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ANOTHER FORM OF QUASI-RELATIVISTIC HARTREE–FOCK EQUATIONS

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The present work is a continuation of the development of techniques for solving the quasi-relativistic Hartree–Fock equations. The equations were formed anew out of Dirac–Hartree–Fock equations in the shape that allowed one to use the conventional rather accurate self-consistent field potential instead of a simplified effective potential. The method is implemented in computer programs and the test results are presented for some ions of the Be, Ne, and Ar isoelectronic sequences. The results are in good coincidence with the results obtained by solving the relativistic Dirac–Hartree–Fock equations.

Keywords: quasi-relativistic Hartree–Fock equations

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1. Introduction

Among the tasks of atomic physics there is a group of problems, such as an exploration of energy spectra of many-electron ions in plasma or X-ray spectra, etc., where the relativistic effects are of importance while calculating the radial orbitals (ROs) of the inner shells that experience a strong nuclear field. In the spectra of atoms and their first ions the direct relativistic effects are only slightly expressed in the outer shells. They can be easily taken into account in the second order of perturbation theory within the Breit–Pauli (BP) approximation. However, the essential changes observed in the ROs of inner shells calculated with account of relativistic effects lead to a considerable rearrangement of the outer shell ROs as well, although there the electron velocities are by no means relativistic. This rearrangement leading to the secondary relativistic effects could be taken into account neither within the BP approximation nor by the conventional calculation of correlation corrections employing the traditional Hartree–Fock functions [1].

To deal with this problem one must solve the relativistic Dirac–Hartree–Fock (DHF) equations [2–4]. But in this case the conventional shells ($l > 0$) split into subshells and their ROs become two-component. As a result, their number grows sharply making the computations slower and more difficult. Moreover, the spectra are then obtained within the jj-coupling instead of the LS-coupling typical for the outer shells of atoms and their first ions.

The way out of this situation is to apply the quasi-relativistic Hartree–Fock (QRHF) equations [5, 6]. The QRHF equations make possible the partial account of the relativistic effects in the calculations of ROs keeping at the same time to the usual Hartree–Fock approach. Solving the QRHF equations appears to be rather urgent task in the cases when the relativistic effects can be taken into account within the BP approximation, where there are no reasons to perform the calculations within jj-coupling.

Unfortunately, a computer program for numerical solution of QRHF equations [7], widely known to scientists, was created long ago and many disadvantages and some inaccuracies of it emerged now. This fact impelled us to create a somewhat different code based on different methods and algorithms. The first steps have been made in papers [8–10].

This work continues the unfolding of techniques for solving the QRHF equations. Here the solution of the problem of describing the potential appearing in the relativistic terms of QRHF equations is proposed. For this purpose the QRHF equations are formed anew out of DHF equations in such a shape that allows one to depart from exploiting the simplified effective potential [7], and instead use an ordinary, quite accurate self-consistent field potential in the relativistic terms of QRHF equations.

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In the next part of the paper the problem of the potential while forming the QRHF equations is described and the solution of the problem is introduced. In the third part the methods used for solving QRHF equations are described. The results are presented and compared with the results of other methods in the fourth part of the work. The conclusions with the prospects of further investigation of the treated problem are made at the end of the paper.

2. Formation of quasi-relativistic Hartree–Fock equations

It is known that the one-electron relativistic effects are of major importance when compared to the two-electron ones. That is why the main attention was paid to forming the one-particle quasi-relativistic equations correctly with all the major one-electron relativistic corrections included into the Hamiltonian. Solving hydrogen-like equations is rather a simple task allowing one to evaluate the applicability of the method under development. However, in switching over to the many-electron QRHF equations some problems appeared while defining the potentials in the relativistic terms of the equations.

Originally the quasi-relativistic equations were formed by simply adding the mass–velocity and the Darwin terms taken from the Pauli equations for one-electron atoms to the usual nonrelativistic one-electron differential equation for the radial function $P(nl|r)$ [7]. Similarly, the local potential quasi-relativistic approximation to the Hartree–Fock equations was formed:

$$\left\{-\frac{\mathrm{d}^2}{\mathrm{d}r^2}+\frac{l(l+1)}{r^2}+V_{\text{eff}}(r)-\frac{\alpha^2}{4}\left[\varepsilon_{nl}-V_{\text{eff}}(r)\right]^2\right.$$
$$-\,\delta(l,0)\frac{\alpha^2}{4}\left[1+\frac{\alpha^2}{4}\left[\varepsilon_{nl}-V_{\text{eff}}(r)\right]\right]^{-1}$$
$$\left.\times\,\frac{\mathrm{d}V_{\text{eff}}(r)}{\mathrm{d}r}\left[\frac{\mathrm{d}}{\mathrm{d}r}-\frac{1}{r}\right]\right\}P(nl|r)=\varepsilon_{nl}P(nl|r)\,. \quad (1)$$

Hereinafter, ε_{nl} denotes the single-electron energy, α is the fine structure constant, $V_{\text{eff}}(r)$ is the central-field potential energy function where the nuclear contribution is $-2Z/r$, the electron interaction energy is also incorporated, and the exchange part of it is taken into account effectively. There are many ways to effectively take into account the electron interaction energy. The several possible models of a simplified effective potential are described and used in [7] and in a computer program based on it.

