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Orbital collapse and dual states of the 5*g* electrons in superheavy elements

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The problem of orbital collapse of the $5g$ and $6f$ electrons in atoms of superheavy elements (SHEs) is considered. Previously, the presence of the orbital collapse was established for the $4f$ and $5f$ elements of the periodic table. Because of the large centrifugal term for the f and g electrons, the effective radial potential has two wells, one narrow and deep and the other wide but shallow. Depending on the external parameters, the electron can be localized in either the outer well with low binding energy and large average radius or the inner well with higher energy and smaller radius. In this paper, we demonstrate the existence of the orbital collapse for the $5g$ electrons when changing the total angular momentum J of the atom. We also find that for some SHEs two different solutions of the same Dirac-Fock equations may coexist, with the $5g$ electron localized in either the inner or outer well. In both cases, the radial wave functions are nodeless. The problem of the dual-state coexistence is studied by the configuration-interaction method in the Dirac-Fock-Sturm orbital basis as well.

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I. INTRODUCTION

The orbital-collapse phenomenon was first predicted in Refs. [1,2]. It was shown that due to the large size of the repulsive centrifugal term, the effective radial potential acting on the $4f$ and $5f$ electrons can have two potential wells: a deep and narrow inner well and a shallow but wide outer well. The formation of the double-well radial potential is determined by the magnitude of the centrifugal term, which increases quadratically with the growth of the orbital quantum number l. Depending on the external parameters, the f orbital can be localized either in the inner well or in the outer one. When these parameters change, an electron initially localized, for example, in the external well, can move into the internal well. At the same time, the radius of the f orbital sharply decreases tenfold, which can lead to a sudden change in various physical and chemical properties of the atom.

As shown in Refs. [3,4], an orbital collapse of the d electrons can also take place for the excited states of atoms. In Ref. [4], the possibility of the collapse of the g electrons in superheavy elements (SHEs) was predicted as well. Orbital collapse can occur in the isoelectronic sequence of atoms and ions [3,5–7], in a series of sequentially ionized atoms [8], in confined (in cavity) and compressed atoms [9,10], in the homologous sequence of the periodic table [11], as a function of the chemical environment of the atom [12,13], in a series of different atomic terms of the same configuration [14], and so on. The effect of the orbital collapse can manifest itself in various experiments, e.g., in photoabsorption, photoionization, etc. *Ab initio* calculations devoted to the study of the orbital-collapse problem were performed previously both by the nonrelativistic Hartree-Fock [5,15,16] and relativistic Dirac-Fock (DF) [6,7,14,17–19] methods. It should be noted that the central-field approximation, employed in the nonrelativistic and relativistic versions of the Hartree-Fock method, does not allow one to study the orbital-collapse effect for atomic configurations involving more than one electron in the shell of interest (for example, the $4f$ shell). The reason is that in the central-field approximation all electrons in the shell possess the same radial wave function. As a result, the state of the atom with more than one electron in the outer well is certainly energetically inefficient.

As already noted, the orbital collapse usually occurs when some external parameters change. As a consequence, an electron can move from the external well to the internal one. However, in Ref. [17] it was found that within the framework of the DF method two different solutions of the same self-consistent field (SCF) equations can be obtained without changing any external parameters. In one of them, the $4f$ electron is localized in the inner well, whereas in the other it is localized in the outer well. In Ref. [17], the coexistence of two different solutions with the same atomic configuration, the "blow" (localized in the outer well) and the "collapse" (localized in the inner well) ones, was shown for the excited state of lanthanum ([Xe]$6s^2 4f_{5/2}$) and the ground state of europium ([Xe]$6s^2 4f^6_{5/2} 4f_{7/2}$). It is noteworthy that both the blow and collapse $4f$ orbitals are nodeless. They can be obtained as the solutions of the SCF equations, provided the initial approximation is appropriately chosen, and correspond to two different stationary values of the DF energy functional. Thus, the DF operator in the converged SCF equations is also different for these two solutions. That is why the coexistence of two different nodeless orbitals

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with the same quantum numbers does not contradict Sturm's oscillation and separation theorems [20].

