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

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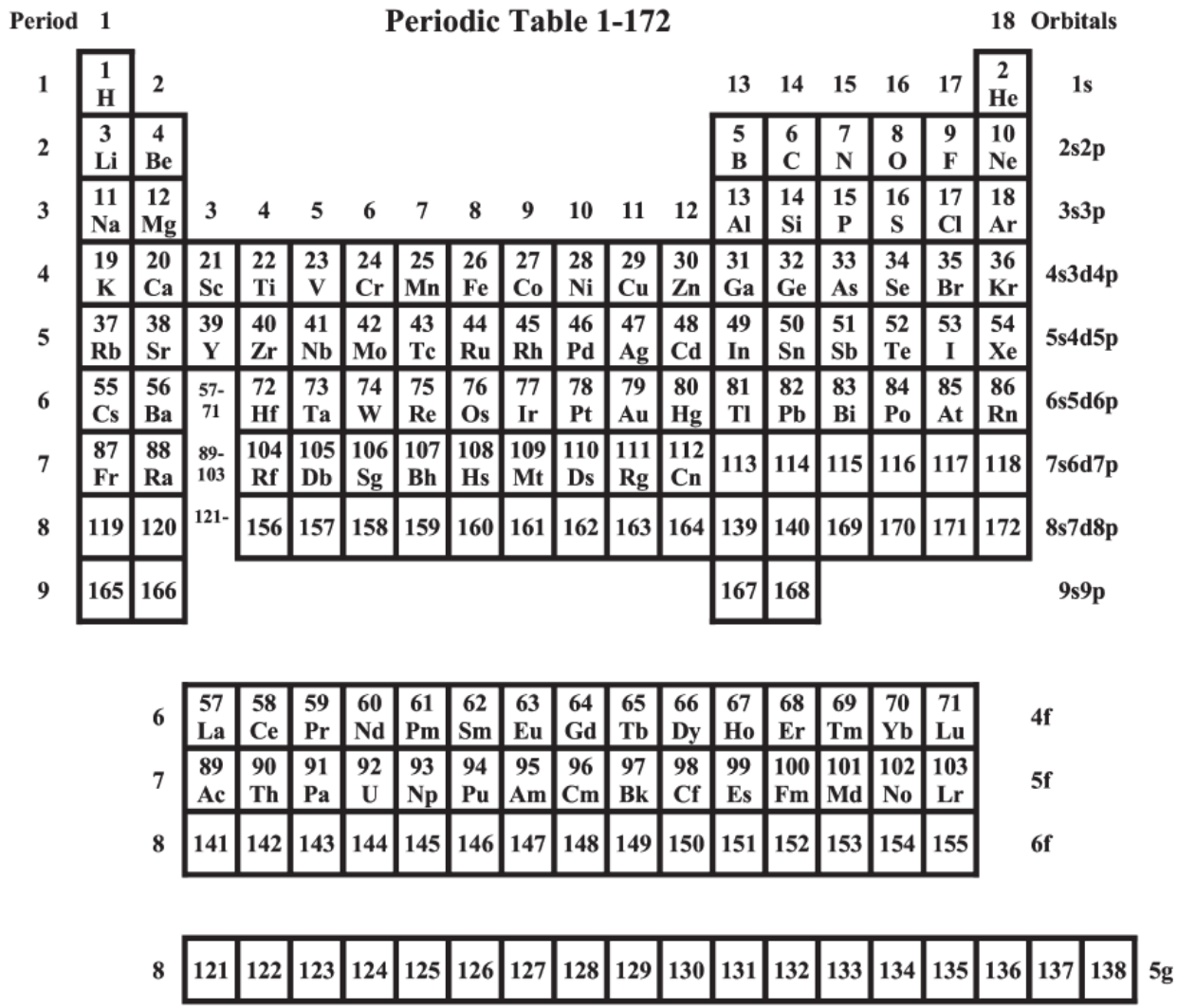
Outline of the Talk

- 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
- Summary and Outlook

Introduction. Pekka Pyykkö periodic table



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

Introduction

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 homologous are performed [1-5].