The mass–velocity and the Darwin terms represent relativistic corrections to the α^2 order. The j-dependent spin–orbit term of the Pauli equation has been omitted in order to obtain the radial wave functions that are independent of j, even though this term is also of α^2 order. So the obtained radial function $P(nl|r)$ forms an approximation to the $(2j+1)$-weighted average of the relativistic functions nlj_+ and nlj_-.

The same quasi-relativistic equations (1) may be obtained from the relativistic Dirac–Hartree–Fock equations:

$$\frac{\mathrm{d}P(nlj|r)}{\mathrm{d}r}=-\frac{\kappa}{r}P(nlj|r)$$
$$+\,\frac{1}{c}\left\{\left[2c^2-\varepsilon_{nlj}+\frac{Z}{r}-V(nlj|r)\right]\right.$$
$$\left.\times\,Q(n\bar{l}j|r)-\chi_{Q}(nlj|r)\right\},$$

$$\frac{\mathrm{d}Q(n\bar{l}j|r)}{\mathrm{d}r}=\frac{\kappa}{r}Q(n\bar{l}j|r)$$
$$+\,\frac{1}{c}\left\{\left[\varepsilon_{nlj}-\frac{Z}{r}+V(nlj|r)\right]\right.$$
$$\left.\times\,P(nlj|r)+\chi_{P}(n\bar{l}j|r)\right\}. \quad (2)$$

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

In order to get the quasi-relativistic equations in the form (1), first, it is necessary to transform the DHF equations. For that one must compose the total potential of an atom or an ion, i. e., to add the exchange part of the potential to the direct part of it and to get in such a way the total potential of an atom or ion. Thus the DHF equations in a local potential approximation appear:

$$\frac{\mathrm{d}P(nlj|r)}{\mathrm{d}r}=$$
$$-\,\frac{\kappa}{r}P(nlj|r)+\frac{1}{c}\left[2c^2-\varepsilon_{nlj}-V_{\text{eff}}(nlj|r)\right]$$
$$\times\,Q(n\bar{l}j|r)\,,$$

$$\frac{\mathrm{d}Q(n\bar{l}j|r)}{\mathrm{d}r} = \frac{\kappa}{r}Q(n\bar{l}j|r) + \frac{1}{c}[\varepsilon_{nlj} + V_{\mathrm{eff}}(nlj|r)] \times P(nlj|r)\,. \tag{3}$$

Now one may get the same quasi-relativistic equations (1) from this local potential approximation to the DHF equations (3) by inserting $Q(n\bar{l}j|r)$, found from the first equation, into the second equation, and then neglecting the spin–orbit term out of the large component equation obtained. Unfortunately, in order to solve the equations one needs to create some kind of an effective potential $V_{\mathrm{eff}}(r)$ that would describe properly the physical qualities of a real potential in atoms and ions.

Usage of this local potential approximation makes the equations simpler and easier to solve. But the approximation used restricts the universality of application of the quasi-relativistic equations since it is complicated to create an effective potential that would describe equally well the properties both of the heavy and of the light atoms and ions. This approximation as any other one degrades the quality of the solutions obtained.

Another approach in solving the problem of the potential in the relativistic terms of the QRHF equations is presented here. The QRHF equations are formed anew in a way different from that described in [7]. Instead of forming quasi-relativistic equations out of Pauli approximation of Dirac equations and then adding the relativistic terms from the last equations to the usual Hartree–Fock equations, the quasi-relativistic Hartree–Fock equations were composed directly from the DHF equations (2) by using the large component equation with the elimination of a small component from those:

$$\left\{\frac{\mathrm{d}^2}{\mathrm{d}r^2} - \frac{l(l+1)}{r^2} - \varepsilon_{nlj} - U(r)\right\} \times P(nlj|r) - \chi_P(nlj|r) \tag{4.1}$$

$$+ \frac{\alpha^2}{4}[\varepsilon_{nlj} + U(r)]^2 P(nlj|r) + \frac{\alpha^2}{4}[\varepsilon_{nlj} + U(r)]\chi_P(nlj|r) \tag{4.2}$$

$$+ \frac{\alpha^2}{4}\left[1 - \frac{\alpha^2}{4}[\varepsilon_{nlj} + U(r)]\right]^{-1} \times \frac{\mathrm{d}U(r)}{\mathrm{d}r}\left(\frac{\mathrm{d}}{\mathrm{d}r} - \frac{X+1}{r}\right) P(nl|r) \tag{4.3}$$

$$+ \frac{\alpha}{2}\left(\frac{\mathrm{d}}{\mathrm{d}r} + \frac{X+1}{r}\right)\chi_Q(nlj|r) \tag{4.4}$$

$$+ \frac{\alpha^2}{4}\left[1 - \frac{\alpha^2}{4}[\varepsilon_{nlj} + U(r)]\right]^{-1} \times \frac{\mathrm{d}U(r)}{\mathrm{d}r}\frac{\alpha}{2}\,\chi_Q(nlj|r) = 0\,. \tag{4.5}$$

