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A UNIVERSAL POTENTIAL FOR QUASIRELATIVISTIC RADIAL ORBITALS

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A possibility to extend the universal Gáspár potential, used for obtaining the initial radial orbitals in iterative solving of quasirelativistic Hartree–Fock equations, is investigated. The extension is achieved via introduction of variable parameters instead of fixed ones that depend on the number of electrons in a configuration and the ionization degree of an atom.

Keywords: universal Gáspár potential, quasirelativistic Hartree–Fock equations, iterative process, initial radial orbitals

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1. Introduction

Although the self-consistent field method by Fock [1] is known since 1930, still for a number of subsequent years the work has been continued in building the potentials that in averaged form describe the field of nuclear charge and its surrounding electrons. One of the results of these efforts was the creation of the universal potential by Gáspár [2]. It was obtained on the basis of statistical methods and analysis of the potential of a many-electron Hg atom. It was enhanced and modified several times afterwards [3], including the works by the Vilnius' specialists in the atomic theory [4]. The rapid development of computational electronics and creation of efficient mathematical methods for solving the integral–differential Hartree–Fock (HF) equations led to wide distribution and use of the programs for obtaining the radial orbitals (RO) of a self-consistent field, and the interest in statistical potentials greatly diminished. Nevertheless, the utility of potentials of this kind is quite high. The point is that for a self-consistent solving of HF equations the initial RO are necessary. In many cases (e. g., the widely known program [5]) the hydrogenic functions with gradual screening of the nuclear charge Z are used as initial RO. But there is no universal and sufficiently accurate method to introduce the screening of nuclear charge, and the RO obtained for differing effective charges of nucleus are not orthogonal and should be additionally orthogonalized before use. As a result, such RO not always sufficiently accurately describe the sought solutions and that in turn may lead to slow self-consistency or even the nonconvergence of the iterative process.

To overcome these problems, in [6] it was proposed to take as initial the RO that are the solutions of equations with the universal Gáspár potential. Using this potential for all the functions describing the given configuration one obtains the RO that are automatically orthogonal. Long-term application of this approach in several versions of programs for solving the HF equations [7] has proven the adequacy of the universal Gáspár potential in description of real potentials for atoms with different nuclear charges at various ionization degrees.

The acquired experience in using the universal Gáspár potential for solving the conventional HF equations was also employed for development of a program for solving the quasirelativistic HF equations described in [8]. There the same form of the potential as for the conventional equations [6] was used. Its application allowed one to obtain the solutions of quasirelativistic equations, but the correspondence of initial RO to the self-consistent solutions appeared to be much worse than in the case of traditional HF equations. In addition, the correspondence visibly worsened with higher ionization degrees, which is in conflict with the tendencies observed in the HF equations' case. As the inadequate initial RO hinder the solving of equations, especially in the case of outer shells of calculated configuration, there arises a need for improving the universal potential used.

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In the next section the method to obtain the new universal potential is described, and in the third one the comparison of characteristics of RO, obtained using a previous and new expressions, with parameters of solutions of quasirelativistic HF equations is performed.

2. Method to obtain the new universal potential

The equation containing the universal potential is obtained from the quasirelativistic HF equation (Eq. (2.22) in [8]) by omitting the exchange part of the potential and substituting the direct part with a local potential. It has the following form:

$$\left\{\frac{\mathrm{d}^2}{\mathrm{d}r^2}-\frac{l(l+1)}{r^2}-2V(r)-\varepsilon_{nl}\right\}P(nl|r) + \frac{\alpha^2}{4}[\varepsilon_{nl}+2V(r)]^2P(nl|r) + \frac{\alpha^2}{4}\left\{1-\frac{\alpha^2}{4}[\varepsilon_{nl}+2V(r)]\right\}^{-1}D(nl|r)P(nl|r) = 0\,. \tag{1}$$

