

Specific features of the electronic structure of super-heavy elements of the 8th period

Ilya Tupitsyn

Atomic group members

Aleksei Malyshev, Yury Kozhedub, Dmitry Glazov, Michael Kaygorodov
and Vladimir Shabaev

Students: Igor Savelyev, Daniil Usov, Anton Ryzhkov and Nikita Dulaev

05 September, 2023

- Introduction
- Ground state electron configurations of superheavy elements (SHE)
- Relativistic effects in the electronic structure of SHE
- Electron density distribution in SHE. Electron localization function (ELF)
- Orbital collapse of the 5g-states
- Dual solutions of the Dirac-Fock equation for 5g-electrons
- Summary and Outlook

Introduction. Pekka Pyykkö periodic table

Periodic Table 1-172

Period 1	Periodic Table 1-172																18 Orbitals		
1	1 H	2											13	14	15	16	17	2 He	1s
2	3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne	2s2p
3	11 Na	12 Mg	3	4	5	6	7	8	9	10	11	12	13 Al	14 Si	15 P	16 S	17 Cl	18 Ar	3s3p
4	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr	4s3d4p
5	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe	5s4d5p
6	55 Cs	56 Ba	57-71 La-Lu	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn	6s5d6p
7	87 Fr	88 Ra	89-103 Ac-Lr	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113	114	115	116	117	118	7s6d7p
8	119	120	121-171	156	157	158	159	160	161	162	163	164	139	140	169	170	171	172	8s7d8p
9	165	166											167	168			9s9p		
6	57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu				4f
7	89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr				5f
8	141	142	143	144	145	146	147	148	149	150	151	152	153	154	155				6f
8	121	122	123	124	125	126	127	128	129	130	131	132	133	134	135	136	137	138	5g

The table is taken from P. Pyykkö Chem. Rev. 112, 371 (2012).

$$Z = 118 \quad 7s^2 7p^6$$

$$Z = 119 - 121$$

$$8s \ 8p$$

$$Z = 145 - 158$$

$$7d \ 6f \ 8p$$

$$Z = 122 - 124$$

$$8p \ 7d \ 6f$$

$$Z = 159 - 166$$

$$7d \ 8p \ 9s$$

$$Z = 125 - 144$$

$$8p \ 7d \ 6f \ 5g$$

$$Z = 167 - 172$$

$$7d \ 8p \ 9s \ 9p$$

In this work, the results of the electronic-structure calculations for a number of super-heavy elements (SHE) of the 7th and 8th periods with atomic numbers $110 \leq Z \leq 170$ and their lighter homologs are performed [1-6].

- Ground state electron configurations of superheavy elements (SHE)
- Ionization potentials
- Electron affinities
- One-particle electron density. Root-mean-square radii (RMS) and widths of the electron-density distribution of valence shells
- Shannon entropy
- Electron localization functions (ELF)
- Quantum electrodynamics (QED) corrections ($110 \leq Z \leq 170$). [5]

1. M. Y. Kaygorodov et al., *Phys. Rev. A* 104, 012819 (2021)
2. I. I. Tupitsyn et al., *Optics and Spectroscopy* 129, 1038 (2021)
3. M. Y. Kaygorodov et al., *Phys. Rev. A* 105, 062805 (2022)
4. I. I. Tupitsyn et al., *Optics and Spectroscopy*, 130, 1022 (2022)
5. A. V. Malyshev et al., *Phys. Rev. A* 106, 012806 (2022)
6. I. M. Savelyev et al., *Phys. Rev. A*, 107, 042803 (2023)

Introduction. Specific features of electronic structure and chemical properties of super-heavy elements of the 7th and 8th periods

How Far Does the Periodic Table Go?

The electronic structure of SHEs is unique in several aspects:

- The Dirac equation for a point nucleus has no solution, starting from $Z=137$. However, if we take into account the finite size of the nucleus, then the solution exists up to the critical value $Z=173$, when $1s$ -level dives into the negative Dirac continuum.
- The concept of the ground configuration for the elements of the 8th period is no longer well-defined, since sets of relativistic atomic terms of different configurations are overlapping [1].
- Strong relativistic effects cause **contraction of the $s_{1/2}$ - and $p_{1/2}$ - orbitals**, i.e., the shift of the maximum of the density distribution of these shells to lower values of the radius and an increase in the binding energies of these electrons.
- Spin-orbital splitting of valence p -shells reaches up about 10 eV for the $7p$ - orbital in Og ($Z=118$) and about 75 eV for the $8p$ -orbital in element with atomic number $Z=165$.

[1] *I. M. Savelyev et al., Phys. Rev. A, 107, 042803 (2023)*

Introduction. Specific features of electronic structure and chemical properties of super-heavy elements of the 7th and 8th periods

- Due to the strong contraction of s- and $p_{1/2}$ -shells and the huge spin-orbit splitting, the $8p_{3/2}$ -shell of elements of the 8th period is populated only starting from $Z=167$, after filling the 9s-shell.
- Example of the atom Og

Og is 118'th element of the 7th period of the 18-th group of noble (inert) gases with configuration $[\text{Rn}] 5f^{14} 6d^{10} 7s^2 7p^6$.

Due to the strong relativistic contraction, the radial distribution of the electron density of the valence $7p_{1/2}$ -shell of the Og atom starts to overlap with the outer core shells.

As a result, the Electronic Localization Function (ELF) is close to 0.5 in the valence region, as for a homogeneous electron gas. In Ref. [1] this effect in Og was interpreted as smearing out the valence electron density distribution and its approaching to the case of **the homogeneous electron gas**.