In this paper, we investigate the problem of the $5g$-electron collapse in atoms of the eighth-period SHEs. As was shown in our paper [21] and in the papers [22–25], the occupation of the $5g$ shell in the ground state starts at $Z = 125$ and continues up to $Z = 144$ (from the multiconfiguration calculations, it follows that this shell becomes closed at $Z = 145$). Since the DF method allows us to study the collapse for only one electron on the $5g_{7/2}$ shell, we restrict ourselves to the calculations of the ground configuration $[\mathrm{Og}]8s^2 8p^1_{1/2} 6f^3_{5/2} 5g^1_{7/2}$ of the atom with $Z = 125$ as well as the excited configurations $[\mathrm{Og}]8s^2 8p^1_{1/2} 6f^2_{5/2} 5g^1_{7/2}$ and $[\mathrm{Og}]8s^2 8p^2_{1/2} 6f^3_{5/2} 5g^8_{7/2} 5g^1_{9/2}$ for $Z = 124$ and 134, respectively. We also obtain the $6f$-orbital dual solutions for the configuration $[\mathrm{Og}]8s^2 8p^2_{1/2} 5g^{18} 7d^1_{3/2} 6f^6_{5/2} 6f^1_{7/2}$ of the SHE with $Z = 148$. The calculations are performed by the single-configuration DF method [26] for individual atomic terms with the given total angular momentum J as well as in the approximation of the gravity center of the relativistic configuration [27,28]. The dual solutions of the DF equations for the aforementioned elements and configurations are obtained using the different initial approximations. In addition, we reproduce the obtained in Ref. [17] dual solutions, the blow and the collapse ones, for lanthanum ($[\mathrm{Xe}]6s^2 4f_{5/2}$) and europium ($[\mathrm{Xe}]6s^2 4f^6_{5/2} 4f_{7/2}$). Finally, in order to determine the mixing of the different many-electron states with the localized and delocalized $5g$ orbitals, we perform the configuration-interaction (CI) calculations in the basis of the Dirac-Fock-Sturm (DFS) orbitals [29,30].

Atomic units (a.u.) are used throughout the paper unless explicitly stated otherwise.

II. DETAILS OF THE CALCULATIONS

In calculations of the DF one-electron wave functions and energies, we use the many-electron Dirac-Coulomb Hamiltonian $\hat{H}^{\mathrm{DC}}$:

$$\hat{H}^{\mathrm{DC}} = \hat{H}^{\mathrm{D}} + \hat{V}^{\mathrm{C}}, \tag{1}$$

where $\hat{H}^{\mathrm{D}}$ is the sum of the one-electron Dirac Hamiltonians,

$$\hat{H}^{\mathrm{D}} = \sum_{i=1}^{N} [(\boldsymbol{\alpha}_i \cdot \boldsymbol{p}_i)c + (\beta_i - 1)mc^2 + V_n(r_i)]. \tag{2}$$

Here $\boldsymbol{\alpha}$ is a vector of the Dirac matrices and $\hat{V}^{\mathrm{C}}$ is the sum of the Coulomb electron-electron interaction operators:

$$\hat{V}^{\mathrm{C}} = \frac{1}{2} \sum_{i \neq j}^{N} \frac{1}{r_{ij}}. \tag{3}$$

All the calculations are performed with the nuclear potential $V_n(r)$ constructed employing the Fermi model for the nuclear-charge distribution. The root-mean-square (rms) radius of the SHE nucleus (in fm) is given by

$$R = \sqrt{\frac{3}{5}} R_{\mathrm{sphere}}, \quad R_{\mathrm{sphere}} = 1.2 A^{1/3}, \tag{4}$$

where for the nucleon number A we use the approximate formula from Ref. [31]:

$$A = 0.00733 Z^2 + 1.30 Z + 63.6. \tag{5}$$

The value of A obtained from Eq. (5) is rounded to the nearest integer. This choice of the nuclear size is consistent with the one made in Ref. [21]. The rms radii of the La and Eu atoms are taken to be 4.8550 fm ($A = 139$) and 5.1115 fm ($A = 153$), respectively [32].

In our DF calculations, the modified Gáspár [33] potential $V_{\mathrm{G}}(r)$ is used as an initial approximation in the SCF procedure. The modification is made by taking into account the self-interaction correction (SIC) [34]. The employed potential reads as

$$V_{\mathrm{G}}(r) = -\frac{Z}{r} + \frac{N_e - 1}{r}\left(1 - \frac{e^{-\lambda r}}{1 + b r}\right), \tag{6}$$

where $\lambda = 0.2075\, Z^{1/3}$, $b = 1.19\, Z^{1/3}$, and N_e is the number of electrons.

It should be noted that in all the cases the $5g$ orbital obtained by solving the one-electron Dirac equation with the local Gáspár potential $V_{\mathrm{G}}(r)$ is localized in the outer well. In order to manage the convergence process in the SCF calculations, we introduce a real parameter α into the DF operator V_{DF}:

$$V_{\mathrm{DF}}(\alpha, r) = V_{\mathrm{DH}}(r) + \alpha\, V_x, \tag{7}$$

where V_{DH} is the Dirac-Hartree potential with the SIC and V_x is the exchange operator. By changing α from zero to unity, the contribution of the exchange interaction can be controlled. This contribution affects the localization of the $5g$ electron in either the inner or the outer well during the SCF calculations. Naturally, at the end of the SCF procedure, when the convergence is achieved, α must be equal to unity.