Here the direct part of the potential is denoted as $U(r) = 2[-Z/r + V(nlj|r)]$, $X = j(j+1) - l(l+1) - s(s+1)$ is a spin–orbit interaction parameter, (4.1) is a non-relativistic part of the equations, (4.2) marks mass–velocity direct and exchange terms, (4.3) are direct contact and spin–orbit interaction terms, (4.4) are exchange contact and spin–orbit interaction terms, and (4.5) are the terms of a higher order. Thus it is possible to use the conventional fairly accurate self-consistent field potential instead of a simplified effective potential in the equations.

In quasi-relativistic approximation the terms of a higher order than α^2 are discarded. Thus further on the relativistic terms (4.5) are omitted. The contact interaction (4.3) is taken into account only in the case of s electrons as it is done in the Breit–Pauli approach and in the quasi-relativistic equations by R.D. Cowan. Since only the large RO component is in use and the small component is indefinite while applying the quasi-relativistic approximation, it is impossible to evaluate the exchange potential χ_Q and to calculate the exchange contact interaction (4.4). In this approach the exchange contact interaction can be incorporated only effectively. Tentative calculations have revealed that the influence of the exchange contact interaction is very small. Therefore it is decided to omit the exchange contact interaction at this stage while developing the QRHF method. This problem might be treated later.

In this way the QRHF equations are formed out of the large component equation from the DHF equations by eliminating the terms of the order higher than α^2 and applying the decribed approximations. Thus the QRHF equations appear:

$$\left\{\frac{\mathrm{d}^2}{\mathrm{d}r^2} - \frac{l(l+1)}{r^2} - \varepsilon_{nlj} - U(r)\right\} P(nlj|r) - \chi_P(nlj|r) + \frac{\alpha^2}{4}[\varepsilon_{nlj} + U(r)]^2\, P(nlj|r)$$

$$+\frac{\alpha^2}{4}[\varepsilon_{nlj}+U(r)]\,\chi_P(nlj|r)$$

$$+\delta(l,0)\frac{\alpha^2}{4}\left[1-\frac{\alpha^2}{4}[\varepsilon_{nlj}+U(r)]\right]^{-1}$$

$$\times\frac{\mathrm{d}U(r)}{\mathrm{d}r}\left(\frac{\mathrm{d}}{\mathrm{d}r}-\frac{X+1}{r}\right)P(nlj|r)=0\,. \qquad (5)$$

In this work the spin–orbit interaction parameter X is put to zero, considering that the spin–orbit interaction averages to zero when the total angular momenta of electrons and the statistical weight of each state are taken into account. So the QRHF equations become j-independent:

$$\left\{\frac{\mathrm{d}^2}{\mathrm{d}r^2}-\frac{l(l+1)}{r^2}-\varepsilon_{nl}-U(r)\right\}P(nl|r)$$

$$-\chi_P(nl|r)+\frac{\alpha^2}{4}[\varepsilon_{nl}+U(r)]^2\,P(nl|r)$$

$$+\frac{\alpha^2}{4}[\varepsilon_{nl}+U(r)]\,\chi_P(nl|r)$$

$$+\delta(l,0)\frac{\alpha^2}{4}\left[1-\frac{\alpha^2}{4}[\varepsilon_{nl}+U(r)]\right]^{-1}$$

$$\times\frac{\mathrm{d}U(r)}{\mathrm{d}r}\left(\frac{\mathrm{d}}{\mathrm{d}r}-\frac{1}{r}\right)P(nl|r)=0\,. \qquad (6)$$

The results obtained applying these QRHF equations are compared with the results obtained using other methods and discussed in Section 4.

3. Methods of calculation

The QRHF equations (6) are solved taking into account the finite size of the nucleus as described in papers [8–10]. Inside the nucleus the QRHF equations are of a simpler form. The exchange interaction between electrons is weak inside the nucleus, so it is omitted in the equations. While the direct electron interaction is taken into account effectively by replacing the nucleus charge Z with the effective charge Z_{eff} that also includes the part of electron densities that are present inside the nucleus region. Thus the equations analogous to the quasi-relativistic equations for hydrogen-like ions [10] are solved inside the nucleus.

While solving the equations inside the nucleus the expression of the potential developed in [8] is used:

$$U(x)=u_0+\sum_{k=1}^{4}u_{2k}\,x^{2k}\,. \qquad (7)$$

Here the variable $x=r/R$, where R is the radius of a nucleus, is used in order to make the calculations simpler. This potential expression allows one to describe all the distributions of charge density in a nucleus treated in [8]. To get the quantitative results the following charge density distribution inside a nucleus has been used in solving the QRHF equations:

$$\rho_6(x)=\frac{3Z_{\mathrm{eff}}}{4\pi R^3}\left(\frac{21}{8}-\frac{63}{8}x^4+\frac{21}{4}x^6\right). \qquad (8)$$

The radius R of the nucleus is defined so that at the centre of the nucleus the charge density is approximately equal to the density obtained by using the Fermi distribution [11–13]. The presented model of a nucleus is equally convenient for the description of both light and heavy nuclei.