[1] *P. Jerabek, B. Schuetrumpf, P. Schwerdtfeger, and W. Nazarewicz, Phys. Rev. Lett. 120, 053001 (2018).*

Introduction. Specific features of electronic structure and chemical properties of super-heavy elements of the 7th and 8th periods

- Formally, the 114th element of the 7th period with the configuration $7s^2 7p^2$ is a homologue of carbon $2s^2 2p^2$ and belongs to the 14th group. However, the spin-orbit splitting of the valence p-orbital in carbon is of the order of 6 meV, and in the 114th element of the order of 6 eV, i.e. **about 1000 times greater**.

For this reason the $7p_{3/2}$ -orbital of the 114th element is not populated with electrons and cannot take part in formation of chemical bonds, in particular **cannot take part in the formation of sp^3 hybridization**.

- Starting from the $Z = 125$ element to $Z=142$, the 5g-shell with the large angular momentum ($l = 4$) is occupied with valence electrons.

The effective radial potential for the 5g-electron, which includes a large centrifugal repulsive term, has two potential wells which leads to the so-called **orbital collapse**.

In our work, we used two independent theoretical calculation methods.

- **Configuration Interaction Dirac-Fock-Sturm method (CI-DFS)**

At the first step, to obtain the one-electron wave functions for the occupied atomic shells, we use the Dirac-Fock method. Then the DFS orbitals are obtained by solving the DFS equations for the vacant shells. At the last step, the relativistic CI+MBPT method is used to obtain the many-electron wave functions and the total energies.

- **Fock Space Coupled-Cluster method (FS-CC)**

DIRAC, a relativistic ab initio electronic structure program, Release DIRAC21 (2021), <http://www.diracprogram.org>. FS-CC method, in contrast to the one-configuration coupled-cluster method is capable of providing not only the ground-state energy of an N-electron system, but also an important fraction of system's excitation spectrum, including ionization potentials, electron affinities, etc.

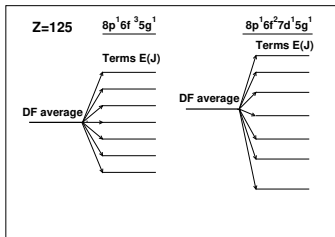
- **To evaluate the QED correction we use the model QED operator approach[1].**

In our recent work [2], the scope of the QEDMOD potential is extended to the region $120 \leq Z \leq 170$.

1. V.M. Shabaev, I.I. Tupitsyn, V.A. Yerokhin, *Comput.Phys.Commun.* 189, 175 (2015)
2. A. V. Malyshev et al., *Phys. Rev. A* 106, 012806 (2022)

Ground state configurations

How do we define the ground state configuration?



The ground configuration is the configuration with the lowest average energy E^{av}

The ground state level is the level with the lowest $E(J)$

$Z = 125$. The lowest Dirac-Fock energy levels within configuration average approximation and for the relativistic terms

Configuration		$E_{\text{DF}}^{\text{av}}$ [a.u.]	J	$E_{\text{DF}}(J)$ [a.u.]
$8p^1 6f^3 5g^1$	E_1	-64627.549597	6.5	-64627.614303
$8p^1 6f^2 7d^1 5g^1$	E_2	-64627.542119	8.5	-64627.638846
	$\Delta E = E_2 - E_1$	0.007478		-0.024543

These configurations have different parity and do not mix.

Ground state configurations

For $Z = 126$ the configurations with the lowest Dirac-Fock (DF) energies within the configuration average approximation are

Configuration	E_{DF}^{av} [a.u.]
$8p^17d^16f^25g^2$	-66298.183666
$8p^16f^35g^2$.183121
$8p^16f^45g^1$.168137
$8p^26f^25g^2$.146963
$8p^17d^26f^15g^2$.114149

The energies of the configurations $8p^17d^16f^25g^2$ and $8p^16f^35g^2$ are almost the same.

- $8p^26f^25g^2$ Mann et al., 1970 (DF)
- $8p^17d^16f^25g^2$ Fricke et al., 1977 (DFS)
- $8p^16f^45g^1$ Umemoto and Saito, 1997 (DF+PZ SIC)
- $8p^16f^35g^2$ (0.98) Nefedov, M. Trzhaskovskaya, 2006 (MCDF)
- $8p^17d^16f^25g^2$ Zhou et al., 2017 (DF)

Таблица: One-electron energies $\varepsilon(nlj)$ and spin-orbit splitting Δ_{SO} [eV]

7-th period			
Z	$\varepsilon(7p_{1/2})$	$\varepsilon(7p_{3/2})$	Δ_{SO}
114	10.4	4.5	5.9
116	14.3	6.1	8.2
118	20.1	8.3	11.8
8-th period			
Z	$\varepsilon(8p_{1/2})$	$\varepsilon(8p_{3/2})$	Δ_{SO}
125	5.3	2.4	2.9
144	13.8	2.7	11.1
145	16.2	2.7	13.5
164	69.9	3.6	66.3
165	79.7	5.0	74.7
166	90.1	6.6	83.5

Shannon entropy as a measure of localization of atomic valence states

According to the formula of K. Shannon [1], the amount of information is defined as:

$$S = - \sum_{i=1}^N p_i \ln p_i \quad (1)$$

where N is the number of random events, p_i is the probability of the i -th event and

$$\sum_{i=1}^N p_i = 1. \quad (2)$$

The *minimum value of S* is reached for the deterministic event when one of the probabilities of p_i is 1, and the rest are zero. In this case, $S = S_{\min} = 0$.