The single-configuration and CI total energies are calculated using the Dirac-Coulomb-Breit Hamiltonian $\hat{H}^{\mathrm{DCB}}$:

$$\hat{H}^{\mathrm{DCB}} = \Lambda^{+}\big(\hat{H}^{\mathrm{DC}} + \hat{V}^{\mathrm{B}}\big)\Lambda^{+}, \tag{8}$$

where Λ^{+} is the product of the one-electron projectors on the positive-energy solutions of the DF equations and $\hat{V}^{\mathrm{B}}$ is the Breit-interaction operator:

$$\hat{V}^{\mathrm{B}} = -\frac{1}{2} \sum_{i \neq j}^{N} \frac{1}{2 r_{ij}} \left[\boldsymbol{\alpha}_i \cdot \boldsymbol{\alpha}_j + \frac{(\boldsymbol{\alpha}_i \cdot \boldsymbol{r}_{ij})(\boldsymbol{\alpha}_j \cdot \boldsymbol{r}_{ij})}{r_{ij}^2} \right]. \tag{9}$$

III. EFFECTIVE RADIAL POTENTIAL

In the DF method, the one-electron radial potential V_a^{DF} for the shell a is a nonlocal operator. For this reason, solely to demonstrate the behavior of the effective radial potential, we replace the nonlocal operator V_a^{DF} by the so-called local DF potential $V_a^{\mathrm{loc}}(r)$ [35] (the procedure of its construction is briefly discussed in the Appendix).

An example of the effective radial potential $V_a^{\mathrm{rad}}(r)$ obtained for the SHE with $Z = 125$ with and without taking into account the exchange is shown in Fig. 1. This potential has two wells (for convenience, the outer well is shown in an enlarged scale in the lower right corner). As can be seen from Fig. 1, the exchange potential actually affects only the depth

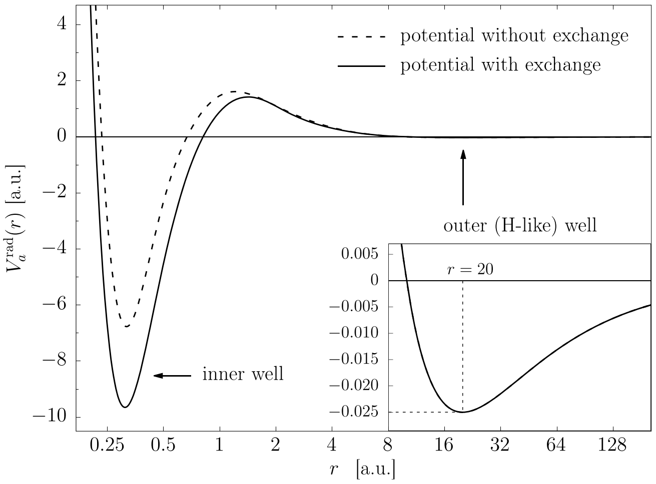

FIG. 1. Effective radial potential $V_a^{\rm rad}(r)$ for the shell $a = 5g_{7/2}$ of the superheavy atom with $Z = 125$. The solid line is the potential with the exchange, while the dashed line is the potential without the exchange.

of the inner well, as it decreases exponentially with increasing the distance.

In the nonrelativistic approximation the effective radial potential $V_a^{\rm rad}(r)$ can be represented as the sum of the local potential $V_a^{\rm loc}(r)$ and the centrifugal term:

$$V_a^{\rm rad}(r) = V_a^{\rm loc}(r) + \frac{l_a(l_a+1)}{2r^2}, \tag{10}$$

where l_a is the orbital quantum number. Because of the rapid exponential decay of the exchange term, the asymptotic form of the local potential $V_a^{\rm loc}(r)$ at large distances is purely Coulombic. Thus, the radial potential $V_a^{\rm rad}(r)$ for a neutral atom in the asymptotic region has the form

$$V_a^{\rm rad}(r) \to -\frac{1}{r} + \frac{l_a(l_a+1)}{2r^2}, \quad r \to \infty. \tag{11}$$

For this reason, for large l_a, the position of the local minimum $r_a^{\rm min}$ of $V_a^{\rm rad}(r)$ corresponding to the outer well and its depth $V_a^{\rm min}$ can be determined with a high degree of accuracy using the expressions

$$r_a^{\rm min} = l_a(l_a+1), \quad V_a^{\rm min} = \frac{1}{2l_a(l_a+1)}. \tag{12}$$

These results are supported by Fig. 1, where for the g orbital one should set $l_a = 4$. Indeed, the minimum of the shallow and wide outer well is located at $r = 20$ a.u., while the depth is of the order of 0.025 a.u. The deep and narrow inner well has the minimum at a small distance $r = 0.32$ a.u. We stress also that in the case of a neutral atom the electron in the outer well can be considered as an electron in the field of a singly charged ion, whose potential at large distances approximately coincides with the Coulomb potential $V_a(r) = -1/r$. Thus, the one-electron energy and the mean radius of the electron in the outer well must be close to the energy $\varepsilon_a^{\rm H}$ and the mean radius $\langle r\rangle_a^{\rm H}$ for the hydrogen atom:

$$\varepsilon_a^{\rm H} = -\frac{1}{2n_a^2}, \quad \langle r\rangle_a^{\rm H} = \frac{1}{2}\left[3n_a^2 - l_a(l_a+1)\right]. \tag{13}$$

TABLE I. $Z = 125$ ([Og]$8s^2 8p_{1/2}^1 6f_{5/2}^3 5g_{7/2}^1$). One-electron energies ε_{5g} and average radii $\langle r\rangle_{5g}$ of the valence $5g_{7/2}$ orbital and the total energies with ($E_{\rm DCB}$) and without ($E_{\rm DC}$) the Breit interaction of the neutral atom. K is the number of energy levels with the given J in the configuration. The energies are shown with the opposite sign. All the values are given in atomic units.