While solving the QRHF equations the usual RO behaviour at the origin is preserved:

$$P(nl|x)=x^{l+1}\sum_{i=1}^{q}a_i\,x^i\,. \qquad (9)$$

Using the expression of the potential inside the nucleus (7) and the RO (9) in the simplified, as described above, QRHF equations one can obtain the recurrent relationship for the RO expansion coefficients a_i. In [9] the RO expansion coefficients for s electrons are presented. In the case of other electrons, the QRHF equations are simpler. These reasonably obtained initial points ensure a proper initial inclination of the RO and improve the results of calculations.

In the region beyond the nucleus, $r>R$, the usual self-consistent field potential is used in solving the QRHF equations in the form (6). Here the equations are solved numerically through Numerov procedure. Since there is no reason to use another variable beyond the nucleus, the equations are solved with the usual radial variable r, not with x. The QRHF equations in the case of s electrons differ from the equations for other electrons by the presence of the first derivative of RO. Seeking to use the same algorithms while solving the equations for any electrons one needs to eliminate the first derivative. In order to achieve these goals a different type of RO is selected while solving the QRHF equations for s electrons:

$$P(ns|r) = \sqrt{1 - \frac{\alpha^2}{4}[\varepsilon_{ns} + U(r)]}\; S(ns|r) \equiv f(r)\, S(ns|r)\,. \tag{10}$$

The multiplier $f(r)$ is chosen so that the sum of coefficients of the first derivative is equal to zero. Inserting the new RO expression (10) into the QRHF equations (6) one can get the QRHF equations for $S(ns|r)$ function, where the first derivative of RO is absent as described in [9]. The appearance of the potentials in these equations for s electrons is different from the equations for other electrons, but instead the same numerical procedure can be used while solving the equations.

All the methods described here are implemented in the computer program for solving the QRHF equations. The equations are solved for a logarithmic variable. Accuracy and duration of calculations depend on the step of the logarithmic variable. Test solutions of the equations and further RO calculations reveal that in order to get fairly accurate results it is necessary to use a logarithmic variable step equal to one hundredth, but not one sixteenth, as it is traditionally done within the widely known program for solving the Hartree–Fock equations [14]. The results obtained by solving the QRHF equations in the described way are discussed in the next section.

4. Results and discussion

The aim of this project is to take into account the relativistic effects in the calculations of ROs while staying at the same time within the usual Hartree–Fock approximation. Later, it is proposed to employ the obtained quasi-relativistic ROs in the well-developed non-relativistic methodology of calculation of spectral characteristics of atoms and ions with account of correlation effects. Therefore the results received while applying the method developed in this work and in the previous papers (marked as QRHF) are compared with the solutions of the non-relativistic Hartree–Fock equations with relativistic effects considered within the conventional Breit–Pauli approximation [14] (marked as HF(BP)), as well as with the results obtained by solving the quasi-relativistic equations (1) using the computer code rcn36 [7] (marked as CW) and with the purely relativistic solutions of the DHF equations (marked as DHF) with the account of the finite size of the nucleus obtained using the GRASP2 program [15].

Table 1. Absolute values of the total energy (a. u.) of ions in Be, Ne, and Ar isoelectronic sequences.

Seq.	Z	HF(BP)	CW	DHF	QRHF
Be	10	110.2418	110.2573	110.2560	110.2547
	30	1091.54	1091.99	1092.27	1092.22
	50	3150.36	3155.83	3159.83	3159.59
	70	6418.49	6466.44	6486.65	6485.96
	99	13727.0	14283.1	14368.4	14366.7
Ne	10	128.6774	128.6931	128.6919	128.6904
	30	1567.712	1568.283	1568.582	1568.455
	50	4704.43	4711.12	4715.83	4714.51
	70	9709.68	9765.54	9792.60	9783.74
	99	20839.4	21461.6	21630.3	21539.7
Ar	20	678.932	679.083	679.104	679.073
	30	1733.58	1734.19	1734.50	1734.33
	50	5408.26	5415.66	5420.59	5418.87
	70	11342.6	11404.3	11433.3	11422.1
	99	24598.4	25282.0	25471.3	25358.7

The calculations were performed for the configurations with all shells closed: for some ions of the beryllium isoelectronic sequence (Z = 10 to 99), of the neon isoelectronic sequence (Z = 10 to 99), and of the argon isoelectronic sequence (Z = 20 to 99). For the calculations and further comparison of the results the configurations with all shells closed were chosen because in this case the solutions of the DHF equations did not depend on the allocations of the electrons to the subshells. The results obtained while solving the DHF equations are j-dependent, so in order to compare them with the output of other methods they need to be averaged by taking into account that $j = l \pm 1/2$ and the statistic weight of each state is equal to $2j+1$. All values in the tables are presented with the accuracy sufficient to see the differences of the methods under comparison.