The *maximum value of S* is reached for an equally probable distribution $p_i = 1/N$. Then, $S_{\max} = \ln(N)$

$$0 \leq S \leq \ln(N) \quad (3)$$

For continuous distribution

$$S = - \int d\mathbf{r} \ln(\rho(\mathbf{r})) \rho(\mathbf{r}), \quad \int d\mathbf{r} \rho(\mathbf{r}) = 1. \quad (4)$$

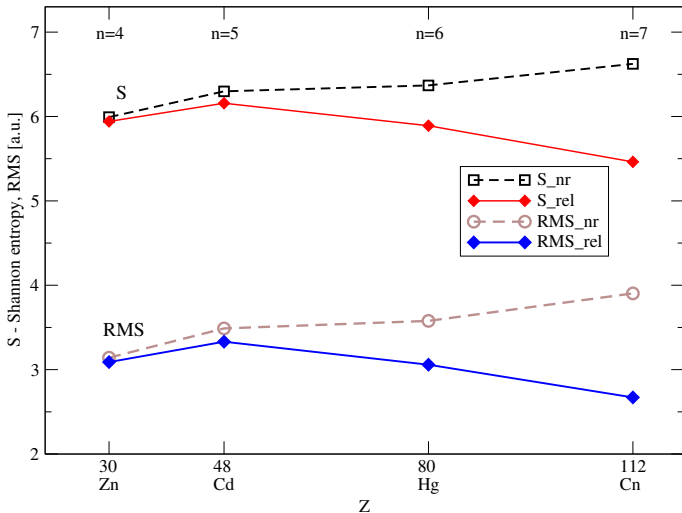
The Shannon entropy increases with increasing delocalization of the valence states.

[1] C.E. Shannon, *Bell Syst. Tech. J.* 27, 379; 623 (1948).

12th group of elements

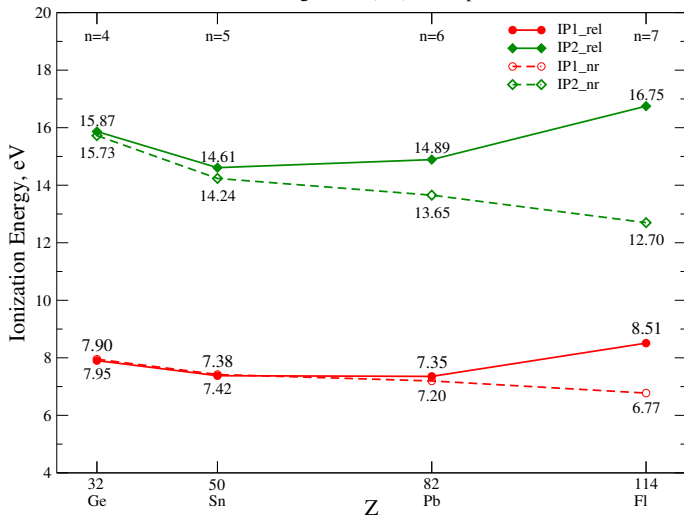
Group 12. Configuration ns^2

Shannon entropy (S), Atomic root mean square (RMS)

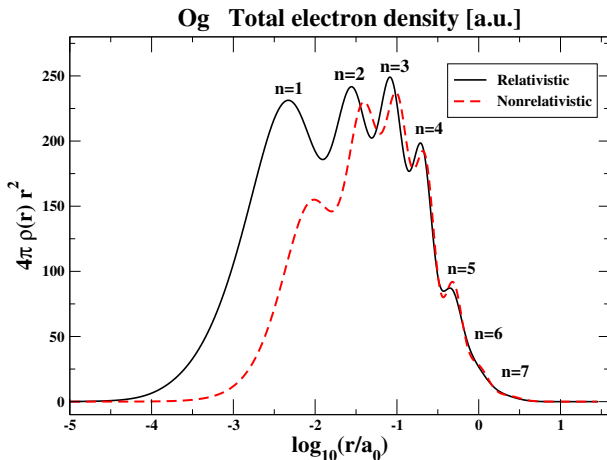


14th group of elements

Group 14: Ionization Potentials
configuration $(n-1)d^{10}ns^2np^2$



Electron density distribution



Radial electron density $4\pi\rho(r)r^2$ plot for Og in both relativistic and non-relativistic approximations.

There is no visible peak in the valence shell region. Electron density alone does not show any valence shell structure

Nonrelativistic Electron Localization Function (ELF)

The probability of finding two particles with the same spins simultaneously at positions 1 and 2 in a multi-electron system is given by the following expression:

$$P_2(\mathbf{r}_1, \mathbf{r}_2) = \sum_{\sigma=\pm 1/2} \rho_2(\mathbf{r}_1 \sigma, \mathbf{r}_2 \sigma | \mathbf{r}_1 \sigma, \mathbf{r}_2 \sigma), \quad (5)$$

where ρ_2 – reduced density matrix of the 2nd order

$$\rho_2(x_1 x_2 | x'_1 x'_2) = \sum_{ijkl} \Gamma_{ij,kl} \varphi_i^*(x_1) \varphi_j^*(x_2) \varphi_k(x'_1) \varphi_l(x'_2), \quad x = (\mathbf{r}, \sigma). \quad (6)$$