J	K	$-\varepsilon_{5g}$	$\langle r\rangle_{5g}$	$-E_{\rm DC}$	$-E_{\rm DCB}$
1/2	2	0.0200016	27.494	64846.13531	64718.58334
3/2	5	0.0200015	27.494	64846.14377	64718.59179
5/2	6	0.0200017	27.493	64846.14376	64718.59179
7/2	6	0.0200017	27.493	64846.14376	64718.59179
9/2	6	0.0200017	27.493	64846.14376	64718.59179
11/2	5	0.0200019	27.493	64846.14377	64718.59179
13/2	3	0.5387971	0.732	64846.37848	64718.85035
15/2	2	0.5348849	0.732	64846.36810	64718.84021
17/2	1	0.5367741	0.733	64846.37428	64718.84636

where n_a is the principal quantum number. In the case of the $5g$ electron, $\varepsilon_{5g}^{\rm H} = -0.02$ a.u. and $\langle r\rangle_{5g}^{\rm H} = 27.5$ a.u. This statement is confirmed by the direct calculations below.

IV. ORBITAL COLLAPSE

In this section, we discuss the orbital collapse of the $5g$ electron in the course of changing the value of the total angular momentum J on the examples of the ground configuration for $Z = 125$ ([Og]$8s^2 8p_{1/2}^1 6f_{5/2}^3 5g_{7/2}^1$) and the excited configuration for $Z = 124$ ([Og]$8s^2 8p_{1/2}^1 6f_{5/2}^2 5g_{7/2}^1$). In Tables I and II, for each value of the total angular momentum J, the values of the one-electron energies and average radii for the $5g_{7/2}$ shell as well as the total energies of atoms are given for $Z = 125$ and 124, respectively. Here the modified Gáspár potential $V_{\rm G}(r)$ defined in Eq. (6) is used as an initial approximation in the SCF procedure. As it will be shown in Sec. V, this initial approximation does not guarantee that the SCF procedure will produce a solution of the DF equations with the lowest total energy for a given value of the total momentum J.

It can be seen from Table I that for all the values of J from $J = 1/2$ to $11/2$ the $5g$ electron has a very large radius

TABLE II. $Z = 124$ ([Og]$8s^2 8p_{1/2}^1 6f_{5/2}^2 5g_{7/2}^1$). One-electron energies ε_{5g} and average radii $\langle r\rangle_{5g}$ of the valence $5g_{7/2}$ orbital and the total energies with ($E_{\rm DCB}$) and without ($E_{\rm DC}$) the Breit interaction of the neutral atom. The notations are the same as in Table I. All values are given in atomic units.

J	K	$-\varepsilon_{5g}$	$\langle r\rangle_{5g}$	$-E_{\rm DC}$	$-E_{\rm DCB}$
0	1	0.01996061	27.567	63308.54698	63185.57955
1	3	0.01998763	27.520	63308.55467	63185.58716
2	4	0.01999968	27.497	63308.55467	63185.58715
3	5	0.01999626	27.504	63308.55460	63185.58704
4	5	0.01999806	27.499	63308.55462	63185.58706
5	4	0.02001107	27.475	63308.55472	63185.58720
6	3	0.02002020	27.457	63308.55474	63185.58722
7	2	0.24072513	0.799	63308.52478	63185.57950
8	1	0.23380541	0.799	63308.50880	63185.56351

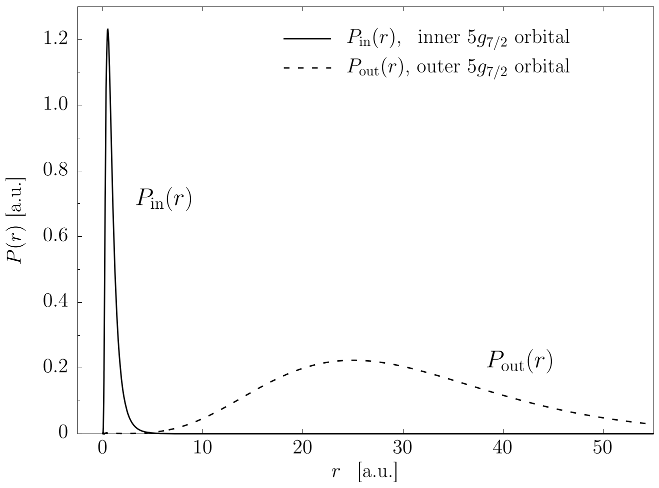

FIG. 2. $Z = 125$ ([Og]$8s^2 8p^1_{1/2} 6f^3_{5/2} 5g^1_{7/2}$). Large components of the radial wave functions: the solid line [$P_{\rm in}(r)$] and dashed line [$P_{\rm out}(r)$] correspond to the $5g_{7/2}$ orbitals localized in the inner and outer wells, respectively. All the values are given in atomic units.

and, hence, it is localized in the outer well. The values of the one-electron energies and mean radii are very close to the hydrogen values (see the discussion at the end of the previous section). For $Z = 125$, the orbital collapse occurs at the transition from $J = 11/2$ to $13/2$. As a result, the one-electron energy $\varepsilon^{\rm H}_{5g}$ increases more than 25 times in magnitude, the mean radius $\langle r\rangle^{\rm H}_{5g}$ decreases almost 40 times, and the total energy changes by about 0.25 a.u.