In Table 1 the absolute values of the total energy of the considered ions obtained by different techniques are presented. The results reveal that, as expected, the quasi-relativistic methods (CW and QRHF) allow one to take into account relativistic effects more effectively than it is possible within the conventional Breit–Pauli approximation HF(BP). As it is seen from the table, the total energies obtained by the considered approach QRHF are in general closer to the relativistic values DHF as compared to the output of the rcn36 code CW. In the case of the Be-like ions, where only s electrons are present, the relative deviations of the QRHF results from the relativistic DHF ones remain almost the same throughout the isoelectronic sequence, whereas the relative deviations of the CW energy values increase as the nucleus charge Z grows. However, in the cases of other isoelectronic sequences, where not

Table 2. Single-electron energy values (a. u.) of ions in Be isoelectronic sequence.

Z	nl	HF	CW	DHF	QRHF
10	$1s$	40.53982	40.58917	40.58839	40.58928
	$2s$	7.49072	7.50140	7.50134	7.50097
30	$1s$	420.069	424.937	425.023	425.051
	$2s$	96.5187	97.9125	97.9250	97.9106
50	$1s$	1199.61	1239.78	1241.32	1241.47
	$2s$	285.553	297.715	297.926	297.851
70	$1s$	2379.15	2546.56	2554.67	2555.12
	$2s$	574.589	626.582	627.779	627.547
99	$1s$	4799.99	5613.74	5648.18	5649.86
	$2s$	1171.32	1429.87	1435.07	1434.19

Table 3. Averaged distances from the origin r (a. u.) of ions in Be isoelectronic sequence.

Z	nl	HF	CW	DHF	QRHF
10	$1s$	0.15617	0.1559	0.15591	0.15592
	$2s$	0.71178	0.7106	0.71064	0.71075
30	$1s$	0.05068	0.04989	0.04987	0.04988
	$2s$	0.21074	0.2076	0.20725	0.20756
50	$1s$	0.03024	0.02892	0.02887	0.02888
	$2s$	0.12377	0.1184	0.11783	0.11833
70	$1s$	0.02155	0.01963	0.01956	0.01957
	$2s$	0.08762	0.07990	0.07906	0.07976
99	$1s$	0.01521	0.01223	0.01215	0.01215
	$2s$	0.06155	0.04981	0.04862	0.04959

only s, but also p electrons are present, the relative deviations of both QRHF and CW results grow along the isoelectronic sequences. Within this work the p electrons are treated in the same way as it has been done in the quasi-relativistic approach by Cowan [7]. Such behaviour of the relative deviations of the energy values impels us to work further on the methodology of the quasi-relativistic Hartree–Fock calculations in the case of $l > 0$ electrons.

Seeking a more detailed evaluation of features of the method under development some single-electron values are presented in Tables 2 and 3 in numerical form and in Figs. 1, 2, and 3 in graphical representation. The results calculated for the ions of Be isoelectronic sequence are shown in the tables. In the figures the relative deviations of the quasi-relativistic values (CW and QRHF) from the relativistic ones (DHF) computed for the ions of Ne isoelectronic sequence are presented.

