Relativistic effects in the electronic structure of the superheavy elements

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Outline of the Talk

- Introduction
- Methods
- Relativistic effects in the electronic structure of SHE
- Dimers and solid phases of noble gases
- Alkali Metal Hydrides
- Electron density distribution and electron localization in SHE
- Orbital collapse of the 5g-states
- Summary and Outlook

Introduction

Our group carries out calculations of the electronic structure of superheavy elements (SHE), as well as molecules and solids containing SHE [1-8].

- Ground state electron configurations of the SHE
- Ionization potentials and Electron affinities of the SHE
- Localization of electronic states in the SHE: one-particle electron density, root-mean-square radii (RMS) and widths of the electron-density distribution of valence shells, electron localization functions (ELF), Shannon entropy
- SHE compounds: potential curves, equilibrium distances, dissociation energies, atomic charges and orbital populations
- Orbital collapse of g-electrons in the SHE of the 8th period
- 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)*
7. *I. I. Tupitsyn, et al., Phys. Rev. A 109, 042807 (2024)*
8. *Dulaev et al., Phys. Rev. D 109, 036008 (2024)*
9. *Dulaev et al., Phys. Rev. D 111, 016018 (2025)*

Introduction. Specific features of electronic structure and chemical properties of superheavy 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 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**, that is, the maximum of the density distribution of these shells shifts to lower values of the radius and the binding energies of these electrons increases.

  This also leads to a decreasing of interatomic distances and an increasing of dissociation energies of the SHE compounds

  The contraction effect is a result of the increasing relativistic mass of electrons whose velocity near the nucleus becomes comparable to the speed of light.
- Spin-orbital splitting of valence 7p- and 8p- shells is very large, and reaches up about 10 eV for the 7p- orbital in Og (Z=118) and about 75 eV for the 8p-orbital in Z=165.
- 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.

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

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

- 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 [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.

  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**.

- Formally, Flerovium (Z=114) 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 Fl of the order of 6 eV, that is, **about 1000 times greater**.

  For this reason the $7p_{3/2}$- orbital of Fl 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 with large centrifugal repulsive term, has two potential wells which leads to the so-called **orbital collapse**.

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

Methods

In our work, we used several 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 (FSCC)**

  DIRAC, a relativistic ab initio electronic structure program, Release DIRAC21 (2021), http://www.diracprogram.org

  FSCC 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.

- **Relativistic Density Functional Theory (DFT)**.

  AMS Band-DFT code is used in calculations of the electronic structure of molecules and solids containing SHE

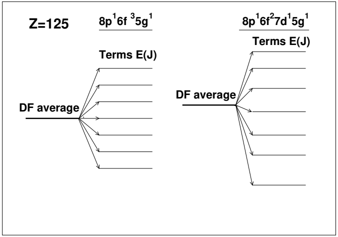
- **Code LAMPS-Mod.Dynamics was used in calculations of solids by molecular dynamics method**

- **To evaluate the QED correction we use the Model QED operator approach.**

  We incorporate the model QED operator (QEDMOD) into the many-electron Hamiltonian and perform two series of the calculations: one with QED included into the Hamiltonian and the other without it. The corresponding QED correction is the difference between these values.

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 $E(J)$

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

Configuration		$E_{\mathrm{DF}}^{\mathrm{av}}$ [a.u.]	J	$E_{\mathrm{DF}}(J)$ [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

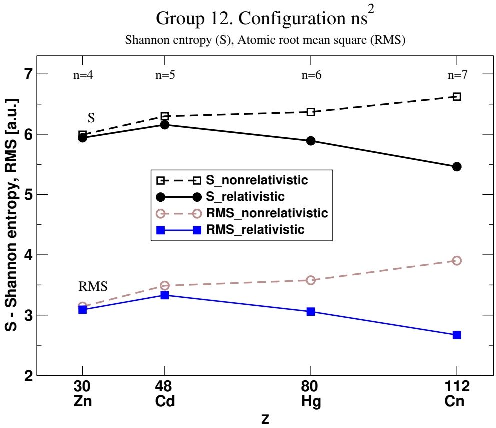
These configurations have different parity and do not mix.