A similar effect is observed for $Z = 124$, as demonstrated in Table II. In this case, the orbital collapse of the $5g$ orbital occurs at $J \geqslant 7$. However, in contrast to $Z = 125$, in this case the total energies of the atomic terms with $J = 7, 8$ are lower by 0.03 and 0.05 a.u. than the energies of the terms $J \leqslant 6$, for which the $5g$ orbital is localized in the outer well. We note that in Table I the total energies for all J in the range $3/2 \leqslant J \leqslant 11/2$ almost coincide with each other and equal -64718.59179 a.u. This value is very close to the value -64718.59196, which is obtained by summing the total energy of the lowest-energy state of the ion with the $5g$ electron removed ($E^{\rm ion} = -64718.57196$) and the one-electron energy of the $5g_{7/2}$ orbital ($\varepsilon_{5g} = -0.020002$); the corresponding ion has $J_{\rm ion} = 5$. Since a polarization of the ionic electron shells by the $5g$ electron located at a very large distance is very weak, all the states of the neutral atom with the total angular momentum $|J_{\rm ion} - 7/2| \leqslant J \leqslant |J_{\rm ion} + 7/2|$ have practically the same energy.

Figure 2 presents the large components of two radial $5g_{7/2}$ wave functions. One of them, $P_{\rm in}(r)$, is localized in the inner well (the solid line) and the other one, $P_{\rm out}(r)$, is localized in the outer well (the dashed line). Both functions are nodeless, which, as was discussed in Sec. I, does not contradict standard quantum-mechanics theorems concerning the number of wave-function nodes. Indeed, these functions are obtained self-consistently in the independent calculations and correspond to the different DF operators. We note that, although these functions are nodeless, they overlap very weakly nonetheless. Namely, their overlap integral is of the order of 0.001.

TABLE III. La, $Z = 57$ ([Xe]$6s^2 4f^1_{5/2}$). One-electron energies ε_{4f} and average radii $\langle r\rangle_{4f}$ of the valence $4f_{5/2}$ orbital and the total energies of the neutral atom with ($E_{\rm DCB}$) and without ($E_{\rm DC}$) the Breit interaction. The labels "in" and "out" indicate two dual states localized in the inner and outer wells, respectively. The column "Hydrogen" shows the values obtained according to Eq. (13). All the values are given in atomic units.

	Ref. [17]	This paper	Hydrogen
$-\varepsilon^{\rm in}_{4f}$	0.2381	0.23830	
$-\varepsilon^{\rm out}_{4f}$	0.0316	0.03180	0.03125
$\langle r\rangle^{\rm in}_{4f}$	1.2591	1.2591	
$\langle r\rangle^{\rm out}_{4f}$	17.062	17.0614	18.0000
$-E^{\rm in}_{\rm DC}$	8493.6246	8493.5521	
$-E^{\rm out}_{\rm DC}$	8493.5512	8493.4767	
$-E^{\rm in}_{\rm DCB}$		8486.5883	
$-E^{\rm out}_{\rm DCB}$		8486.5096	

V. DUAL STATES

The dual solutions of the DF equations, the blow and the collapse ones, were first obtained in lanthanum ($Z = 57$, [Xe]$6s^2 4f^1_{5/2}$) and europium ($Z = 63$, [Xe]$6s^2 4f^6_{5/2} 4f^1_{7/2}$) in Ref. [17]. It was done by "pushing" the $4f$ electron at the first iterations slightly to the inner or outer wells (see the details in Ref. [17]). In the present paper, we have also found the dual solutions in La and Eu. We calculated the total energies both with ($E_{\rm DCB}$) and without ($E_{\rm DC}$) the Breit interaction in order to compare our data with the results of Ref. [17], where the Breit interaction was not taken into account.

To obtain the $4f$ orbitals localized in the inner well, we have included the full exchange interaction, i.e., $\alpha = 1$ in Eq. (7). The $4f$ orbital localized in the outer well was obtained by the following way. At the first stage, we have performed the SCF calculation excluding the exchange interaction, i.e., $\alpha = 0$. In the no-exchange case, the inner well becomes less deep (see Fig. 1), and the solution of the Hartree equation with the SIC for the $4f$ electron localizes in the outer well. On the next step, we have repeated the SCF calculation with a full exchange, $\alpha = 1$, using the one-electron functions obtained at the first stage as the initial approximation.

The results of the calculations of the dual states in La and Eu are presented in Tables III and IV, respectively. As can be seen from both tables, our data are in a good agreement with the results of Ref. [17]. Despite the fact that the average radii of the $4f$ states obtained in this paper and in Ref. [17] coincide, the one-electron energies differ slightly. This may be related to the use of another coefficient for converting atomic energy units into eV, different nuclear rms, as well as rounding errors. We have used the value 1 a.u. = 27.211386245988 eV taken from Ref. [36] in order to convert the data from Ref. [17] from eV to atomic units.