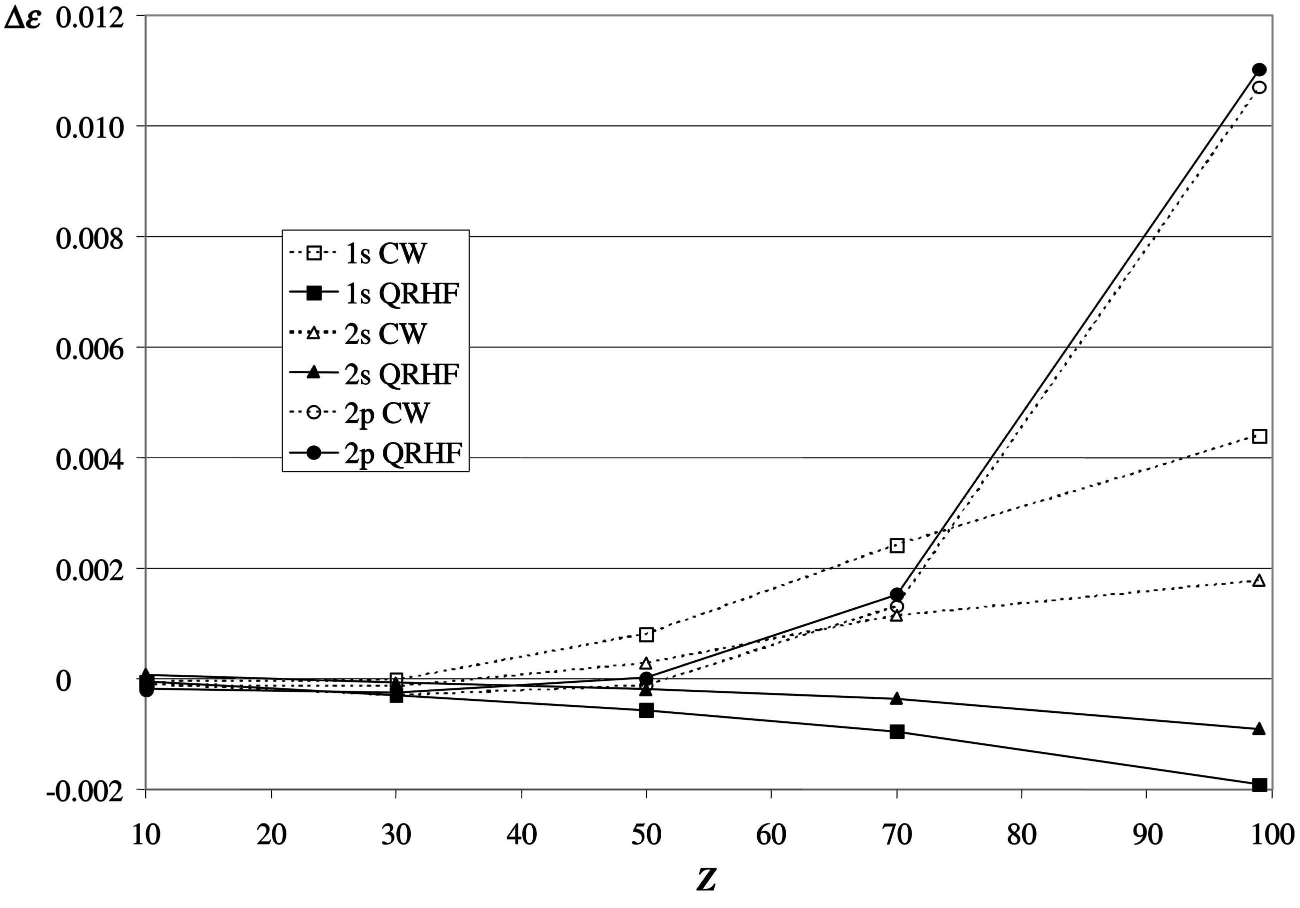

Fig. 1. Relative deviations of the single-electron energy values of ions in Ne isoelectronic sequence.