Spin-orbit splitting

Table 1: One-electron energies ε(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

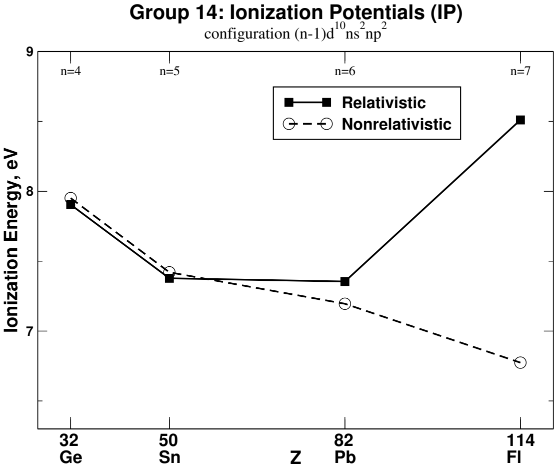
12th group of elements



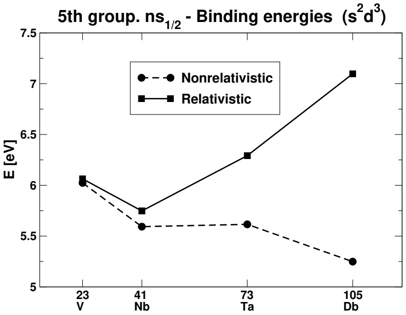
The figure shows that the average radius of the valence shell and the Shannon entropy, which characterizes the localization degree of electrons, behave similarly depending on the atomic number.

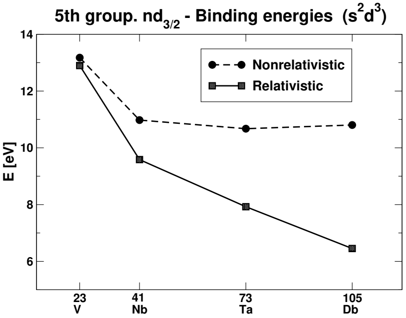
Relativistic curves (solid line) in contrast to non-relativistic ones (dashed lines), indicate an increase in the degree of electron localization with increasing atomic number.

14th group of elements



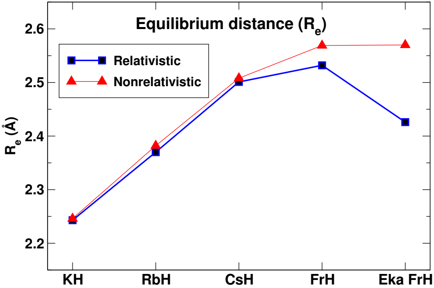
5th group of elements


5th group. ns$_{1/2}$ - Binding energies (s^{2}d^3)


5th group. nd$_{3/2}$ - Binding energies (s^{2}d^3)

- The direct relativistic effect leads to contraction of s-electrons and an increasing their binding energy
- On the contrary, an indirect effect, which consists in the fact that the contraction of s- and $p_{1/2}-$ electrons increases the screening of the charge of the nucleus, leads to a decrease in the binding energy of $d-$ electrons

Alkali Metal Hydrides (MeH)



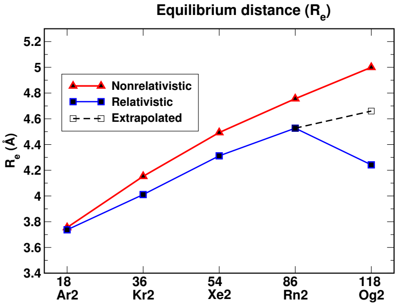
Relativistic $Q_{\rm rel}$ and nonrelativistic ($Q_{\rm nr}$) values
of alkali metal atomic charges $\Delta Q = Q_{\rm nr} - Q_{\rm rel}$

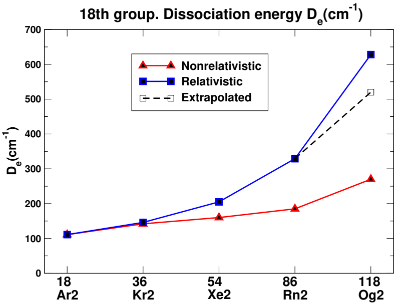
MeH	$Z_{\rm Me}$	Nonrelativistic	Relativistic	ΔQ
LiH	3	0.473	0.473	0.0
NaH	11	0.421	0.421	0.0
KH	19	0.453	0.451	0.002
RbH	37	0.462	0.455	0.007
CsH	55	0.458	0.429	0.029
FrH	87	0.503	0.451	0.052
Eka FrH	119	0.533	0.388	0.145

In the relativistic case, the contribution of ionic bonding decreases in comparison with non-relativistic one, that correlates with the increase of the ionization potential.