The one-electron energies ε_{4f} of the $4f$ electron localized in the outer well are about ten times smaller than the corresponding energies for the inner well, whereas the average radii

TABLE IV. Eu, $Z = 63$ ([Xe]$6s^2 4f^6_{5/2} 4f^1_{7/2}$). One-electron energies ε_{4f} and average radii $\langle r \rangle_{4f}$ of the valence $4f_{7/2}$ orbital and the total energies of the neutral atom with (E_{DCB}) and without (E_{DC}) the Breit interaction. The notations are the same as in Table III. All the values are given in atomic units.

	Ref. [17]	This paper	Hydrogen
$-\varepsilon^{\mathrm{in}}_{4f}$	0.3609	0.36073	
$-\varepsilon^{\mathrm{out}}_{4f}$	0.0316	0.03146	0.03125
$\langle r \rangle^{\mathrm{in}}_{4f}$	0.94877	0.94877	
$\langle r \rangle^{\mathrm{out}}_{4f}$	17.709	17.7087	18.0000
$-E^{\mathrm{in}}_{\mathrm{DC}}$	10846.7756	10846.6533	
$-E^{\mathrm{out}}_{\mathrm{DC}}$	10846.6727	10846.5483	
$-E^{\mathrm{in}}_{\mathrm{DCB}}$		10836.8226	
$-E^{\mathrm{out}}_{\mathrm{DCB}}$		10836.7123	

$\langle r \rangle_{4f}$ of the state in the outer well are about 15 times larger than their inner-well counterparts. It should be noted that the one-electron energies and average radii of the $4f$ orbitals in the outer well are close to the hydrogen values shown in the last columns in Tables III and IV. The comparison of the total energies E_{DC} and E_{DCB} of the dual states shows that in both cases the state with the electron localized in the inner well is energetically more favorable.

The dual solutions for the atoms with $Z = 124, 125$ (the corresponding configurations are indicated at the bottom of Table V) have been obtained as follows. As can be seen from Tables I and II, when the Gáspár potential is used as the initial approximation, the collapse occurs in the transitions from the atomic state with total angular momentum $J = 6$ to 7 and from $J = 11/2$ to $13/2$ for $Z = 124$ and 125, respectively. In order to obtain the solutions localized in the inner wells, it is sufficient to take the orbitals obtained for the terms $J = 7$ and $13/2$ as the initial approximations for all the other values of J for $Z = 124$ and 125, respectively. In contrast, to obtain the orbitals localized in the outer wells, the orbitals evaluated for $J = 6$ and $11/2$ can be used as the initial approximations for $Z = 124$ and 125, respectively. For the SHE atoms with $Z = 134$ and 148, also presented in Table V, we have used the procedure described above for the Eu and La atoms.

The second, third, and fourth columns in Table V present the one-electron energies ε_{5g} and the average radii $\langle r \rangle_{5g}$ of the $5g$ orbitals for two different nodeless radial solutions of the same DF equations for the SHE atoms with $Z = 124, 125, 134$. The fifth column shows similar results for two $6f$ orbitals localized in the inner and outer wells for the element with $Z = 148$. Both radial parts of these $6f$ orbitals have two nodes. The notations "in" and "out" mean that the corresponding orbital is localized in the inner and in the outer well, respectively. The data reported in Table V are obtained for the atomic terms J, which have the lowest total energies E_{DCB} for the configurations shown at the bottom of the table.

It can be seen from Table V that the one-electron energies and the average radii of the $5g$ electrons in the outer well are very close to the hydrogen values $\varepsilon^{\mathrm{H}}_{5g} = 0.02$ a.u. and $\langle r \rangle^{\mathrm{H}}_{5g} = 27.5$ a.u., respectively. It is noteworthy that, although the localized in the outer well $6f$ orbital of the atom with $Z = 148$ has two nodes at the points $r_1 = 0.193$ a.u. and $r_2 = 0.510$ a.u., it is very similar to the nodeless hydrogen $4f$ orbital at the larger distances. This is in consistency with the fact that the values of the one-electron energy 0.03169 a.u. and average radius 17.5938 a.u. for the $6f$ orbital in the outer well are close to the hydrogen values $\varepsilon^{\mathrm{H}}_{4f} = 0.03125$ a.u. and $\langle r \rangle^{\mathrm{H}}_{4f} = 18.0$ a.u.

The total SHE energies given in the last two rows of Table V are calculated by diagonalizing the matrix of the DCB Hamiltonian (8) in the basis of the configuration-state functions (CSFs), which are the eigenstates of the $\hat{J}^2$ and $\hat{J}_z$ operators. The CSFs are the linear combinations of the Slater determinants for a single relativistic configuration. This approach is equivalent, in fact, to the single-configuration DF method. The diagonalization of the Hamiltonian matrix is necessary because there are many states with the given value of the total angular momentum J in the complex atomic configurations of the SHE (see Tables I and II).