Here the first term determines the kinetic energy and the nonrelativistic interaction with a nucleus, the next one describes the mass dependence on velocity, and the last term in the equation describes the contact interaction with a nucleus in the form proposed in [9]:

$$D(nl|r)=\left[\delta(l,0)+\frac{1}{3}\delta(l,1)\right]2\frac{\mathrm{d}V(r)}{\mathrm{d}r}\left\{\frac{\mathrm{d}}{\mathrm{d}r}-\frac{1}{r}\times\left[\alpha^2Z^2\delta(l,1)\left(-\frac{37}{30}-\frac{5}{9n}+\frac{2}{3n^2}\right)+1\right]\right\}. \tag{2}$$

The local potential is defined as follows:

$$V(r)=\begin{cases}\dfrac{1}{32}\dfrac{Z}{r_{\mathrm{nuc}}}\left[-63+42\left(\dfrac{r}{r_{\mathrm{nuc}}}\right)^2-18\left(\dfrac{r}{r_{\mathrm{nuc}}}\right)^6+7\left(\dfrac{r}{r_{\mathrm{nuc}}}\right)^8\right], & r<r_{\mathrm{nuc}}\,,\\ U(r)\,, & r\geq r_{\mathrm{nuc}}\,.\end{cases} \tag{3}$$

As seen from (3), definition of potential inside the nucleus remains the same and, as proposed in [10], the potential is expanded in even powers of radial variable. In obtaining the initial RO, the universal Gáspár potential

$$U(r)=-\frac{I}{r}-\frac{(Z-I)}{r}\cdot\frac{\exp\left(-B_0Z^{1/3}r\right)}{1+A_0Z^{1/3}r} \tag{4}$$

outside the nucleus is used, where I is the atom ionization degree in spectroscopic notation (1 for neutral atom), and the parameters of potential have the following values [6]:

$$A_0=1.19\,,\quad B_0=0.2075\,. \tag{5}$$

The potential calculated using parameters (5) will be denoted by U_{G}.

As mentioned before, the potential U_{G} does not provide the opportunity to obtain sufficiently accurate initial quasirelativistic RO, which makes it difficult to solve the equations. As the very form of the potential is physically sound enough and gives good asymptotic behaviour at zero and at infinity, it has been decided not to change the formulas but to restrict ourselves to adjusting the values of parameters A and B.

At first the optimal values of parameters for a definite value of nuclear charge and ionization degree of the ground configuration were determined. To this end the quasirelativistic equations for the investigated ion were being solved and the numerical values of a great number of points of the direct potential U_{QR} for the outer shell were being calculated. The potential of the outer shell has been chosen due to the fact that it has been necessary to obtain as accurate as possible values for the characteristics of outer electrons. Afterwards, employing the least squares method providing coincidence of potential (4) with numerically determined U_{QR}, the optimal values of parameters $A_{Z,I}$ and $B_{Z,I}$ for this ion have been determined. The least squares method has also been used for adjusting the paramaters $A^q_{Z,I}$ and $B^q_{Z,I}$ not of the potential itself but of the effective charge defined as the ratio of value of potential to the corresponding value of radial variable. This corresponds to the fact that in the least squares method the radial variable is used as weighting factor for points of potential.

Such calculations have been performed for a wide variety of ground configurations with number of electrons N from 5 to 86. Neutral atoms as well as ions with nuclear charge up to 100 have been considered. The full list of investigated isoelectronic sequences is given in Table 1. Most of the results presented in Table 1 were not possible using the original Gáspár potential. In order to achieve appropriate and self-consistent solutions, the empirical fitting for Gáspár potential characteristics has been crucial. There and further for marking the isoelectronic sequences the total number of electrons $N=Z-I+1$ has been used without specifying the distribution of electrons in shells, because the ground states have been treated in all the cases. As seen from the table, the data on potentials and their corresponding

Table 1. Numbers of electrons N in the investigated sequences and the charges of nucleus Z.

