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Orbital collapse of the $5g$-electrons in the superheavy elements of the 8th period

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The presence of the orbital collapse of the g-orbitals in the excited state of the atom with the nuclear charge number $Z = 124$ and in the ground state of the atom with $Z = 125$, which belong to the 8th period of the extended periodic table, is demonstrated. In both cases, the orbital collapse occurs within the same configuration when increasing the total angular momentum J, which characterizes the relativistic term of the atom in the jj coupling. All calculations are performed by means of the relativistic Dirac-Fock method.

Keywords: Superheavy elements, g electrons, orbital collapse, multielectron relativistic terms, Dirac-Fock method.

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Introduction

The orbital collapse of excited states of lanthanides and other atoms and ions with open $4f$ and $3d$ shells is understood as the process of a sharp decrease in the radius of $4f$ or $3d$ orbitals when various parameters that determine the state of the system change. This phenomenon was predicted in the paper [1], where it was shown that due to the large value of the centrifugal term, the effective radial f potential can have two quantum wells: a deep and narrow inner well and a shallow but wide outer well. The formation of a double-well potential depends on the magnitude of the centrifugal term, which increases quadratically with increasing 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 localized, for example, in an outer well, can move into an inner well. In this case, the radius of the f orbital will sharply decrease tens of times, which can lead to abrupt changes in various physical and chemical properties of the atom. As was shown in papers [2,3], for excited states of atoms, orbital collapse of d electrons can also occur. The paper [3] predicted the potential presence of collapse in g electrons of superheavy elements (SHE).

The first calculations by the Hartree-Fock method, in which a double-well radial potential was obtained and the presence of collapse of f electrons was demonstrated, were performed in papers [4–7]. In the papers [4,5] the non-relativistic Hartree-Fock method was used. The collapse of $4f$ electrons in the excited state of the La atom and in the ground state of Eu was calculated by the Dirac-Fock method in papers [6,7]. The orbital collapse in isoelectronic series of neutral atoms and ions was studied in papers [8–12]. In particular, the collapse of $4f$ electrons in the excited $4d^9 4f^1$ configuration of the isoelectronic Xe series was calculated by the nonrelativistic Hartree-Fock method in paper [9]. The isoelectronic series of the Cs atom with $[\mathrm{Xe}]4f^1$ and $[\mathrm{Xe}]5d^1$ configurations, where there is the orbital collapse of $4f$ and $5d$ electrons, was calculated by the Dirac-Fock method in paper [10]. In a later work [12], the collapse of the $5f$ and $5d$ orbitals in the isoelectronic series of the Yb^{1+} ion was studied by the Dirac-Fock method together with the relativistic model potential method. The orbital collapse is also observed for „compressed atoms“ with boundary conditions in a box as the size of the box decreases [13].

In this paper, we investigated the problem of the collapse of g electrons of superheavy element atoms of the 8th period with atomic numbers $Z = 124$ and $Z = 125$. As it was shown in our paper [14] and in earlier papers [15,16], the $5g$ shell in the ground configuration is filled starting from $Z = 125$ and continues to be filled up to $Z = 144$ (from the multi-configuration calculation it follows that this shell becomes closed at $Z = 145$). However, standard single-configuration and multi-configuration Dirac-Fock methods do not allow one to study the problem of the localization of one $g_{7/2}$ electron in an external well for a configuration containing several $g_{7/2}$ electrons, since the radial wave functions of all electrons of one shell are the same in these methods. In this regard, in this paper we focused on studying the orbital collapse for the ground configuration $[\mathrm{Og}]8s^2 8p^1_{1/2} 6f^3_{5/2} 5g^1_{7/2}$ of the atom with $Z = 125$ and for the excited configuration $[\mathrm{Og}]8s^2 8p^1_{1/2} 6f^2_{5/2} 5g^1_{7/2}$ of the

atom with $Z = 124$. Calculations were performed using the single-configuration Dirac-Fock method [17,18] for individual terms, as well as in the approximation of the center of gravity of the configuration. We calculated both the total atomic energies and single-electron energies and the average radii of valence g orbitals for various multielectron terms with the total angular momentum $J = 1/2,\ 3/2,\ \ldots,\ 17/2$ for $Z = 125$ and with $J = 0,\ 1,\ \ldots,\ 8$ for $Z = 124$. The calculation results indicate the presence of orbital collapse of the g electron, which occurs as the value of the quantum number J increases.