The calculations were carried out using the FSCC method by students of our group Amir Saetgaraev and Daniil Usov.

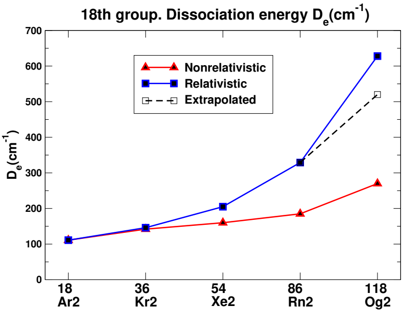
Noble gas dimers



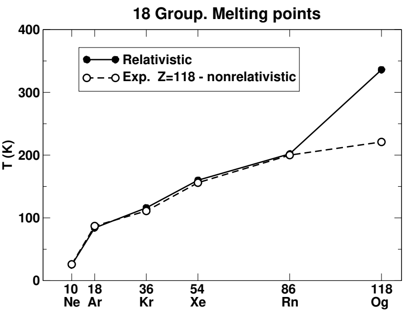


When going from Rn2 to Og2, we see a strong relativistic effect that contradicts to the extrapolation values for both equilibrium distances and dissociation energies.

The calculations were carried out using the FSCC method by Daniil Usov.



The calculations were performed by Daniil Usov.



The calculations were performed by Nikita Dulaev.

It is evident from the graphs that when moving from lighter homologous to Og, a strong increase in the dissociation energy of dimers and the melting temperature of solids is observed.

Noble gases in the solid phase

Relativistic DFT calculations of noble gases in the FCC (face-centered cubic) solid state phase with taking into account spin-orbit interaction and dispersion corrections.

Noble gases bond lengths (Å)

Functional	Xe	Rn	Og
revPBE-D3BJ	4.497	4.614	4.432
PBEsol-D3BJ	4.267	4.297	4.277
revPBE-D4	4.535	4.635	4.443
PBEsol-D4	4.343	0.366	4.307
Experiment[a]	4.336	–	–

Noble gases cohesive energies (eV)

Functional	Xe	Rn	Og
revPBE-D3BJ	0.191	0.237	0.338
PBEsol-D3BJ	0.194	0.285	0.585
revPBE-D4	0.158	0.199	0.298
PBEsol-D4	0.138	0.206	0.504
Experiment[a]	0.164	–	–

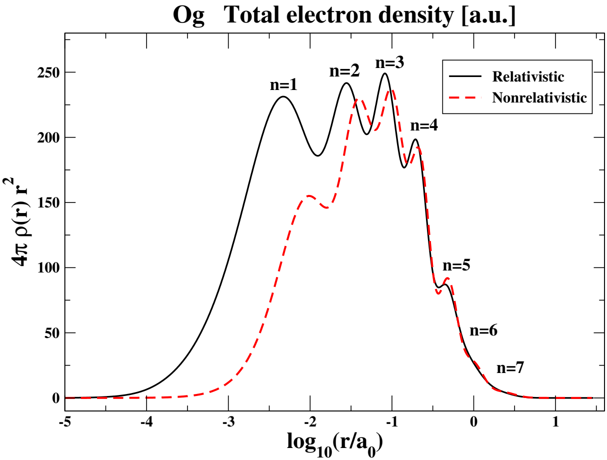
[a] Schwalbe L. A. et al., J. Chem. Phys. 66, 4493 (1977).

(The calculations were performed by students of our group Anton Ryzhkov and Daniil Usov using relativistic DFT method)

As can be seen from the table, the cohesive energy increases strongly with increasing of the atomic number, which is a result of the strong relativistic effect

The large discrepancy of cohesive energies is probably due to the fact that the DFT theory is poorly adapted to the calculations of dispersion interactions.