Here $\Gamma_{ij,kl}$ is second-order reduced density matrix (RMD2) in the basis $\varphi_i(x)$

$$\Gamma_{ij,kl} = \frac{1}{2} \langle \Psi | a_i^\dagger a_j^\dagger a_l a_k | \Psi \rangle. \quad (7)$$

The probability density to find two electrons with parallel spins in the same point is equal to zero

$$P_2(\mathbf{r}, \mathbf{r}) = 0. \quad (8)$$

Nonrelativistic Electron Localization Function (ELF)

Consider the **conditional density probability** $P_x(\mathbf{r}_1, \mathbf{r}_2)$, which is equal to the probability density of finding one electron at the point $\mathbf{r} + \mathbf{s}$, when another electron is at \mathbf{r}

$$P_x(\mathbf{r}, \mathbf{r} + \mathbf{s}) = \frac{P_2(\mathbf{r}, \mathbf{r} + \mathbf{s})}{\rho(\mathbf{r})} \quad (9)$$

where ρ is the one-electron density.

We define $D(\mathbf{r})$ as the first nonzero coefficient of the of the spherically averaged Taylor expansion of the conditional density probability P_x on the displacement \mathbf{s} . The first expansion coefficients vanished by the Pauli principle, the second is vanished after spherical averaging. Then

$$D(\mathbf{r}) = \frac{1}{2} \Delta_s P_x(\mathbf{r}, \mathbf{r} + \mathbf{s}) \Big|_{\mathbf{s}=\mathbf{0}} = \frac{1}{2} \Delta_s \frac{P_2(\mathbf{r}, \mathbf{r} + \mathbf{s})}{\rho(\mathbf{r})} \Big|_{\mathbf{s}=\mathbf{0}} . \quad (10)$$

The more highly localized is the reference electron, the smaller is the probability of finding another electron near the reference point.

[1] A. D. Becke and K. E. Edgecombe, *J. Chem. Phys.* v.92, 5397 (1990).

Nonrelativistic Electron Localization Function (ELF)

The *electron localization function* (ELF) characterizes the degree of localization of electrons in atoms and molecules. ELF was introduced in the quantum chemistry in the paper [1]

$$\text{ELF}(\mathbf{r}) = \left(1 + \left[\frac{D(\mathbf{r})}{D_0(\mathbf{r})} \right]^2 \right)^{-1}, \quad (11)$$

In the Hartree-Fock approximation

$$D(\mathbf{r}) = \frac{1}{2} \left[\tau - \frac{1}{4} \frac{|\nabla \rho(\mathbf{r})|^2}{\rho(\mathbf{r})} \right], \quad \text{and} \quad \tau = \sum_{i,\sigma} |\nabla \varphi_{i\sigma}(\mathbf{r})|^2. \quad (12)$$

Here ρ is total density and τ the kinetic energy density.

$D_0(\mathbf{r})$ corresponds to a uniform electron gas (Thomas-Fermi) kinetic energy density

$$D_0(\mathbf{r}) = \frac{3}{10} (3\pi^2)^{2/3} \rho^{5/3}(\mathbf{r}). \quad (13)$$

The ELF values lie between zero and one $0 \leq \text{ELF} \leq 1$. Small values are typical for the region between two electron shells. *In a homogeneous electron gas* $\text{ELF} = 0.5$.

[1] A. D. Becke and K. E. Edgecombe, *J. Chem. Phys.* v.92, 5397 (1990).

Relativistic Electron Localization Function (ELF)

$$D(\mathbf{r}) = \sum_{\lambda=1,2} \left[W^\lambda(r) T^\lambda(\mathbf{r}) - \frac{1}{8} \frac{|\nabla \rho^\lambda(r)|^2}{\rho(r)} \right], \quad (14)$$

where $\rho(r)$ – total electron density

$$\rho(r) = \sum_{\lambda=1,2} \rho^\lambda(r), \quad \rho^\lambda(r) = \frac{4\pi}{r^2} \sum_a q_a \begin{cases} P_a^2(r), & \lambda = 1, \\ Q_a^2(r), & \lambda = 2. \end{cases} \quad (15)$$

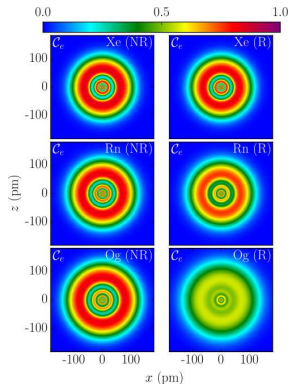
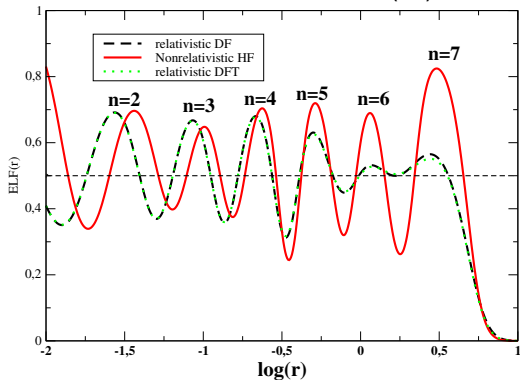
$T^\lambda(\mathbf{r})$ in formula (14) is the relativistic analogue of the non-relativistic kinetic energy density