Atomic system of units is used herein ($\hbar = e = m = 1$).

1. Effective radial potential

In this section, we describe the procedure for constructing an approximate effective radial potential $V_a^{\rm rad}(r)$ for a visual interpretation of the orbital collapse problem for of the $5g$ orbital in the superheavy elements of the 8th period.

In the Dirac-Fock method, the potential $V_a^{\rm DF}$, which acts on the single-electron shell wave function a, is a nonlocal operator, since the exchange operator is nonlocal. In order to study the properties of the effective radial potential, we replace the nonlocal operator $V_a^{\rm DF}$ with the so-called local Dirac-Fock potential $V_a(r)$. This potential was proposed in the paper [19] (equation (56)). We determine the effective radial potential $V_a^{\rm rad}(r)$, which acts on an electron located on the shell a with the orbital quantum number l_a, by adding to the local potential $V_a(r)$ the nonrelativistic expression for the centrifugal term:

$$V_a^{\rm rad}(r) = V_a(r) + \frac{l_a(l_a+1)}{2r^2}. \qquad (1)$$

The figure shows a graph of the effective radial potential $V_a^{\rm rad}(r)$. As can be seen from the figure, the potential $V_a^{\rm rad}(r)$ has two wells (for convenience, the outer well is shown enlarged along the vertical axis in the inset in the lower right corner of the figure). One of the wells is deep and narrow and has a minimum in the region of small distances at $r = 0.32$ a.u., the other is shallow, with a depth of approximately 0.025 a.u., but wide, with a minimum at the point $r = 20$ a.u.

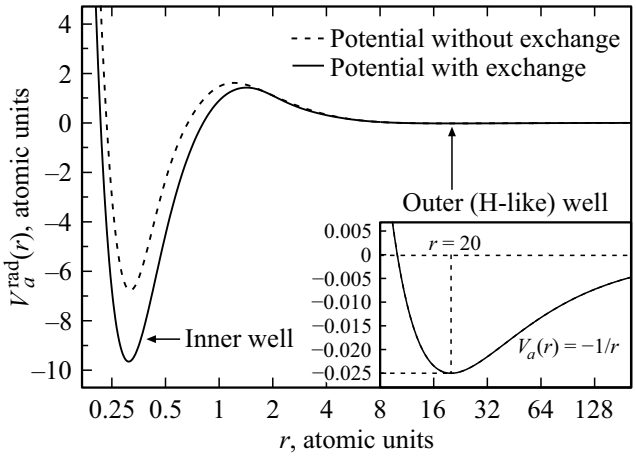
The asymptotic behavior of the local potential $V_a(r)$ at large distances is purely Coulomb, therefore the effective radial potential $V_a^{\rm rad}$ in the asymptotic area for a neutral atom has the form

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

The radial potential (2) has a wide well with a minimum at point $r_{\min} = l_a(l_a+1)$ and depth $V_{\min} = [2l_a(l_a+1)]^{-1}$. For the $5g$ potential ($l_a = 4$) we obtain

$$r_{\min} = 20 \text{ a.u.}, \qquad V_{\min} = 0.025 \text{ a.u.} \qquad (3)$$

The position of the minimum $r_{\min}$ and the depth at the minimum point $V_{\min}$, obtained for the external well within the Dirac-Fock method, differ from the given analytical values by amounts of the order of 10^{-5} a.u. and 10^{-9} a.u., respectively. From this we can conclude that the external well for the g electron is indeed located in the asymptotic area, where the local Dirac-Fock potential is almost Coulomb $V_a(r) = -1/r$



Effective radial potential $V_a^{\rm rad}(r)$ for the $a = 5g_{7/2}$ shell in the superheavy element atom with $Z = 125$. Solid line — potential with exchange, dashed line — without exchange.

In our calculations of the total and single-electron energies and average radii, the local Dirac-Fock operator approximation was not used. Depending on the value of the total angular momentum J, the Dirac-Fock wave function turns out to be localized either in the inner or outer wells.