Electron density distribution



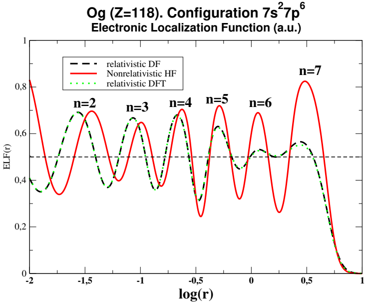
Radial electron density $4\pi\rho(r)r^2$ plot for Og in both relativistic and non-relativistic approximations.

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)

To describe the distribution and localization of electron density, it is better to use the so-called electron localization function (ELF) [1]

Modification of the ELF for the case of strong relativistic effects was done in our paper [2]



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

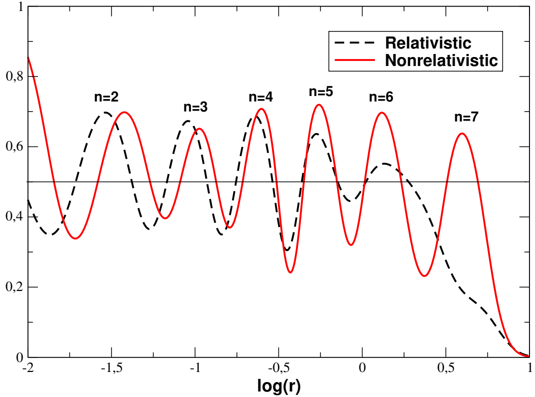
[1] *A. D. Becke and K. E. Edgecombe, J. Chem. Phys. v.92, 5397 (1990).*

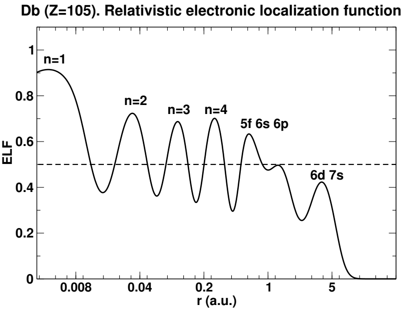
[2] *I.I Tupitsyn et al., Optics and Spectroscopy, 130, 1022 (2022)*

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

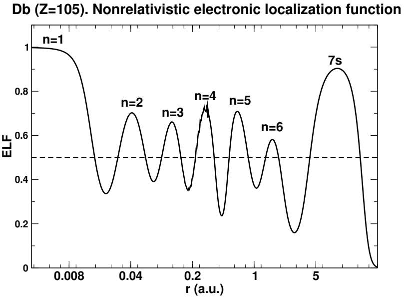
Fl (Z=114). Configuration $7s^2 7p^2$

Electronic Localizatiom Function (a.u.)





Db (Z=105). Relativistic electronic localization function



Db (Z=105). Nonrelativistic electronic localization function

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.
- 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.
- The orbital collapse effect was then considered in various papers and reviews (see [1-4] and references therein).

[1] *M. Goeppert 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 $l(l+1)/r^2$ wich dominates at small r.

$$V_{\mathrm{rad}}(r) = V(r) + \frac{l(l+1)}{2r^2}\,. \tag{1}$$

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.
It should be noted that well capacity is proportional to the width of the well and the square root of its depth.

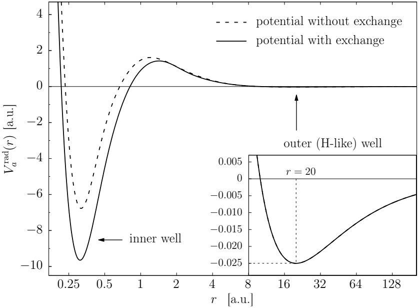


Figure 1: Z=125. The effective radial potential for the shell is $a = 5g_{7/2}$. The solid line is the potential with exchange and the dashed line is the potential without exchange.