N	Z
5	5–13, 15, 17, 20, 25, 30, 45, 50, 55, 60, 70, 80, 90
6	6–16, 18, 20, 22, 24, 26, 28, 30, 35, 37, 40, 45, 50, 55, 60, 70, 80, 90
8	8–20, 22, 24, 26, 28, 30, 32, 35, 37, 40, 45, 50, 55, 60, 70, 80, 90
10	10–18, 20, 22, 24, 26, 28, 30, 32, 35, 37, 40, 45, 50, 55, 60, 70, 80, 90
19	21–30, 32, 35, 37, 47, 50, 55, 60, 70, 80, 90
37	37–45, 47, 48, 49, 50, 52, 60, 62, 65, 67, 70, 80, 90
47	47–55, 60, 62, 65, 67, 70, 75, 80, 85, 90, 95
54	54–64, 66, 68, 70, 72, 74, 76, 78, 82, 84, 85, 90, 100
68	68–75, 77, 80, 83, 85, 87, 90, 95, 100
70	70–80, 82, 84, 86, 88, 90, 92, 95, 97
80	80–100
86	86–100

parameters for more than 360 configurations have been obtained.

With that, it has become clear that the considered parameters quite strongly depend on the nuclear charge and ionization degree. This is demonstrated in Table 2, which contains the values of parameters of potential for some configurations at different ionization degrees. As can be seen from the table, even for neutral atoms the obtained parameter values quite essentially differ from the traditional nonrelativistic values (4) as well as between themselves. At higher ionization degrees the parameter values markedly increase and depart more from (4). The indicated dependence is due to the increasing difference of quasirelativistic RO from solutions of ordinary HF equations, on the basis of which the universal potential has been obtained, with nuclear charge increase. All these differences equally pertain to the coefficient in the denominator of the expression for the universal potential (3) as well as to the power index. The obtained data indicates that it is complicated to get any constant values of universal potential parameters that would well describe the real potentials appearing at different nuclear charges and ionization degrees. In connection with all mentioned above it has been decided to use paramaters as functions of I and N instead of constant ones.

In the second stage of calculations the dependences of parameters on ionization degrees for every investigated isoelectronic sequence have been obtained in the form of expansions in powers of I. While getting the expansions different polynomials have been investigated. It has come out that it is quite sufficient to restrict oneself to powers from zero to two:

$$A_N(I) = a_{N,0} + a_{N,1}\,I + a_{N,2}\,I^2\,,$$

$$B_N(I) = b_{N,0} + b_{N,1}\,I + b_{N,2}\,I^2\,. \tag{6}$$

Table 2. Values of the universal potential coefficients for various configurations.

N	Z	$A_{Z,I}$	$B_{Z,I}$	$A^q_{Z,I}$	$B^q_{Z,I}$
5	5	1.62032	0.20831	1.26956	0.33166
	20	3.44975	1.54327	3.04767	1.69331
	90	13.72749	4.43528	10.89147	5.69662
10	10	1.21844	0.35235	0.71740	0.62183
	30	1.98049	1.98947	0.69184	2.91732
	90	5.82775	4.59036	2.08609	7.18321
47	47	1.26364	0.21482	1.01503	0.32111
	60	1.54802	0.42217	0.95682	0.73315
	95	2.32521	0.84315	1.11545	1.55156
68	68	1.17250	0.24217	1.06008	0.29117
	100	1.78699	0.55665	1.00978	0.98909
86	86	1.21932	0.21328	1.24412	0.20502
	100	1.47495	0.31793	1.22395	0.43567

The values of coefficients $a_{n,k}$ and $b_{n,k}$ were determined by the least squares method for all possessed values of parameters. For example, in the case of neon isoelectronic sequence ($N = 10$) the following expressions have been obtained:

$$A_{10}(I) = 1.31218 + 0.0205382\,I + 0.000411654\,I^2\,,$$

$$B_{10}(I) = 0.320836 + 0.0874033\,I - 0.000434845\,I^2\,,$$

$$A^q_{10}(I) = 0.76862 - 0.0125168\,I + 0.000343317\,I^2\,,$$

$$B^q_{10}(I) = 0.605271 + 0.1183522\,I - 0.000470773\,I^2\,.$$

In the case of xenon isoelectronic sequence ($N = 54$) the sought-after expansions have this form:

$$A_{54}(I) = 1.27101 + 0.0166506\,I + 0.000062368\,I^2\,,$$

$$B_{54}(I) = 0.162205 + 0.0140429\,I - 0.000074148\,I^2\,,$$

$$A^q_{54}(I) = 1.17482 + 0.0031170\,I + 0.000123055\,I^2\,,$$

$$B^q_{54}(I) = 0.197017 + 0.0210473\,I - 0.000097442\,I^2\,,$$

and for the radon isoelectronic sequence ($N = 86$)

$$A_{86}(I) = 1.19485 + 0.0236577\,I - 0.000336049\,I^2\,,$$

$$B_{86}(I) = 0.207530 + 0.0069973\,I + 0.000022466\,I^2\,,$$

$$A^q_{86}(I) = 1.24591 - 0.0083329\,I + 0.000471499\,I^2\,,$$

$$B^q_{86}(I) = 0.187453 + 0.0202794\,I - 0.000255235\,I^2\,.$$

Just as expected, the coefficients in presented expansions depend on the number of electrons in configuration. To take into account this dependence in general form, the expansion in powers of number of electrons has been used. Similarly to the previous expansion, it turns out that it is possible to restrict oneself to quadratic dependence

$$a_{N,k} = \alpha_0 + \alpha_1 N + \alpha_2 N^2\,,$$

$$b_{N,k} = \beta_0 + \beta_1 N + \beta_2 N^2\,. \tag{7}$$

Coefficients α_i and β_i have been determined by the least squares method taking into account all the considered isoelectronic sequences. Substitution of their values into (6) leads to the following general expressions for the parameters of the universal potential (3):

$$\begin{aligned}A(N,I) &= 1.68292295 - 1.54855956\cdot 10^{-2}N + 1.18613040\cdot 10^{-4}N^2\\ &+ I\,(6.80267876\cdot 10^{-2} - 1.95268774\cdot 10^{-3}N + 1.79791804\cdot 10^{-5}N^2)\\ &+ I^2\,(5.62961892\cdot 10^{-4} - 1.42822397\cdot 10^{-5}N + 4.29849376\cdot 10^{-8}N^2)\,,\end{aligned} \tag{8}$$

$$\begin{aligned}B(N,I) &= 2.53862830\cdot 10^{-1} - 1.93417591\cdot 10^{-3}N + 1.81755849\cdot 10^{-5}N^2\\ &+ I\,(9.43884981\cdot 10^{-2} - 2.50023623\cdot 10^{-3}N + 1.77429131\cdot 10^{-5}N^2)\\ &+ I^2\,(-4.73906019\cdot 10^{-4} + 1.22191182\cdot 10^{-5}N - 7.41630927\cdot 10^{-8}N^2)\,.\end{aligned} \tag{9}$$

The potential (3) calculated using parameters (8) and (9) is further denoted as U_N. When the effective charge is approximated instead of the potential itself, the following expressions for the parameters are obtained:

$$\begin{aligned}A^q(N,I) &= 1.09270806 - 5.08422790\cdot 10^{-3}N + 7.29722952\cdot 10^{-5}N^2\\ &+ I\,(5.26634851\cdot 10^{-2} - 2.02788199\cdot 10^{-3}N + 1.61348845\cdot 10^{-5}N^2)\\ &+ I^2\,(3.16546385\cdot 10^{-4} - 1.17222742\cdot 10^{-5}N + 1.50926909\cdot 10^{-7}N^2)\,,\end{aligned} \tag{10}$$

$$\begin{aligned}B^q(N,I) &= 5.30964547\cdot 10^{-1} - 7.21449090\cdot 10^{-3}N + 4.39624106\cdot 10^{-5}N^2\\ &+ I\,(1.08641267\cdot 10^{-1} - 2.52982224\cdot 10^{-3}N + 1.82931326\cdot 10^{-5}N^2)\\ &+ I^2\,(-3.83202815\cdot 10^{-4} + 1.05096094\cdot 10^{-5}N - 1.05488797\cdot 10^{-8}N^2)\,.\end{aligned} \tag{11}$$

The potential (3) calculated using parameters (10) and (11) is further denoted as U^q_N.