- 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., Opt. Spectr. 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)*

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

The electronic structure of SHEs is unique in several aspects:

- Strong relativistic effects cause contraction of the s- and p- orbitals
- Spin-orbital splitting of valence p-shells reaches up about 10 eV in Og (Z=118) and about 420 eV for the 7p-orbital and about 75 eV for the 8p-orbital in element with atomic number Z=165.
- As a result, 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 and ELF is close to 0.5 in the valence region.
  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.
- Starting from the Z = 125 element, the 5g-shell with the large angular momentum (l = 4) is occupied with 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*.

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

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.

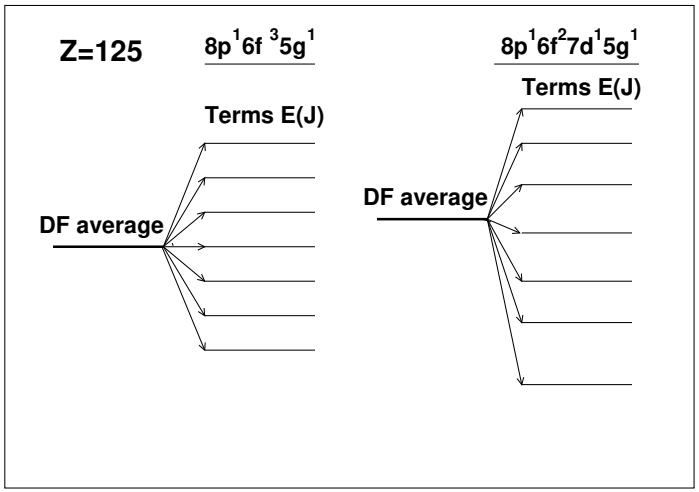
- **To evaluate the QED correction we use the model QED operator approach**[1].

  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 $E^{\rm av}$
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		$E^{\rm av}_{\rm DF}$ [a.u.]	J	$E_{\rm DF}(J)$ [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-Fcok (DF) energies* within the configuration average approximation are

Configuration	$E_{\mathrm{DF}}^{\mathrm{av}}$ [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: 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).

Spin-orbit splitting

Table: 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

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:

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

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

$$\sum_{i=1}^{N} p_i = 1 \, . \tag{2}$$

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

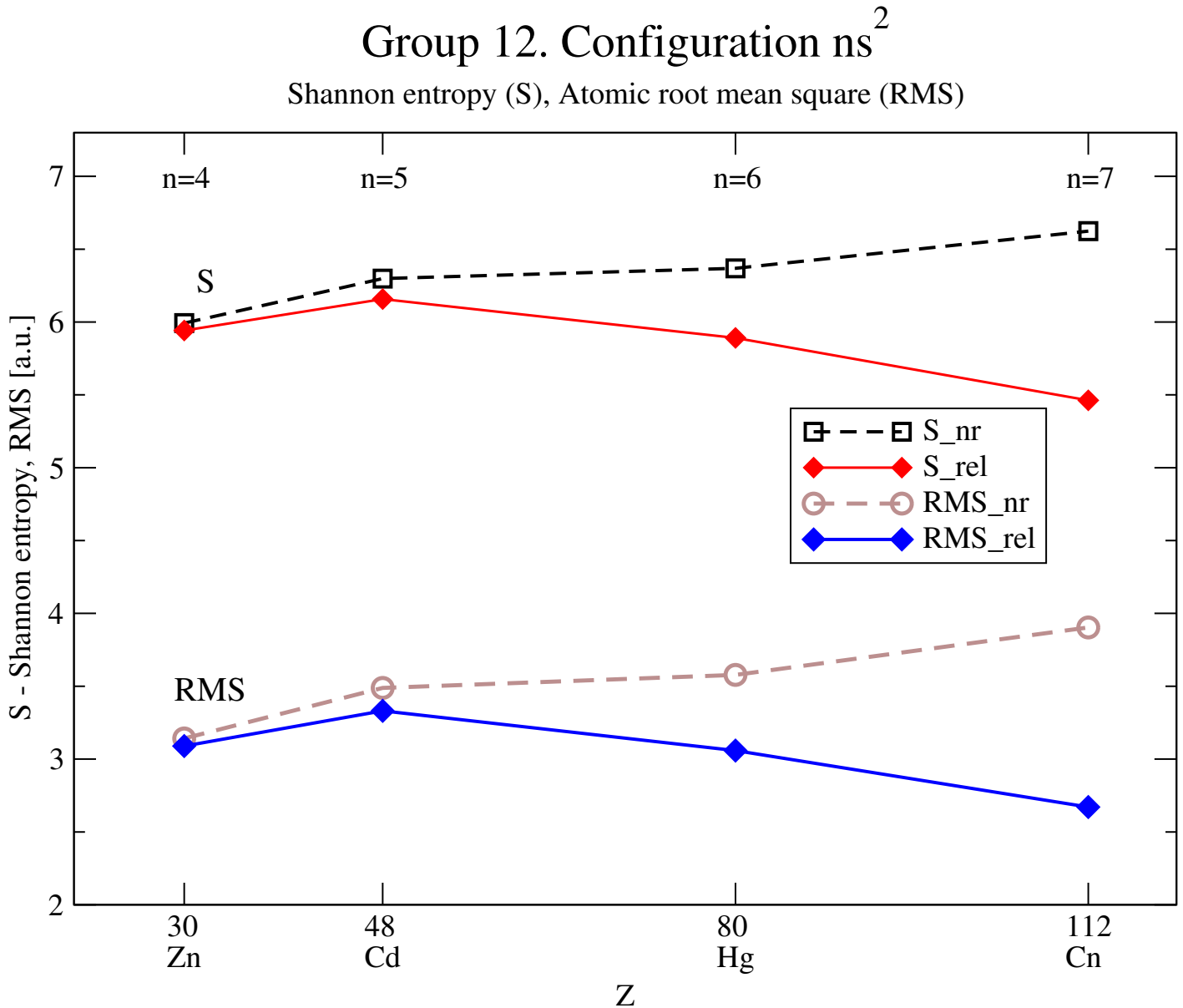