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 $V_{\mathrm{rad}}(r)$ in the asymptotic region for a neutral atom has the form

$$V_{\mathrm{rad}}(r) = -\frac{1}{r} + \frac{l(l+1)}{2r^2}\,, \qquad r \to \infty\,. \tag{2}$$

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

$$r_{\min} = l\,(l+1)\,. \tag{3}$$

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

$$V_{\min} = -\left[2l(l+1)\right]^{-1}\,. \tag{4}$$

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

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

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

$$r_{\min} = 20\ \text{a.u.}, \qquad V_{\min} = -0.0250\ \text{a.u.} \tag{6}$$

and

$$\varepsilon^{\mathrm{H}}_{5g} == -0.02000\ \text{a.u.}, \qquad \langle r\rangle^{\mathrm{H}}_{5g} = 27.5\ \text{a.u.} \tag{7}$$

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

Table 2: 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]$8s^2 8p^1_{1/2} 6f^3_{5/2} 5g^1_{7/2}$

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

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

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

Table 3: 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.

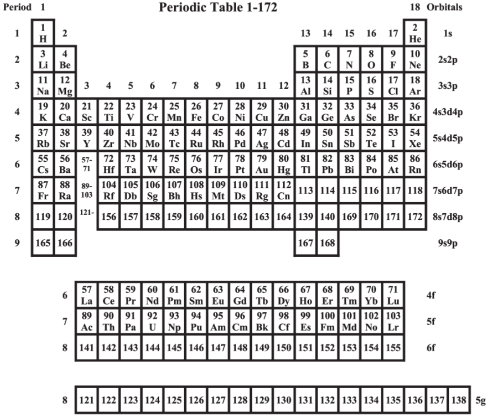
Z=124 [Og]$8s^2 8p^1_{1/2} 6f^2_{5/2} 5g^1_{7/2}$

Relativistic			Nonrelativistic		
Term (J)	ε_{5g}	$\langle r \rangle_{5g}$	Term (LS)	ε_{5g}	$\langle r \rangle_{5g}$
0	-0.019961	27.567	^{1}S	-1.920833	0.631
1	-0.019988	27.520	^{3}S	-1.917294	0.630
2	-0.020000	27.497	^{5}S	-1.912106	0.630
3	-0.019996	27.504	^{1}P	-1.912189	0.630
4	-0.019998	27.499	^{3}P	-1.913845	0.630
5	-0.020011	27.475	^{5}P	-1.917600	0.631
6	-0.020020	27.457	^{1}D	-1.912618	0.629
7	-0.240725	0.799	^{3}D	-1.915445	0.630
8	-0.233805	0.799	^{5}D	-1.921194	0.630

1. *I. I. Tupitsyn et al., Optics and Spectroscopy 131, 895 (2023)*
2. *I. I. Tupitsyn, et al., Phys. Rev. A 109, 042807 (2024)*

Thank You for Attention.

Introduction. Pekka Pyykkö periodic table



Periodic Table 1-172

Period	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	Orbitals
1	1 H																	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											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	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	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-	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).

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

$Z = 119 - 121 \quad 8s\,8p$
$Z = 122 - 124 \quad 8p\,7d\,6f$
$Z = 125 - 144 \quad 8p\,7d\,6f\,5g$

$Z = 145 - 158 \quad 7d\,6f\,8p$
$Z = 159 - 166 \quad 7d\,8p\,9s$
$Z = 167 - 172 \quad 7d\,8p\,9s\,9p$

Introduction. Methods

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

For $\mathbf{Z = 126}$ the configurations with the *lowest Dirac-Fcok (DF) energies* **within the configuration average approximation are**

Configuration	$E_{\rm DF}^{\rm av}$ [a.u.]
$8p^1 7d^1 6f^2 5g^2$	-66298.183666
$8p^1 6f^3 5g^2$	.183121
$8p^1 6f^4 5g^1$	.168137
$8p^2 6f^2 5g^2$	.146963
$8p^1 7d^2 6f^1 5g^2$	.114149

The enrgies of the configurations $8p^1 7d^1 6f^2 5g^2$ and $8p^1 6f^3 5g^2$ are almost the same.