As both adjustments and simplifications have been indispensable in obtaining parameters of the new universal potential, it is necessary to check its validity, which is done in the next section. This is accomplished using as a criterion the results obtained by self-consistently solving the quasirelativistic equations that take into account both direct and exchange interaction of electrons. The potential obtained in this way is denoted as U_{QR}.

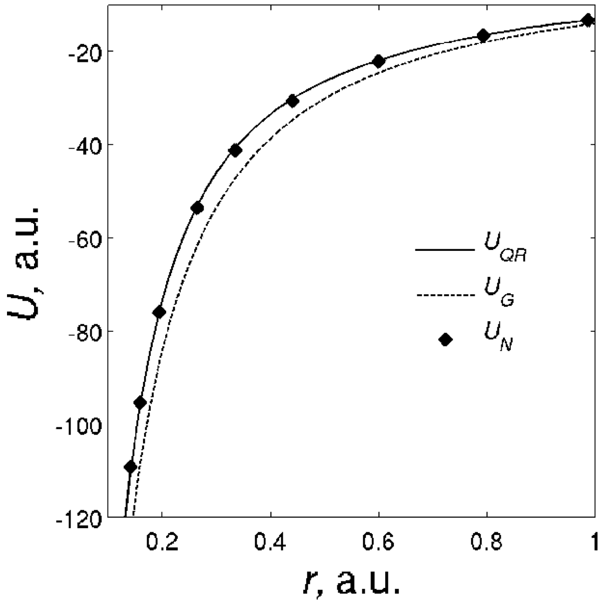

Fig. 1. Potentials U_{QR}, U_G, and U_N for the case of Ti XV ion ($Z = 22$) of the oxygen isoelectronic sequence.

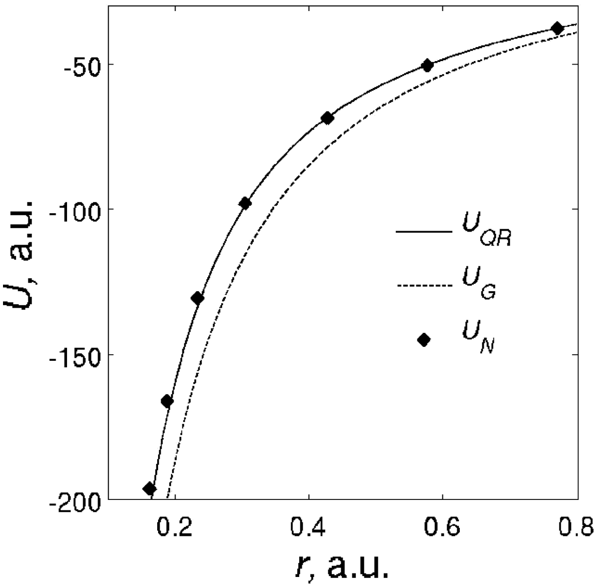

Fig. 2. Potentials U_{QR}, U_G, and U_N for the case of Sn XXII ($Z = 50$) of the copper isoelectronic sequence.

3. Results of using the new universal potential

The investigated potentials U_{QR}, U_G, and U_N for the cases of Ti XV ion ($Z = 22$) of the oxygen ($N = 8$) isoelectronic sequence, Sn XXII ($Z = 50$) of the copper ($N = 22$) isoelectronic sequence, and U XCII ($Z = 92$) of the mercury ($N = 80$) isoelectronic sequence are graphically depicted in Figs. 1, 2, and 3. In the graphs as well as in all further tables the atomic system of units is used. The potential U_{QR} has been calculated for the outer shells of the considered configurations. As the potentials, according to (3), are asymptotically the same at zero and at infinity, the figures depict only the intermediate regions where the greatest differences are observed. Physically important are the differences in potential values corresponding to the same distance from the origin of coordinate. It is seen from the figures that the new universal potential in all the presented cases essentially better coincides with the potential obtained solving the quasirelativistic equations. The differences of values $|U_{\mathrm{QR}}(r) - U_N(r)|$ as compared to $|U_{\mathrm{QR}}(r) - U_G(r)|$ become many times smaller. This is observed not just in these three presented examples but for all the treated potentials as well. The behaviour of potential U_N^q in the cases of Ti XV and Sn XXII when pictured graphically is practically the same as that of U_N. In the U XCII case the potential practically coincides with U_{QR}, as is the case with the potential U_N in Figs. 1, 2.