2. Orbital collapse. Results and discussion

In this paper, using the single-configuration many determinant Dirac-Fock method, we performed calculations of various relativistic terms of atoms of the 8th period with atomic numbers $Z = 124$ and $Z = 125$. The so-called Dirac-Coulomb Hamiltonian was used as the Hamiltonian of the atom (not taking into account the Breit interaction). In both cases, we considered configurations with one valence g electron, namely, $[\mathrm{Og}]8s^2 8p^1_{1/2} 6f^3_{5/2} 5g^1_{7/2}$ and $[\mathrm{Og}]8s^2 8p^1_{1/2} 6f^2_{5/2} 5g^1_{7/2}$ for atoms with $Z = 125$ and $Z = 124$, respectively.

The configurations listed above have several open shells, which leads to the appearance of a large number of atomic terms, some of which coincide. Table 1 shows all the terms (J) of both configurations and their multiplicities (K). Here, by term multiplicity we mean the number of repeated terms. In this paper, we performed the calculations of the lowest energy term for all values of the total angular momentum J in the basis of Slater determinants of one configuration.

Tables 2 and 3 show our calculated values of the single-electron energies and average radii of the $5g_{7/2}$ shell and

Table 1. List of values of the total angular momentum J (relativistic terms) and the number K of repeating (identical) terms of the configurations $[\mathrm{Og}]8s^2 8p^1_{1/2} 6f^3_{5/2} 5g^1_{7/2}$ of the $Z = 125$ atom and $[\mathrm{Og}]8s^2 8p^1_{1/2} 6f^2_{5/2} 5g^1_{7/2}$ of the $Z = 124$ atom

$Z = 125$		$Z = 124$	
Term J	K	Term J	K
1/2	2	0	1
3/2	5	1	3
5/2	6	2	4
7/2	6	3	5
9/2	6	4	5
11/2	5	5	4
13/2	3	6	3
15/2	2	7	2
17/2	1	8	1

Table 2. Single-electron energies ε_{5g} and average radii $\langle r\rangle_{5g}$ of the valence $5g_{7/2}$ orbital, as well as total energies of the neutral atom with $Z = 125$. All values are given in atomic units

Term (J)	ε_{5g}	$\langle r\rangle_{5g}$	Total Energy
1/2	−0.0200016	27.494	−64846.13530
3/2	−0.0200015	27.494	−64846.14377
5/2	−0.0200017	27.493	−64846.14376
7/2	−0.0200017	27.493	−64846.14376
9/2	−0.0200017	27.493	−64846.14376
11/2	−0.0200019	27.493	−64846.14377
13/2	−0.5387971	0.732	−64846.37848
15/2	−0.5348849	0.732	−64846.36810
17/2	−0.5367741	0.733	−64846.37428

Table 3. Single-electron energies ε_{5g} and average radii $\langle r\rangle_{5g}$ of the valence $5g_{7/2}$ orbital, as well as total energies of the neutral atom with $Z = 124$. All values are given in atomic units

Term (J)	ε_{5g}	$\langle r\rangle_{5g}$	Total Energy
0	−0.01996061	27.567	−63308.54698
1	−0.01998763	27.520	−63308.55467
2	−0.01999968	27.497	−63308.55467
3	−0.01999626	27.504	−63308.55460
4	−0.01999806	27.499	−63308.55462
5	−0.02001107	27.475	−63308.55472
6	−0.02002020	27.457	−63308.55474
7	−0.24072513	0.799	−63308.52478
8	−0.23380541	0.799	−63308.50880

the total atomic energies for each value J. From Table 2 it is clear that for all values, starting from $J = 1/2$ up to $J = 11/2$, the orbital of $5g$ electron has a very large radius and is localized in the outer well. An electron in the outer well can be considered as an electron with a large orbit radius placed in the field of a singly charged ion, the potential of which at large distances coincides with good accuracy with the Coulomb one, $V_{5g}(r) = -1/r$. The exchange potential with the electrons of the ion is practically zero due to the negligible overlap of the $5g$ orbital of large radius with the orbitals of the ion. This overlap is still small because near zero the radial part of the $g_{7/2}$ orbital behaves like r^5. Thus, the energy and average radius of the electron in the outer well should be close to the energy $\varepsilon^{\mathrm{H}}_{5g}$ and the average radius $\langle r\rangle^{\mathrm{H}}_{5g}$ of the hydrogen atom in the state with the principal quantum number $n = 5$:

$$\varepsilon^{\mathrm{H}}_{5g} = -\frac{1}{2n^2} = -0.02 \text{ a.u.},$$

$$\langle r\rangle^{\mathrm{H}}_{5g} = \frac{1}{2}\left[3n^2 - l(l+1)\right] = 27.5 \text{ a.u.} \qquad (4)$$

The value of the single-electron energy of the $5g$ orbital localized in the outer well, which is presented in Table 2, coincides with the hydrogen value by five digits after the decimal point, and the average radius differs by one at the fourth significant digit. It is worth paying attention to the fact that the total energies of the terms with $3/2 \leqslant J \leqslant 11/2$ of the atom with $Z = 125$ are almost similar. This fact is also explained by the lack of overlap between the wave functions of the g electron in the outer well and the wave functions of the ion.

As can be seen from Table 2, for the terms with $J = 13/2$, $15/2$ and $17/2$, there is a collapse of the $5g_{7/2}$ orbital, which results is the localized on $5g$ orbital in the inner well. In this case, there is a sharp (more than 30 times) decrease in the average radius and an increase (more than 20 times) in the binding energy of the $5g$ orbital. The total energy of the $J \geqslant 13/2$ terms turns out to be lower than that of the $J \leqslant 11/2$ terms by approximately 0.23 a.u.

A similar collapse is observed for the $[\mathrm{Og}]8s^2 8p^1_{1/2} 6f^2_{5/2} 5g^1_{7/2}$ configuration of the atom with $Z = 124$, which is demonstrated in Table 3. In this case, the orbital collapse of the $5g$ orbital occurs at $J \geqslant 7$. Here, on the contrary, the energies of the $J = 7$ and 8 terms, where there is a collapse, lie higher than the energies of the $J \leqslant 6$ terms with the delocalized $5g$ orbital.

3. Conclusion

It was found that in atoms of the 8th period with atomic numbers $Z = 125$ and $Z = 124$ for the configurations containing one $5g_{7/2}$ electron, the effective radial potential is double-well and when the configuration term changes, the wave function of the g electron, localized in a wide and shallow outer well, sharply shrinks and becomes localized in the inner well. In this case, the average radius of the g orbital decreases by more than 30 times, and the binding energy of the g electron increases by more than 20 times. The state of the $5g$ electron in the outer well can be described with high accuracy by the hydrogen-like wave function.

The orbital collapse of $5g$ orbitals is an analogue of the previously widely studied collapse of $4f$ orbitals of atoms

and ions with the unfilled $4f$ shell. It should also be noted that in the study of the orbital collapse of $4f$ orbitals in the configurations $6s^2 4f_{5/2}$ of the La atom and $6s^2 4f^6_{5/2} 4f_{7/2}$ of the Eu atom, two solutions of the Dirac-Fock equations were discovered, describing two different states of the atom. Both solutions were obtained using different initial approximations in a process of self-consistency for the same configuration and the same term. In one of the states, the $4f$ electron was localized in the outer hydrogen-like well, and in the other state, in the inner deep well.

In this paper, in all calculations, the initial approximation in the self-consistency procedure was based on the use of the modified Gaspar potential [20]. The modification consisted in taking into account the self-interaction correction [21] (equation (3)):

$$V_{\mathrm{G}}(r) = -\frac{Z}{r} + \frac{N_e - 1}{r}\left(1 - \frac{e^{-\lambda r}}{1 + A r}\right), \qquad (5)$$

where $\lambda = 0.2075\, Z^{1/3}$ and $A = 1.19\, Z^{1/3}$, and N_e is the number of electorns. We will discuss the issue of the existence of other solutions to the Dirac-Fock equations obtained using other initial approximations in a subsequent publication.

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Conflict of interest

The authors declare that they have no conflict of interest.

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