In the present paper we have obtained two different solutions of the DF equations for the same configuration. An interesting question is how strongly they interact with each other. For this purpose, we have performed the calculations of the total energies and the many-electron wave functions for the [Xe]$6s^2 4f_{5/2}$ configuration of the La atom by the CI

TABLE V. Dual states of the SHE atoms with $Z = 124, 125, 134, 148$. One-electron energies ε_a and average radii $\langle r \rangle_a$ of the collapsing a orbitals and the total energies E_{DCB} of the neutral atoms. The labels "in" and "out" indicate two dual states localized in the inner and outer wells, respectively. All the values are given in atomic units.

Property	$Z = 124$[a] $a = 5g_{7/2}$, $J = 7$	$Z = 125$[b] $a = 5g_{7/2}$, $J = 6.5$	$Z = 134$[c] $a = 5g_{9/2}$, $J = 6$	$Z = 148$[d] $a = 6f_{7/2}$, $J = 4$
$-\varepsilon^{\mathrm{in}}_a$	0.240725	0.538797	0.534678	0.124697
$-\varepsilon^{\mathrm{out}}_a$	0.019998	0.020002	0.020001	0.031689
$\langle r \rangle^{\mathrm{in}}_a$	0.7990	0.7317	0.6304	1.5742
$\langle r \rangle^{\mathrm{out}}_a$	27.5007	27.4934	27.4977	17.5938
$-E^{\mathrm{in}}_{\mathrm{DCB}}$	63185.579	64718.850	80420.248	114885.579
$-E^{\mathrm{out}}_{\mathrm{DCB}}$	63185.587	64718.592	80420.067	114885.578

[a] [Og]$8s^2 8p^1_{1/2} 6f^2_{5/2} 5g^1_{7/2}$.

[b] [Og]$8s^2 8p^1_{1/2} 6f^3_{5/2} 5g^1_{7/2}$.

[c] [Og]$8s^2 8p^2_{1/2} 6f^3_{5/2} 5g^8_{7/2} 5g^1_{9/2}$.

[d] [Og]$8s^2 8p^2_{1/2} 5g^{18} 7d^1_{3/2} 6f^6_{5/2} 6f^1_{7/2}$.

TABLE VI. The CI-DFS calculations of La, $Z = 57$ ([Xe]$6s^2 4f^1_{5/2}$). $E_{\rm CI}$ is the total CI energies, and $q_{4f_{5/2}}$ are the atomic populations of the $4f_{5/2}$ shell. The labels "in" and "out" indicate two dual states. All the values are given in atomic units.

	$-E_{\rm CI}$	$q^{\rm in}_{4f_{5/2}}$	$q^{\rm out}_{4f_{5/2}}$	q_{6s}
In state	8486.7738	0.98766	0.02583	1.83645
Out state	8486.5441	0.00006	0.96557	1.66580

method in the DFS basis [29,30]. The conventional DFS basis contains the one-electron DF functions as occupied and active orbitals as well as a set of virtual DFS orbitals being the solutions of the DFS equations. In our case, two different solutions of the SCF equations specify different mutually nonorthogonal sets of the occupied DF orbitals. To construct a unified basis set of the one-electron functions, we proceed as follows. The radial wave functions of the occupied atomic shells except for the $4f$ shell are defined by

$$P_a(r) = 0.5\big[P_a^{\rm (in)}(r) + P_a^{\rm (out)}(r)\big]$$
$$Q_a(r) = 0.5\big[Q_a^{\rm (in)}(r) + Q_a^{\rm (out)}(r)\big] \qquad (14)$$

where the index a, as before, enumerates the atomic shells, $P_a^{\rm (in)}(r)$ and $Q_a^{\rm (in)}(r)$ are the large and small components of the radial orbitals being the solutions of the DF equations when the $4f$ orbital is localized in the inner well, and $P_a^{\rm (out)}$ and $Q_a^{\rm (out)}$ are the same quantities for the case when the $4f$ orbital is in the outer well. Then, both $4f_{5/2}$ orbitals and a set of the virtual DFS orbitals are added to this unified basis, followed by an orthonormalization. In our calculations, besides the occupied DF orbitals, we have included $5d$ as the active orbital and $7s$–$10s$, $6p$–$10p$, $6d$–$9d$, $5f$–$9f$, and $5g$–$6g$ as the virtual DFS ones.

To interpret our results, we employed an atomic-population analysis based on the use of a one-particle density matrix ρ in the atomic basis, or, in other words, the first-order reduced density matrix:

$$\rho_{ij} = \langle \Psi \mid \hat{a}_i^+ \, \hat{a}_j \mid \Psi \rangle, \qquad q_a = \sum_{i \in a} \rho_{ii}, \qquad (15)$$

where Ψ is the many-electron wave function, $\hat{a}_i^+$ and $\hat{a}_j$ are the creation and annihilation operators of the ith and jth electron, respectively, q_a is the population of the shell a, and the index i enumerates all atomic orbitals of the shell a. Based on the population analysis, we have identified two eigenvectors of the CI matrix that give the configuration closest to [Xe]$6s^2 4f^1_{5/2}$. One of these states, where the $4f$ electron is localized in the inner well, we denote as the "in-state," and the other one, where the $4f$ electron is localized in the outer well, is referred to as the "out-state." As can be seen from Table VI, the in-state and out-state interact weakly. This can be explained by the small overlap of the $4f$ orbitals localized in the inner and outer wells. We also note that in this case the in-state is energetically more favorable.