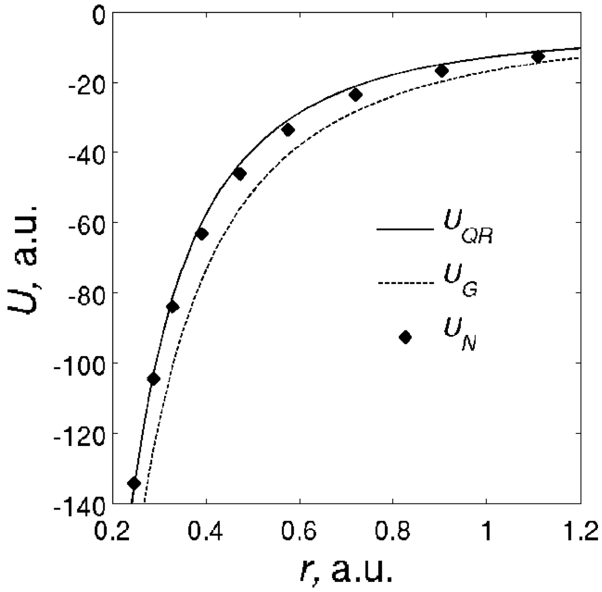

Fig. 3. Potentials U_{QR}, U_G, and U_N for the case of U XCII ($Z = 92$) of the mercury isoelectronic sequence.

However, the good behaviour of potentials U_N and U_N^q does not yet guarantee their applicability in calculations. It is more important what RO are obtained after solving (1) employing the new universal potential. The characteristics of RO obtained solving the equations with potentials U_G, U_N, and U_N^q are compared to the characteristics of RO obtained solving the quasirelativistic HF equations. Hereafter we will call the results of self-consistent solving the exact ones. As an indicator of methods used for obtaining the characteristics, the index of a potential employed in determining the RO is used both in the text and in tables.

The most important characteristic of RO that essentially influences the convergence of iterative process is the single-electron energy ε_{nl}. Here ε_{nl} traditionally imply the positive quantities entering Eq. (1). For obtaining the measured single-electron energies the presented values must be multiplied by -0.5. The other characteristics used are the mean distance to the origin

$$r_{nl} = \int\limits_0^\infty r P^2(nl|r)\,\mathrm{d}r \tag{12}$$

and the mean inverse distance to the origin

$$r_{nl}^{-1} = \int\limits_0^\infty r^{-1} P^2(nl|r)\,\mathrm{d}r\,, \tag{13}$$

which determines the potential energy of interaction between electron and nucleus.

Control calculations of RO have been performed for the isoelectronic sequences used in obtaining the parameters of potential (Table 1) as well as for a series of new sequences. No principal differences in these results have been detected. To restrict the volume of this paper, only the results for two new sequences, with low number of electrons ($N = 12$) and with high one ($N = 74$), are presented further.

As a first example, the characteristics that have been obtained in treating the magnesium isoelectronic sequence are presented in Table 3. For illustrative purposes the exact results in this and the following tables are distinguished in bold. As seen in the table, practically everywhere the single-electron energies obtained with the new potentials agree with the exact values better. The single exception is ε_{1s} for sulphur ion ($Z = 16$). In all the cases usage of U_G leads to significantly elevated values of single-electron energies. The usage of new potentials, on the contrary, makes the above-mentioned quantities too low. This probably is due to the fact that only the direct potentials have been used in approximation, while the electron exchange interaction has the sign opposite to their direct interaction and makes the absolute values of single-electron energies higher. The mean distances to the origin of coordinate behave analogously. The relative discrepancies in this case are noticeably lower than the corresponding discrepancies in single-electron energies, though. The same tendencies are seen in comparing the inverse distances r_{nl}^{-1}. Naturally, the deviations from the exact values in this case have the opposite sign compared to r_{nl}. It should be noted that there are no principal differences between results obtained using U_N and U_N^q. The fact that the accuracy of these results becomes higher for outer shells is caused by the usage of outer orbitals for potential approximation and corresponds to the posed task to enhance the accuracy of initial radial orbitals for outer shells.