$$0 \leq S \leq \ln(N) \tag{3}$$

For continuous distribution

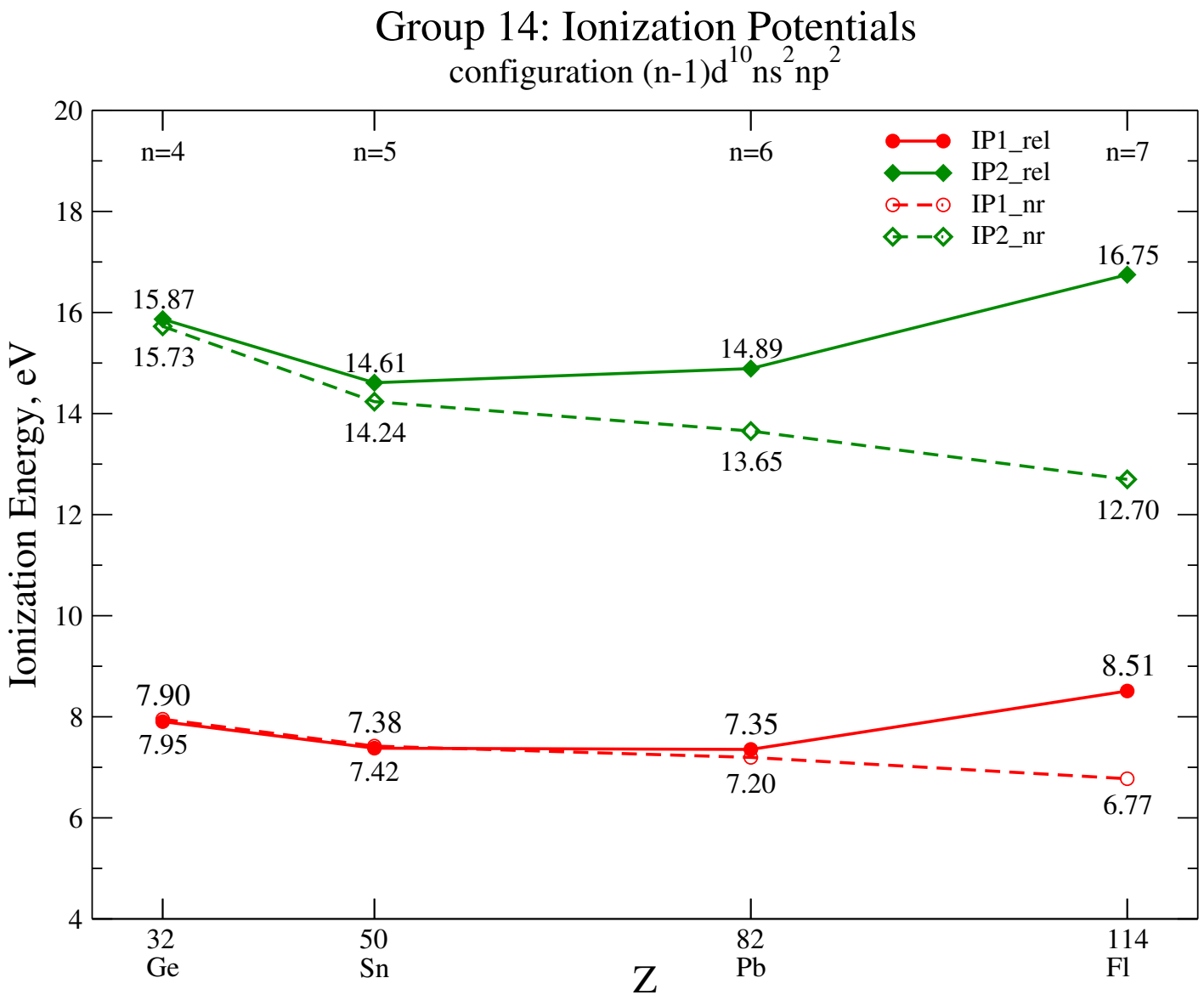
$$S = -\int d\boldsymbol{r} \, \ln(\rho(\boldsymbol{r})) \, \rho(\boldsymbol{r}) \, , \qquad \int d\boldsymbol{r} \, \rho(\boldsymbol{r}) = 1 \, . \tag{4}$$