It should be noted, however, that our conclusion that the interaction between the in-state and the out-state is weak should be considered as preliminary. It is based on the calculations with a moderate-size configuration space. The ultimate answer can be obtained from the calculations with a larger configuration space.

VI. CONCLUSIONS

In the present paper, it was found that the effective $5g$ or $6f$ radial potentials for the eighth-period elements of the periodic table with the atomic numbers $Z = 125$, 124, 134, and 148 are double-well ones. As a consequence, the orbital collapse is observed in these elements. For example, it has been shown that, when the atomic term J is changed in atoms with $Z = 124$, 125, the wave function of the $5g$ electron, localized in the wide and shallow outer well, shrinks strongly and turns out to be localized in the inner well. As a result, the average radius of the $5g$ orbital decreases by a factor of almost 40, and the binding energy of the $5g$ electron increases by a factor of more than 25. It is shown that the state of the $5g$ electron in the outer well can be described with high accuracy by the hydrogen wave function. The state of the neutral atom with one electron in the outer well can be interpreted as the motion of an electron in the Coulomb field of a singly charged positive ion. The orbital-collapse effect for the $5g$ electrons is manifested more strongly than for the $4f$ and $6f$ electrons because of the larger magnitude of the centrifugal term.

In this paper, we have confirmed the coexistence of the dual SCF solutions of the same DF equations for La and Eu atoms observed earlier in Ref. [17]. In one of these solutions, the $4f$ electron is localized in the inner well, whereas in the other solution it is localized in the outer well. The similar dual states were found for the $5g$ electrons in the atoms with $Z = 124$, 125, 134 and for the $6f$ electron in the atom with $Z = 148$.

In order to verify the coexistence of the dual states in the many-electron approach, on the example of the [Xe]$6s^2 4f^1_{5/2}$ configuration of the La atom, we have performed the CI calculations including both states into the many-electron CSF basis. Using the atomic-population analysis, it was found that both dual states remain sufficiently stable when the configuration interaction is taken into account. The final answer on the question whether these dual states are actually physically observable requires large-scale multiconfiguration calculations.

In all examples of the orbital collapse and coexistence of the dual solutions, we considered the configurations with one electron in the $4f_{5/2}$, $4f_{7/2}$, $5g_{7/2}$, $5g_{9/2}$, and $6f_{7/2}$ shells. This does not mean that these effects cannot be observed for a larger number of electrons in these shells. However, in these cases, it is necessary to discard the central-field approximation, according to which the radial functions of the different orbitals of the same shell must be identical, and a configuration with more than one electron in the outer well is energetically unfavorable.

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APPENDIX: LOCAL DIRAC-FOCK POTENTIAL

The DF equations for the large $P_a(r)$ and small $Q_a(r)$ radial components of the one-electron wave function are given by

$$\left(-\frac{d}{dr}+\frac{\kappa_a}{r}\right)Q_a+\left(V_n+\frac{Y_a(r)}{r}-\varepsilon_a\right)P_a=-\frac{X^Q(r)}{r},$$
$$\left(\frac{d}{dr}+\frac{\kappa_a}{r}\right)P_a+\left(V_n+\frac{Y_a(r)}{r}-\varepsilon_a-2c^2\right)Q_a=-\frac{X^P(r)}{r} \tag{A1}$$

where ε_a is the one-electron energy, κ_a is the relativistic angular quantum number, $V_n(r)$ is the nuclear potential, and $Y_a(r)/r$ is the screening Coulomb potential [27,28]. The functions $X^Q(r)/r$ and $X^P(r)/r$ include the result of the action of the exchange-interaction operator on the radial wave functions P_a and Q_a and the contribution from the nondiagonal Lagrange multipliers. The local DF potential is defined by

$$V_a^{\text{loc}}(r)=V_n(r)+\frac{Y_a(r)}{r}+V_a^{\text{ex}}(r), \tag{A2}$$

where

$$V_a^{\text{ex}}(r)=\frac{1}{\bar{\rho}_a(r)}\sum_{\substack{b\\(n_b\leqslant n_a)}}\delta_{\kappa_b,\kappa_a}\,w_{ab}\left[\frac{X_b^Q(r)}{r}P_b+\frac{X_b^P(r)}{r}Q_b\right]. \tag{A3}$$

Here n_a is the principal quantum number of the shell a, and

$$\bar{\rho}_a(r)=\sum_{\substack{b\\(n_b\leqslant n_a)}}\delta_{\kappa_b,\kappa_a}\,w_{ab}\left[P_b^2(r)+Q_b^2(r)\right]. \tag{A4}$$

In these calculations, the weights w_{ab} were chosen to be equal to the ratio of the one-electron energies:

$$w_{ab}=\varepsilon_a/\varepsilon_b. \tag{A5}$$

A more detailed description of the local DF potential is given in Ref. [35].

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