- $8p^2 6f^2 5g^2$ Mann et al., 1970 (DF)
- $8p^1 7d^1 6f^2 5g^2$ Fricke et al., 1977 (DFS)
- $8p^1 6f^4 5g^1$ Umemoto and Saito, 1997 (DF+PZ SIC)
- $8p^1 6f^3 5g^2$ (0.98) Nefedov, M. Trzhaskovskaya, 2006 (MCDF)
- $8p^1 7d^1 6f^2 5g^2$ Zhou et al., 2017 (DF)

Ground electron configurations

Table 4: Ground state electron configurations

Z	Conf.	J	Ref[1]	Ref[2]
Core: [Og] $8s^{2}$				
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] $8s^{2}$ $8p^{2}_{1/2}$				
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).

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:

$$S = -\sum_{i=1}^{N} p_i \, \ln p_i \tag{8}$$

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

$$\sum_{i=1}^{N} p_i = 1 \, . \tag{9}$$

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, $S_{\max} = \ln(N)$

$$0 \leq S \leq \ln(N) \tag{10}$$

For continuous distribution

$$S = -\int d\boldsymbol{r} \, \ln(\rho(\boldsymbol{r})) \, \rho(\boldsymbol{r}) \, , \qquad \int d\boldsymbol{r} \, \rho(\boldsymbol{r}) = 1 \, . \tag{11}$$

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

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

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:

$$P_2(\boldsymbol{r}_1, \boldsymbol{r}_2) = \sum_{\sigma=\pm 1/2} \rho_2(\boldsymbol{r}_1\, \sigma\,, \boldsymbol{r}_2\, \sigma | \boldsymbol{r}_1\, \sigma\,, \boldsymbol{r}_2\, \sigma)\,, \tag{12}$$

where ρ_2 – reduced density matrix of the 2nd order

$$\rho_2(x_1\, x_2 | x_1'\, x_2') = \sum_{ijkl} \Gamma_{ij,kl}\, \varphi_i^*(x_1)\, \varphi_j^*(x_2)\, \varphi_k(x_1')\, \varphi_l(x_2')\,, \qquad x = (\boldsymbol{r}, \sigma)\,. \tag{13}$$

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

$$\Gamma_{ij,kl} \;=\; \frac{1}{2}\, \langle \Psi \mid a_i^+\, a_j^+\, a_l\, a_k \mid \Psi \rangle\,. \tag{14}$$

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

$$P_2(\boldsymbol{r}, \boldsymbol{r}) = 0\,. \tag{15}$$

Nonrelativistic Electron Localization Function (ELF)

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

$$P_x(\boldsymbol{r}, \boldsymbol{r} + \boldsymbol{s}) = \frac{P_2(\boldsymbol{r}, \boldsymbol{r} + \boldsymbol{s})}{\rho(\boldsymbol{r})} \tag{16}$$

where ρ is the one-electron density.

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

$$D(\boldsymbol{r}) = \frac{1}{2}\,\Delta_s\, P_x(\boldsymbol{r}, \boldsymbol{r} + \boldsymbol{s})\Big|_{\boldsymbol{s}=0} = \frac{1}{2}\;\Delta_s \frac{P_2(\boldsymbol{r}, \boldsymbol{r} + \boldsymbol{s})}{\rho(\boldsymbol{r})}\,\Bigg|_{\boldsymbol{s}=\boldsymbol{0}} \;. \tag{17}$$

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) characterize the degree of localization of electrons in atoms and molecules. ELF was introduced in the quantum chemistry in the paper [1]

$$\mathrm{ELF}(\boldsymbol{r}) = \left(1 + \left[\frac{D(\boldsymbol{r})}{D_0(\boldsymbol{r})}\right]^2\right)^{-1} , \tag{18}$$

In the Hartree-Fock approximation

$$D(\boldsymbol{r}) = \frac{1}{2}\left[\tau - \frac{1}{4}\frac{|\boldsymbol{\nabla}\rho(\boldsymbol{r})|^2}{\rho(\boldsymbol{r})}\right] , \qquad \text{and} \qquad \tau = \sum_{i,\sigma} |\boldsymbol{\nabla}\varphi_{i\sigma}(\boldsymbol{r})|^2 . \tag{19}$$

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

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

$$D_0(\boldsymbol{r}) = \frac{3}{10}(3\,\pi^2)^{2/3}\rho^{5/3}(\boldsymbol{r}) . \tag{20}$$