Table 3. Parameters of RO of magnesium isoelectronic sequence (a. u.).

nl	Z	ε_{nl}			
		U_{QR}	U_{G}	U_N	U_N^q
1s	16	**94.60**	97.99	82.81	85.34
	26	**280.31**	303.06	260.51	263.73
	50	**1165.90**	1244.25	1117.46	1123.49
2s	16	**11.24**	13.87	9.24	9.09
	26	**48.16**	59.92	44.48	44.22
	50	**247.64**	288.38	237.83	237.26
2p	16	**8.87**	12.26	7.09	6.94
	26	**43.30**	57.53	39.79	39.52
	50	**231.43**	279.23	221.78	221.04
3s	16	**2.61**	3.68	2.55	2.49
	26	**16.65**	21.51	16.42	16.31
	50	**98.54**	116.76	97.42	97.22
nl	Z	r_{nl}			
		U_{QR}	U_{G}	U_N	U_N^q
1s	16	**0.0967**	0.0964	0.0999	0.0986
	26	**0.0584**	0.0577	0.0596	0.0592
	50	**0.0290**	0.0287	0.0294	0.0293
2s	16	**0.4715**	0.4408	0.5105	0.5055
	26	**0.2617**	0.2426	0.2723	0.2714
	50	**0.1227**	0.1162	0.1256	0.1255
2p	16	**0.4385**	0.3885	0.4904	0.4835
	26	**0.2317**	0.2065	0.2430	0.2419
	50	**0.1074**	0.0992	0.1101	0.1100
3s	16	**1.4831**	1.2161	1.5175	1.5410
	26	**0.6856**	0.5918	0.6939	0.6965
	50	**0.2983**	0.2716	0.3011	0.3015
nl	Z	r_{nl}^{-1}			
		U_{QR}	U_{G}	U_N	U_N^q
1s	16	**15.67**	15.71	15.25	15.43
	26	**25.99**	26.24	25.56	25.70
	50	**53.10**	53.58	52.49	52.67
2s	16	**3.11**	3.36	2.86	2.89
	26	**5.70**	6.21	5.46	5.47
	50	**12.66**	13.49	12.34	12.35
2p	16	**2.97**	3.30	2.67	2.72
	26	**5.51**	6.12	5.26	5.30
	50	**11.80**	12.72	11.54	11.57
3s	16	**0.92**	1.17	0.93	0.91
	26	**2.09**	2.50	2.10	2.09
	50	**5.07**	5.69	5.07	5.06

As a second example, the characteristics of RO for isoelectronic sequence of tungsten in the cases of mercury ($Z = 80$) and thorium ($Z = 90$) ions are presented in Table 4. As seen from the table, in the case of ions with high nuclear charge both new potentials provide much higher accuracy of ε_{nl} for all shells without an exception. Meanwhile, the usage of U_G leads

Table 4. Parameters of RO of tungsten isoelectronic sequence (a. u.) for the outer shells 5s, 5p, 5d, 6s. Mean square deviations (%) calculated including the inner shells 1s . . . 4f as well.

nl	Z	ε_{nl}			
		U_{QR}	U_{G}	U_N	U_N^q
5s	80	**8.59**	12.01	8.96	7.89
	90	**22.00**	33.14	23.64	21.75
5p	80	**6.42**	9.69	6.98	6.04
	90	**18.24**	28.95	20.13	18.43
5d	80	**3.86**	6.47	4.33	3.61
	90	**13.87**	23.30	15.41	13.95
6s	80	**2.86**	4.17	3.25	2.90
	90	**10.41**	15.42	11.51	10.72
σ	80		46.9	6.2	10.0
	90		55.2	6.5	2.2