$$T^\lambda(\mathbf{r}) = \sum_a q_a t_a^\lambda(\mathbf{r}), \quad t_a^\lambda(\mathbf{r}) = \frac{1}{2} \frac{1}{2j_a + 1} \sum_{\mu_a, \sigma} |\nabla \phi_{a\mu_a}^\lambda(\mathbf{r}, \sigma)|^2 \quad (16)$$

and $W^\lambda(r)$ is a weight function that has the form

$$W^\lambda(r) = \frac{\rho^\lambda(r)}{\rho(r)}. \quad (17)$$

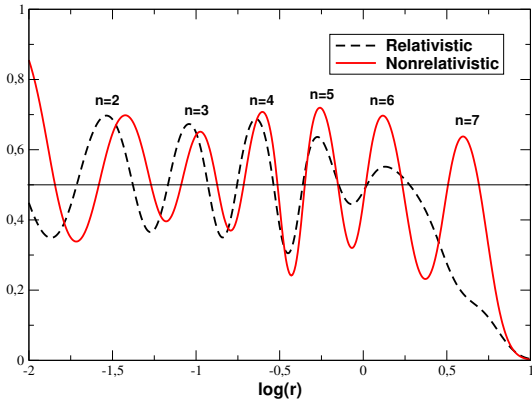
Og (Z=118). Configuration $7s^2 7p^6$
Electronic Localization Function (a.u.)

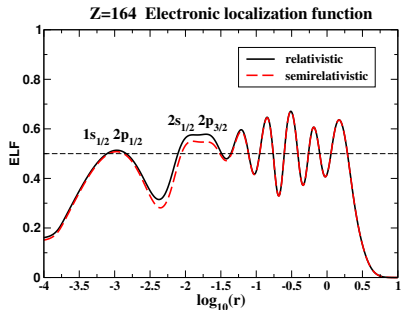
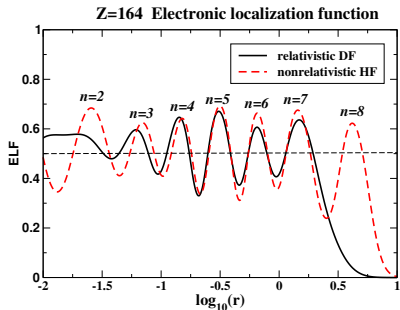


“Spin-orbit splitting in the $7p$ electronic shell becomes so large (~ 10 eV) that Og is expected to show uniform-gas-like behavior in the valence region” [1].

[1] P. Jerabek, B. Schuetrumpf, P. Schwerdtfeger, and W. Nazarewicz, *Phys. Rev. Lett.* **120**, 053001 (2018).

Fl (Z=114). Configuration $7s^2 7p^2$
Electronic Localization Function (a.u.)





Z164 Electron configuration: $[\text{Og}]5g^{18}6f^{14}7d^{10}$.

One-electron energies ε and mean radii of the core electrons

	ε [keV]	$\langle r \rangle$ [a.u.]
1s 1/2	-770.6	0.0028
2p 1/2	-343.0	0.0038
2s 1/2	-196.3	0.0130
2p 3/2	-66.2	0.0279

$$mc^2 = 510.7 \text{ keV}$$

Orbital collapse. Double-well effective potential

- The orbital collapse effect occurs in atoms with open d- and f-shells as a consequence of the fact that the effective radial potential acting on the electrons of these shells contains two wells: a deep narrow inner well and a shallow but wide outer well.
- The effect of orbital collapse was predicted in [1], where it was shown, that the formation of a double-well potential is a consequence by the sum of two contributions of different signs: the screened potential of the nucleus and the centrifugal term, increasing quadratically with increasing orbital quantum number l . This effect was then considered in various papers and reviews (see [1-4] and references therein).
- With small changes in the various parameters determining this effective potential, the average radius and energy of the orbital can change by a factor of ten depending on which of the wells it's localised in.
- This phenomenon can have a significant influence on the properties of free atoms and ions, as well as atoms in molecules, clusters and crystals.

[1] *M. Goepfert Mayer, Phys. Rev. 60, 184 (1941)*

[2] *J. P. Connerade, Contemp. Phys. 19, 415 (1978)*

[3] *R. I. Karaziya, Usp. Fiz. Nauk 135, 79 (1981)*

[4] *J.-R Connerade and R.C. Kamatak, Handbook on the Physics and Chemistry of Rare Earths, v. 28, p. 1 (2000)*

Orbital collapse. Double-well effective potential

The radial Dirac-Fock equation for f- and g- electrons ($l=3,4$) contains a large centrifugal term $l(l+1)/r^2$ which dominates at small r .

$$V_{\text{rad}}(r) = V(r) + \frac{l(l+1)}{2r^2}. \quad (18)$$

As a result, it may turn out that the effective one-electron potential has two wells: a narrow deep localized well and a tiny, but very wide, delocalized well.

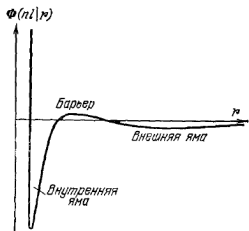
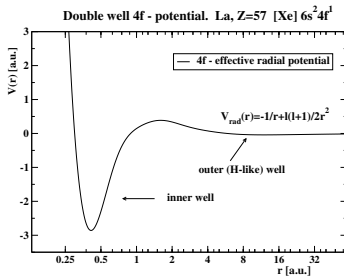


Рис. 1. Двухямный эффективный потенциал (схематический вид).



Orbital collapse. Double-well effective potential

The asymptotics of the local potential $V(r)$ at large distances is purely Coulombic. The exchange interaction of 5g-electrons localised in the outer well with the remaining electrons of the ion is practically equal to zero due to the negligible overlapping of their wave functions.