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

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

Relativistic Electron Localization Function (ELF)

$$D(\boldsymbol{r}) = \sum_{\lambda=1,2} \left[W^{\lambda}(r)\, T^{\lambda}(\boldsymbol{r}) - \frac{1}{8}\, \frac{\left|\boldsymbol{\nabla}\rho^{\lambda}(r)\right|^2}{\rho(r)} \right] , \tag{21}$$

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

$$\rho(r) = \sum_{\lambda=1,2} \rho^{\lambda}(r)\,, \qquad \rho^{\lambda}(r) = \frac{4\pi}{r^2} \sum_a q_a \left\{ \begin{array}{ll} P_a^2(r), & \lambda = 1, \\ Q_a^2(r), & \lambda = 2\,. \end{array} \right. \tag{22}$$

$T^{\lambda}(\boldsymbol{r})$ in formula (21) is the relativistic analogue of the non-relativistic kinetic energy density

$$T^{\lambda}(\boldsymbol{r}) = \sum_a q_a\, t_a^{\lambda}(\boldsymbol{r})\,, \qquad t_a^{\lambda}(\boldsymbol{r}) = \frac{1}{2}\, \frac{1}{2j_a + 1} \sum_{\mu_a,\sigma} |\boldsymbol{\nabla}\phi_{a\mu_a}^{\lambda}(\boldsymbol{r},\sigma)|^2 \tag{23}$$

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

$$W^{\lambda}(r) = \frac{\rho^{\lambda}(r)}{\rho(r)}\,. \tag{24}$$

I.I Tupitsyn et al., Optics and Spectroscopy, 130, 1022 (2022)

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

$$r_{\min} = 12 \text{ a.u.}, \qquad V_{\min} \simeq -0.0417 \text{ a.u.} \tag{25}$$

and

$$\varepsilon^{\mathrm{H}}_{4f} = -0.03125 \text{ a.u.}, \qquad \langle r \rangle^{\mathrm{H}}_{4f} = 18.0 \text{ a.u.} \tag{26}$$

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

$$r_{\min} = 20 \text{ a.u.}, \qquad V_{\min} = -0.0250 \text{ a.u.} \tag{27}$$

and

$$\varepsilon^{\mathrm{H}}_{5g} == -0.02000 \text{ a.u.}, \qquad \langle r \rangle^{\mathrm{H}}_{5g} = 27.5 \text{ a.u.} \tag{28}$$

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

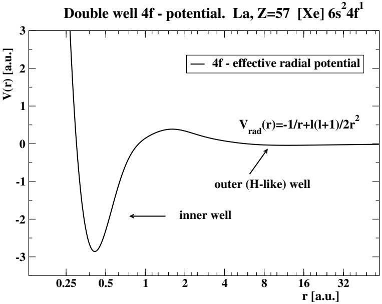
Table 5: List of values of total angular momentum J (relativistic terms) and number K of similar (identical) terms of configurations [Og]$8s^2 8p^1_{1/2} 6f^3_{5/2} 5g^1_{7/2}$, $Z = 125$ and [Og]$8s^2 8p^1_{1/2} 6f^2_{5/2} 5g^1_{7/2}$, $Z = 124$ of atoms with Z=125 and Z=124 respectively

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

Orbital collapse

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

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

$$\hat{V}_{\mathrm{DF}}(r) = V_{\mathrm{H}} + \alpha\,\hat{V}_{\mathrm{x}}\,, \tag{29}$$

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

- In the first step, we adjust the parameter a 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.

$$V_{\mathrm{G}}(r) = -\frac{Z}{r} + \frac{N_e - 1}{r}\left(1 - \frac{e^{-\lambda r}}{1 + A\,r}\right)\,, \tag{30}$$

  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 6f-electrons (Z=148)

Z=148. Configuration: [Og]8s^2 8$\mathrm{p}_{1/2}^2$ 5g^{18} 7$\mathrm{d}_{3/2}$ 6$\mathrm{f}_{5/2}^6$ 6$\mathrm{f}_{7/2}^1$

Table 6: 6f-orbital localized in the inner well

Level J	Total energy	$\varepsilon_{6\mathrm{f}}$	<r>
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

Table 7: 6f-orbital localized in the outer well

Level J	Total energy	$\varepsilon_{6\mathrm{f}'}$	<r>
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

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.