nl	Z	r_{nl}			
		U_{QR}	U_{G}	U_N	U_N^q
5s	80	**0.8909**	0.7749	0.8671	0.8866
	90	**0.6811**	0.5678	0.6576	0.6682
5p	80	**0.9981**	0.8352	0.9580	0.9903
	90	**0.7468**	0.5983	0.7098	0.7250
5d	80	**1.2280**	0.9529	1.1663	1.2540
	90	**0.8432**	0.6396	0.7987	0.8286
6s	80	**1.9293**	1.5312	1.7820	1.9051
	90	**1.2635**	0.9915	1.1826	1.2326
σ	80		10.8	3.9	3.4
	90		14.3	2.6	2.2

nl	Z	r_{nl}^{-1}			
		U_{QR}	U_{G}	U_N	U_N^q
5s	80	**1.54**	1.84	1.61	1.56
	90	**2.10**	2.66	2.23	2.17
5p	80	**1.33**	1.64	1.41	1.35
	90	**1.82**	2.37	1.96	1.90
5d	80	**1.05**	1.40	1.13	1.04
	90	**1.57**	2.12	1.69	1.61
6s	80	**0.68**	0.88	0.75	0.69
	90	**1.09**	1.46	1.19	1.13
σ	80		13.9	4.6	3.0
	90		18.6	3.7	2.8

to essentially elevated values of ε_{nl}, and the discrepancies with the exact values may markedly exceed 50%. The comparison of results obtained by using two new potentials reveals that in the case of heavy atoms the single-electron energies calculated with potential U_N are of somewhat lower accuracy than those calculated with potential U_N^q. This is particularly noticeable for the outer shells of considered configurations. This feature of U_N^q is undoubtedly related to the way of obtaining this potential. All the above comments about the single-electron energies are also true of r_{nl} and r_{nl}^{-1}.

For the averaged evaluation of suitability of the investigated potentials, in the last two rows of Table 4 the relative mean square deviations σ from the exact values, in percent, are given, which are defined as

$$\sigma(x_U) = \sqrt{N^{-1}\sum_{nl}\frac{N_{nl}(x_{\mathrm{QR}} - x_U)^2}{x_{\mathrm{QR}}^2}} \cdot 100\% \,. \qquad (14)$$

Here x_U denotes each of the characteristics considered, and the sum is taken over all the shells of each ion. The presented values of σ clearly demonstrate the advantages of the new potentials. Also, some advantage of potential U_N^q over U_N emerges.

4. Conclusion

The transition from fixed values A_0 and B_0 of the universal Gáspár potential parameters to parameters $A(N,I)$ and $B(N,I)$ or $A^q(N,I)$ and $B^q(N,I)$ that depend on the number of electrons in a configuration and the ionization degree has enabled us to obtain radial orbitals which correspond significantly better to the self-consistent solutions of quasirelativistic HF equations at ionization degrees in the range from several units to those maximally possible. The usage of the new universal potentials in obtaining the initial functions allows one to obtain the solutions in the cases when the usage of conventional universal Gáspár potential does not lead to convergence of the iterative process. The potentials, both U_N and U_N^q, give sufficiently adequate radial orbitals in a very wide range of variable ionization degrees and the usage of all three potentials for solving the quasirelativistic HF equations in the program essentially extends its capabilities.

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UNIVERSALUS POTENCIALAS KVAZIRELIATYVISTINĖMS RADIALIOSIOMS ORBITALĖMS

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Santrauka

Pakeitus fiksuotas parametrų A_0 ir B_0 vertes Gáspár potenciale parametrais, priklausančiais nuo elektronų skaičiaus konfigūracijoje bei jonizacijos laipsnio, $A(N,I)$ ir $B(N,I)$ arba $A^q(N,I)$ ir $B^q(N,I)$, žymiai padidėja potencialo tikslumas, o gaunamos orbitalės gerokai efektyviau tinka spręsti kvazireliatyvistines Hatree ir Foko lygtis esant ir mažai, ir maksimaliai jonizacijai. Šis potencialas veiksmingas ir tada, kai nepavyksta iteraciškai išspręsti kvazireliatyvistinių lygčių naudojant paprastąjį Gáspár potencialą atitinkančias pradines funkcijas.