Therefore the radial potential $V_{\text{rad}}(r)$ in the asymptotic region for a neutral atom has the form

$$V_{\text{rad}}(r) = -\frac{1}{r} + \frac{l(l+1)}{2r^2}, \quad r \rightarrow \infty. \quad (19)$$

The minimum of the effective potential $V_{\text{rad}}(r)$ in the outer well is at the point

$$r_{\text{min}} = l(l+1). \quad (20)$$

The depth V_{min} of this minimum is equal to

$$V_{\text{min}} = -[2l(l+1)]^{-1}. \quad (21)$$

The energy and mean radius of the electron in the outer well must be close to the non-relativistic hydrogen values of the energy $\varepsilon_{nl}^{\text{H}}$ and the mean radius $\langle r \rangle_{nl}^{\text{H}}$ with principal quantum number n and orbital quantum number l .

$$\varepsilon_{nl}^{\text{H}} = -\frac{1}{2n^2} \text{ a.u.}, \quad \langle r \rangle_{nl}^{\text{H}} = \frac{1}{2} [3n^2 - l(l+1)] \text{ a.u.} \quad (22)$$

Orbital collapse. Double-well effective potential

For the 4f-electron ($n=4, l=3$) of a neutral atom localised in the outer well, we obtain

$$r_{\min} = 12 \text{ a.u.}, \quad V_{\min} \simeq -0.0417 \text{ a.u.} \quad (23)$$

and

$$\varepsilon_{4f}^{\text{H}} = -0.03125 \text{ a.u.}, \quad \langle r \rangle_{4f}^{\text{H}} = 18.0 \text{ a.u.} \quad (24)$$

For the 5g-electron ($n = 5, l = 4$) we have

$$r_{\min} = 20 \text{ a.u.}, \quad V_{\min} = -0.0250 \text{ a.u.} \quad (25)$$

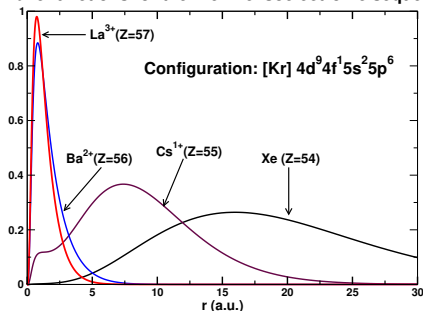
and

$$\varepsilon_{5g}^{\text{H}} = -0.02000 \text{ a.u.}, \quad \langle r \rangle_{5g}^{\text{H}} = 27.5 \text{ a.u.} \quad (26)$$

Orbital collapse. $4d \rightarrow 4f$ E1-transition

Example of the 4f-orbital collapse of the excited configuration $4d^9 4f$ in the Xe-like isoelectronic series.

Wave functions for the Xe-like isoelectronic sequence



[1] K. T. Cheng, C. Froese Fischer, *PRA*, 28, 2811 (1983)

5g-orbital collapse in the SHE with $Z=124$ and $Z=125$

Таблица: List of values of total angular momentum J (relativistic terms) and number K of similar (identical) terms of configurations $[\text{Og}]8s^2 8p_{1/2}^1 6f_{5/2}^3 5g_{7/2}^1$, $Z = 125$ and $[\text{Og}]8s^2 8p_{1/2}^1 6f_{5/2}^2 5g_{7/2}^1$, $Z = 124$ of atoms with $Z=125$ and $Z=124$ respectively

Z=125		Z=124	
Терм J	K	Терм 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

5g-orbital collapse in the SHE with $Z=124$ and $Z=125$

Таблица: The one-electron energies of the ε_{5g} and the mean radii $\langle r \rangle_{5g}$ of the valence $5g_{7/2}$ -orbital, and total Dirac-Fock energies of the neutral atom with $Z = 125$. All values are given in atomic units

$Z=125$. [Og] $8s^2 8p_{1/2}^1 6f_{5/2}^3 5g_{7/2}^1$

Терм (J)	ε_{5g}	$\langle r \rangle_{5g}$	Полная энергия
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

1. I. I. Tupitsyn et al., *Optics and Spectroscopy* 131, 895 (2023)

5g-orbital collapse in the SHE with $Z=124$ and $Z=125$

Таблица: The one-electron energies ε_{5g} and mean radii $\langle r \rangle_{5g}$ of the valence $5g_{7/2}$ -orbital, and the total energies of the neutral atom with $Z = 124$. All quantities are given in atomic units.

$$Z=124 \text{ [Og]} 8s^2 8p_{1/2}^1 6f_{5/2}^2 5g_{7/2}^1$$

Терм (J)	ε_{5g}	$\langle r \rangle_{5g}$	Полная энергия
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

1. I. I. Tupitsyn et al., *Optics and Spectroscopy* 131, 895 (2023)

Orbital collapse. Dirac-Fock double solutions

We consider configurations with only one f- or g- electron outside closed relativistic shell, since in the restricted Hartree-Fock method all electrons of the one shell have the same radial wave function, and only one electron can be localized in the outer well.

In some cases, depending on the initial approximation, two different solutions can be obtained: one localised in a narrow inner well and the other in a wide outer well.

The dual solutions were first found in Ref [1]. Using the mixing of the initial and final wave functions in the iterative procedure the authors obtained two Dirac-Fock solutions for lanthanum with configuration $6s^2 4f_{5/2}$ and for europium $6s^2 4f_{5/2}^7 4f_{7/2}$.