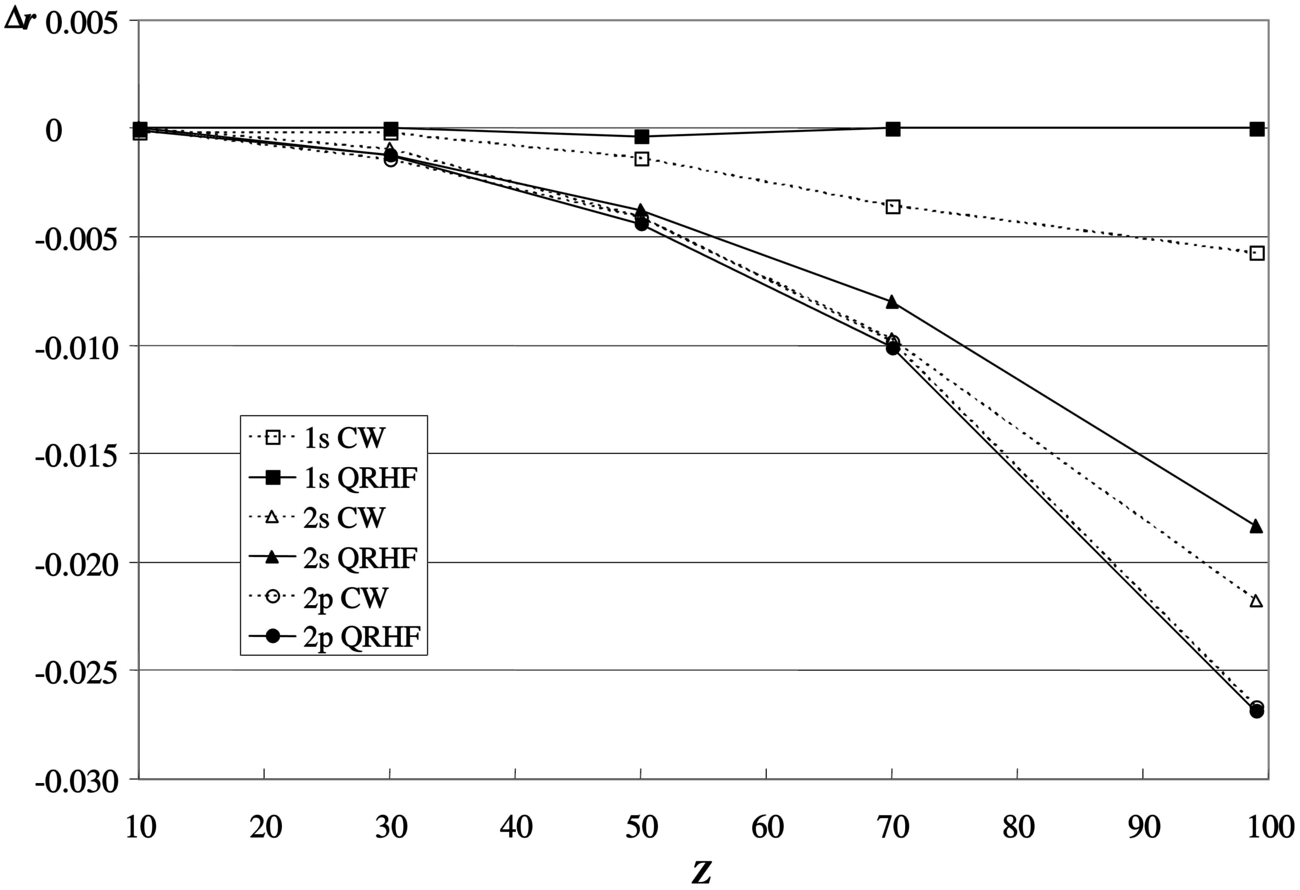

Fig. 2. Relative deviations of the averaged distances from the origin r of ions in Ne isoelectronic sequence.

The relative deviations of the single-electron energies ε are calculated as follows:

$$\Delta\varepsilon_{\mathrm{CW}} = \frac{\varepsilon_{\mathrm{DHF}} - \varepsilon_{\mathrm{CW}}}{\varepsilon_{\mathrm{DHF}}},$$

$$\Delta\varepsilon_{\mathrm{QRHF}} = \frac{\varepsilon_{\mathrm{DHF}} - \varepsilon_{\mathrm{QRHF}}}{\varepsilon_{\mathrm{DHF}}}, \tag{11}$$

and marked in Fig. 1 as CW and QRHF, respectively. The relative deviations of the averaged distances from the origin r and of the opposite quantities $1/r$ are calculated and marked in the same way. The relative deviations of the single-electron quantities obtained within the usual Hartree–Fock approach from the relativistic ones (DHF) are not presented in the figures, because they are of different order of magnitude and require figures of different scale. Moreover, they are not of the main interest in the work. The presentation of both the numerical values and the relative deviations shown graphically allows one to have a clearer idea of the properties of the methods.

The single-electron energies presented in Table 2 and their relative deviations plotted in Fig. 1 for Be and Ne isoelectronic sequences reveal that in the case of s electrons the QRHF results are in general closer to the relativistic DHF ones. However, Fig. 1 shows that in the case of p electrons the relative deviations of CW and QRHF results from the DHF solutions are very small. That is an expected outcome keeping in mind that the p electrons are treated in the same way within the both mentioned methods. Therefore, it is necessary to apply some different methods rather than those used in [7] for the treatment of the $l > 0$ electrons. It is also seen from the table and the figure that the single-electron energy values QRHF are in some cases deeper than the relativistic values DHF. However, in the case of hydrogen-like ions presented in [9, 10] the single-electron energies of s electrons were found to be very close to the relativistic values DHF. Possibly, some many-electron effects are not properly taken into account. These facts provide us with the materials for further investigations.

Since the main purpose of the work is to get the correct ROs for further usage, the averaged distances from the origin r and the relative deviations of these and of the opposite quantities $1/r$ obtained in the mentioned different ways are presented in Table 3 and in Figs. 2 and 3 for Be and Ne isoelectronic sequences.

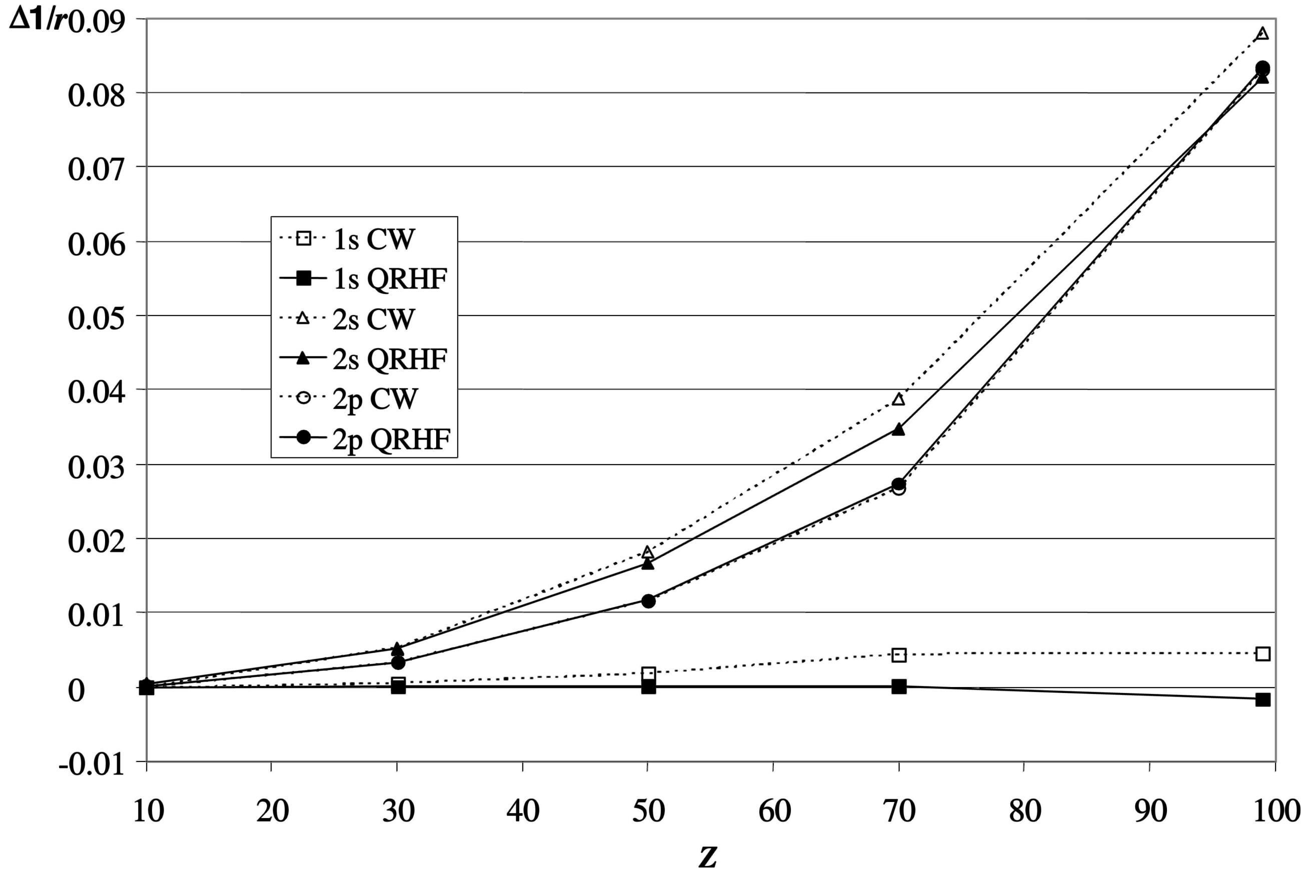

Fig. 3. Relative deviations of the averaged inverse distances from the origin $1/r$ of ions in Ne isoelectronic sequence.

As seen from the table and the figures, these values in the treated QRHF case are pretty close to the relativistic values DHF. The difference between the non-relativistic (HF) and the quasi-relativistic (QRHF) results presented in Table 3 is especially obvious. It is expected that the usage of the quasi-relativistic ROs instead of non-relativistic ones in further calculations of the spectral characteristics of atoms and ions will affect them in a positive way. The differences of the behaviour of the relative deviations of r and $1/r$ in the case of $1s$ and $2s$ electrons plotted in Figs. 2 and 3 for Ne isoelectronic sequence are caused most likely by the lack of orthogonalization.

5. Conclusion

The new form of the QRHF equations presented in the paper is free of the additional approximations such as the creation of an artificial effective potential. The developed methods for solving the equations with account of the finite size of the nucleus ensure the proper behaviour of the RO in the vicinity of the origin and give additional opportunities for the calculation of nuclear effects. The obtained test results demonstrate that the relativistic corrections applied in the described way are rather effective, even though one keeps staying within the usual Hartree–Fock approach. At the same time it is obvious that there is still a lot of space for improvement of the method. The presented test results show that the direct contact interaction might be overestimated for the s electrons and underestimated in other cases. Also the question of the exchange contact interaction might be investigated deeper. All these are the matter of further investigations.

In the presented work the problem of orthogonality of the ROs of equal l and different n is not investigated, because the CW results are not orthogonalized. We also do not employ the orthogonalization in our calculations in order to see the differences between the methods caused purely by the usage of potentials, nuclear models, methods of calculations, but not by the lack of orthogonalization, since the aim of this work is to treat the problem of the potential while solving the QRHF equations. The problem of orthogonality of the ROs will be investigated in the future.

The QRHF calculations seem to be promising enough new possibilities in the calculations of spectral characteristics of atoms and ions in the future. The development of this method will be continued taking into consideration the assumptions mentioned above.

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KITAS KVAZIRELIATYVISTINIŲ HARTRIO IR FOKO LYGČIŲ PAVIDALAS

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Santrauka

Toliau plėtojama kvazireliatyvistinių Hartrio (Hartree) ir Foko (Fock) lygčių sprendimo metodika. Iš Dirako (Dirac), Hartrio ir Foko lygčių gauta nauja kvazireliatyvistinių Hartrio ir Foko lygčių forma, kuri leidžia atsisakyti supaprastinto efektinio potencialo, o naudoti pakankamai tikslų įprastą suderintinio lauko potencialą. Kaip ir ankstesniuose darbuose, kvazireliatyvistinės Hartrio ir Foko lygtys sprendžiamos, atsižvelgiant į baigtinį branduolio tūrį. Pateikti bandomųjų skaičiavimų rezultatai kai kuriems Be, Na ir Ar izoelektroninių sekų jonams. Šitie rezultatai pakankamai gerai sutampa su tikslių reliatyvistinių Dirako, Hartrio ir Foko lygčių sprendiniais, gautais atsižvelgiant į baigtinį atomo branduolio tūrį. Paskutiniame darbo skyriuje nurodytos tolimesnės metodo plėtojimo perspektyvos.