1. *I.M. Band and V.I. Fomichev, Phys.Letters A, 75, 178 (1980)*

Orbital collapse. Dirac-Fock double solutions

In order to obtain two solution we use the following procedure.

- We introduce the parameter α as a multiplier in the exchange interaction and represent the Dirac-Fock operator in the form of

$$\hat{V}_{\text{DF}}(r) = V_{\text{H}} + \alpha \hat{V}_{\text{x}}, \quad (27)$$

where V_{H} – Hartree potential with self-interaction correction, and \hat{V}_{x} – exchange operator.

- In the first step, we adjust the parameter α in order to obtain the required solution. Thus, for example, $\alpha = 0$, as a rule, gives us a solution localised in the outer well. At this stage we use the eigenfunctions of the Dirac operator with the modified Gaspar potential [1] as an initial approximation. The modification has been done in [2] to take into account self-interaction correction.

$$V_{\text{G}}(r) = -\frac{Z}{r} + \frac{N_e - 1}{r} \left(1 - \frac{e^{-\lambda r}}{1 + A r} \right), \quad (28)$$

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

- Then we change the parameter α in order to go directly or gradually to the value $\alpha = 1$, using as an initial approximation the wave functions obtained at the previous value of α .

[1] R. Gaspar. J. Chem. Phys., 20, 1863 (1952).

[2] A. E. S. Green. Advances in Quantum Chemistry, 7, 221 (1973).

Orbital collapse. Two solutions for f-electrons (La, Z=57)

A coexistence of two different states of an atom with the same electronic configuration both for lanthanum ($6s^2 4f_{5/2}$)

Comparison our results with [1] for the La configuration ($6s^2 4f_{5/2}$) in [a.u.]

4f – localized (inner) orbital, 4f' – delocalized (outer) orbital, ϵ_{4f}^H – nonrelativistic H-like energy for n=4.

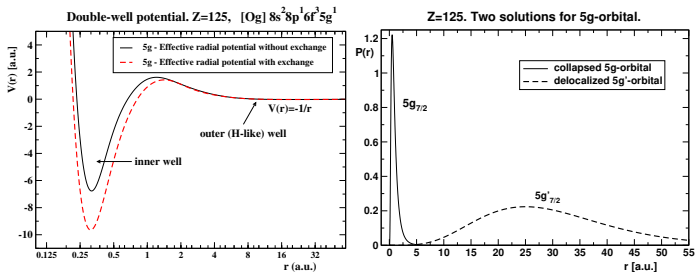
$$\begin{array}{llll} \epsilon_{4f} & = & -0.23830 & \langle r \rangle_{4f} & = & 1.2591 \\ \epsilon_{4f'} & = & -0.03180 & \langle r \rangle_{4f'} & = & 17.0614 \\ \epsilon_{4f'}[1] & = & -0.0316 & & & -- \\ \epsilon_{4f}^H & = & -0.03125 & \langle r \rangle_{4f}^H & = & 17.9999 \end{array} \quad (29)$$

Total Energies (J=2.5):

$$\begin{array}{llll} E_{\text{inner}} & = & -8493.5521 & E_{\text{inner}}[1] & = & -8493.6247 \\ E_{\text{outer}} & = & -8493.4767 & E_{\text{outer}}[1] & = & -8493.5512 \end{array} \quad (30)$$

1. I.M. Band and V.I. Fomichev, *Phys.Letters A*, **75**, 178 (1980)

Orbital collapse. Two solutions for g-electrons (Z=125)



One-electron energies and radii of two states in [a.u.]

5g – localized (inner) orbital, 5g' – delocalized (outer) orbital, ϵ_{5g}^H – nonrelativistic H-like energy for n=5.

$$\begin{array}{ll}
 \epsilon_{5g} & = -0.51464169 \text{ a.u.} & \langle r \rangle_{5g} & = 0.71289 \text{ a.u.} \\
 \epsilon_{5g'} & = -0.02000147 \text{ a.u.} & \langle r \rangle_{5g'} & = 27.4943 \text{ a.u.} \\
 \epsilon_{5g}^H & = -0.02000001 \text{ a.u.} & \langle r \rangle_{5g}^H & = 27.5000 \text{ a.u.}
 \end{array} \tag{31}$$

Total Energies (J=0.5):

$$\begin{array}{ll}
 E_{\text{inner}} & = -64846.2788 \text{ a.u.} \\
 E_{\text{outer}} & = -64846.0878 \text{ a.u.}
 \end{array} \tag{32}$$

Orbital collapse. Two solutions for 6f-electrons (Z=148)

Z=148. Configuration: [Og]8s² 8p_{1/2}¹ 6f_{5/2}⁶ 6f_{7/2}¹

Таблица: 6f-orbital localized in the inner well

Level J	Total energy	ϵ_{6f}	$\langle r \rangle$
2.0	-115208.5829	-0.10466	1.570
3.0	-115208.6011	-0.11633	1.566
4.0	-115208.6145	-0.12470	1.574
5.0	-115208.5860	-0.10774	1.562

Таблица: 6f-orbital localized in the outer well

Level J	Total energy	$\epsilon_{6f'}$	$\langle r \rangle$
2.0	-115208.6203	-0.0309	18.206
3.0	-115208.6208	-0.0314	17.798
4.0	-115208.6210	-0.0317	17.594
5.0	-115208.6205	-0.0311	18.058

One-electron model QED potential

The model self-energy (SE) operator V^{SE} for $5 \leq Z \leq 120$ was introduced in our papers [1-3]

$$V^{\text{SE}} = V_{\text{loc}}^{\text{SE}} + \sum_{i,k=1}^n |\phi_i\rangle \Delta B_{ik} \langle \phi_k|, \quad (33)$$

where

$$\Delta B_{ik} = \sum_{j,l=1}^n (D^{-1})_{ji} \Delta \Sigma_{jl} (D^{-1})_{lk}, \quad (34)$$

$$\Delta \Sigma_{ik} = \Sigma_{ik} - \langle \psi_i^{(0)} | V_{\text{loc}}^{\text{SE}} | \psi_k^{(0)} \rangle \text{ and } \Sigma_{ij} = \langle \psi_i^{(0)} | \hat{\Sigma} | \psi_j^{(0)} \rangle.$$

Here Σ_{ij} are the matrix elements of the exact one-loop energy-dependent SE operator $\hat{\Sigma}$, calculated with hydrogen like wave functions $\psi_i^{(0)}$ [1].

At the present time, the scope of model QED operator has been expanded up to $Z=170$ [4].

1. V.M. Shabaev, I.I. Tupitsyn, V.A. Yerokhin, *Phys. Rev. A*, **88**, 012513 (2013)
2. V.M. Shabaev, I.I. Tupitsyn, V.A. Yerokhin, *Computer Phys. Comm.*, **189**, 175 (2015)
3. I.I. Tupitsyn, M.G. Kozlov, M.S. Safronova, V.M. Shabaev, and V.A. Dzuba, *PRL*, **117**, 253001 (2016)
4. A. V. Malyshev, D. A. Glazov, V. M. Shabaev, I. I. Tupitsyn, V. A. Yerokhin, and V. A. Zaytsev, *Phys. Rev. A* **106**, 012806 (2022)

Thank You for Attention.

Ground electron configurations

Таблица: Ground state electron configurations

Core: [Og] 8s ²				
Z	Conf.	J	Ref[1]	Ref[2]
125	5g ¹ 6f ² 7d ¹ 8p ¹	8.5	5g ¹ 6f ³ 8p ¹	5g ¹ 6f ² 8p ²
126	5g ² 6f ² 7d ¹ 8p ¹	10	5g ² 6f ² 7d ¹ 8p ¹	5g ² 6f ³ 8p ¹
127	5g ³ 6f ² 7d ¹ 8p ¹	13.5	5g ³ 6f ² 8p ²	5g ³ 6f ² 8p ²
Core: [Og] 8s ² 8p _{1/2} ²				
144	5g ¹⁸ 6f ¹ 7d ³	4.0	5g ¹⁸ 6f ¹ 7d ³	5g ¹⁷ 6f ¹ 7d ³
145	5g ¹⁸ 6f ³ 7d ²	6.5	5g ¹⁸ 6f ³ 7d ²	5g ¹⁸ 6f ³ 7d ²
162	5g ¹⁸ 6f ¹⁴ 7d ⁸	4.0	5g ¹⁸ 6f ¹⁴ 7d ⁸	5g ¹⁸ 6f ¹⁴ 7d ⁷ 9s ¹
163	5g ¹⁸ 6f ¹⁴ 7d ⁹	2.5	5g ¹⁸ 6f ¹⁴ 7d ⁹	5g ¹⁸ 6f ¹⁴ 7d ⁸ 9s ¹
164	5g ¹⁸ 6f ¹⁴ 7d ¹⁰	0.0	5g ¹⁸ 6f ¹⁴ 7d ¹⁰	5g ¹⁸ 6f ¹⁴ 7d ⁹ 9s ¹
165	5g ¹⁸ 6f ¹⁴ 7d ¹⁰ 9s ¹	0.5	5g ¹⁸ 6f ¹⁴ 5g ¹⁸ 7d ¹⁰ 9s ¹	—
166	5g ¹⁸ 6f ¹⁴ 7d ¹⁰ 9s ²	0.0	5g ¹⁸ 6f ¹⁴ 5g ¹⁸ 7d ¹⁰ 9s ²	—

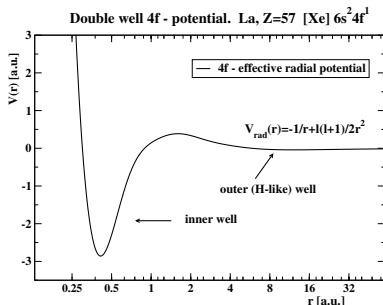
[1] B. Fricke and G. Soff, *Atomic Data and Nuclear Data Tables* 19, 83 (1977).

[2] V.I. Nefedov, M. Trzhaskovskaya, *Dokl. Phys. Chem.* 408, 149 (2006).

Orbital collapse

The radial Dirac-Fock equation for f- and g- electrons ($l=3,4$) contains a large centrifugal term $l(l+1)/r^2$ which dominates at small r . As a result, it may turn out that the effective one-electron potential has two wells: a narrow deep localized well and a tiny, but very wide, delocalized well.

This leads to the fact that with small changes in the atomic parameters *the delocalized solution can collapse into a highly localized one* [1], for example, depending on the value of total angular momentum J .



[1] Griffin et al, Phys Rev 177, 62. (1969)

No orbital collapse of the 6f-electrons

There is no collapse of the 6f-orbital for the elements of 8th period, since the 6f-radial potential has only one inner well.