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

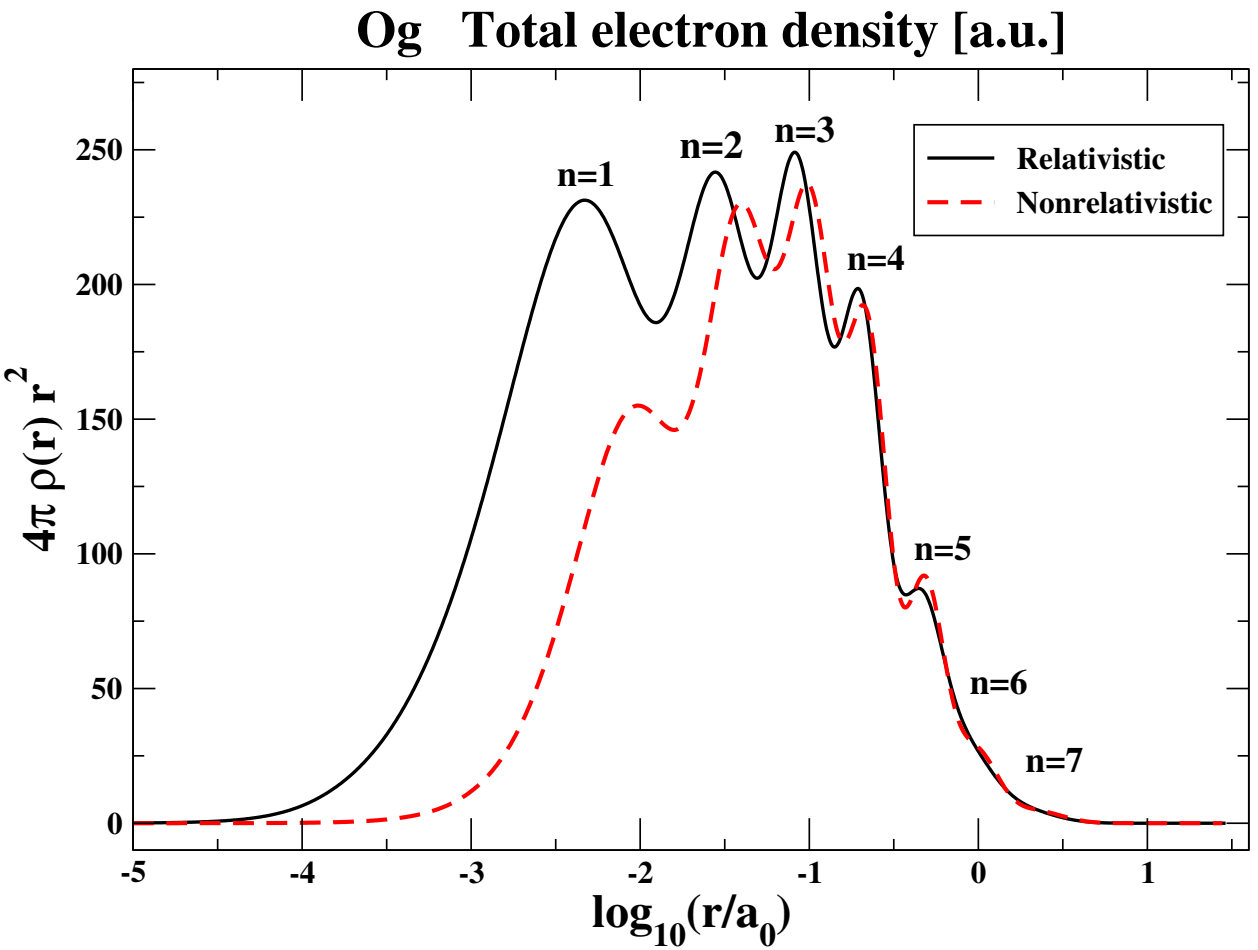
[1] *C.E. Shannon, Bell Syst. Tech. J. 27, 379; 623 (1948).*


Group 12. Configuration ns2
Shannon entropy (S), Atomic root mean square (RMS)
n=4
n=5
n=6
n=7
S
RMS
S_nr
S_rel
RMS_nr
RMS_rel
S - Shannon entropy, RMS [a.u.]
7
6
5
4
3
2
30
Zn
48
Cd
80
Hg
112
Cn
Z

14th group of elements



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 electron localization function characterize the degree of localization of electrons in atoms and molecules. ELF was introduced in the quantum chemectry in the paper [1]. ELF is defined by

$$\mathrm{ELF}(\boldsymbol{r}) = \left(1 + \left[\frac{D(\boldsymbol{r})}{D_0(\boldsymbol{r})}\right]^2\right)^{-1}, \tag{5}$$

where $D(\boldsymbol{r})$ is *the coefficient of non-zero leading term of the Taylor expansion of the conditional probability of finding a second electron near the reference electron with the same spin, which is located at position* $\boldsymbol{r}$.

In the Hartree-Fock approximation

$$D(\boldsymbol{r}) = \frac{1}{2}\left[\tau - \frac{1}{4}\frac{|\boldsymbol{\nabla}\rho(\boldsymbol{r})|^2}{\rho(\boldsymbol{r})}\right], \qquad \text{and} \qquad \tau = \sum_{i,\sigma} |\boldsymbol{\nabla}\varphi_{i\sigma}(\boldsymbol{r})|^2 . \tag{6}$$

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

$$D_0(\boldsymbol{r}) = \frac{3}{10}(3\,\pi^2)^{2/3}\rho^{5/3}(\boldsymbol{r})\,. \tag{7}$$

The ELF values lie between zero and one $0 \leq \mathrm{ELF} \leq 1$. 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)

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

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

$$\rho(r) = \sum_{\lambda=1,2} \rho^{\lambda}(r)\,, \qquad \rho^{\lambda}(r) = \frac{4\pi}{r^2} \sum_a q_a \begin{cases} P_a^2(r), & \lambda = 1, \\ Q_a^2(r), & \lambda = 2\,. \end{cases} \tag{9}$$

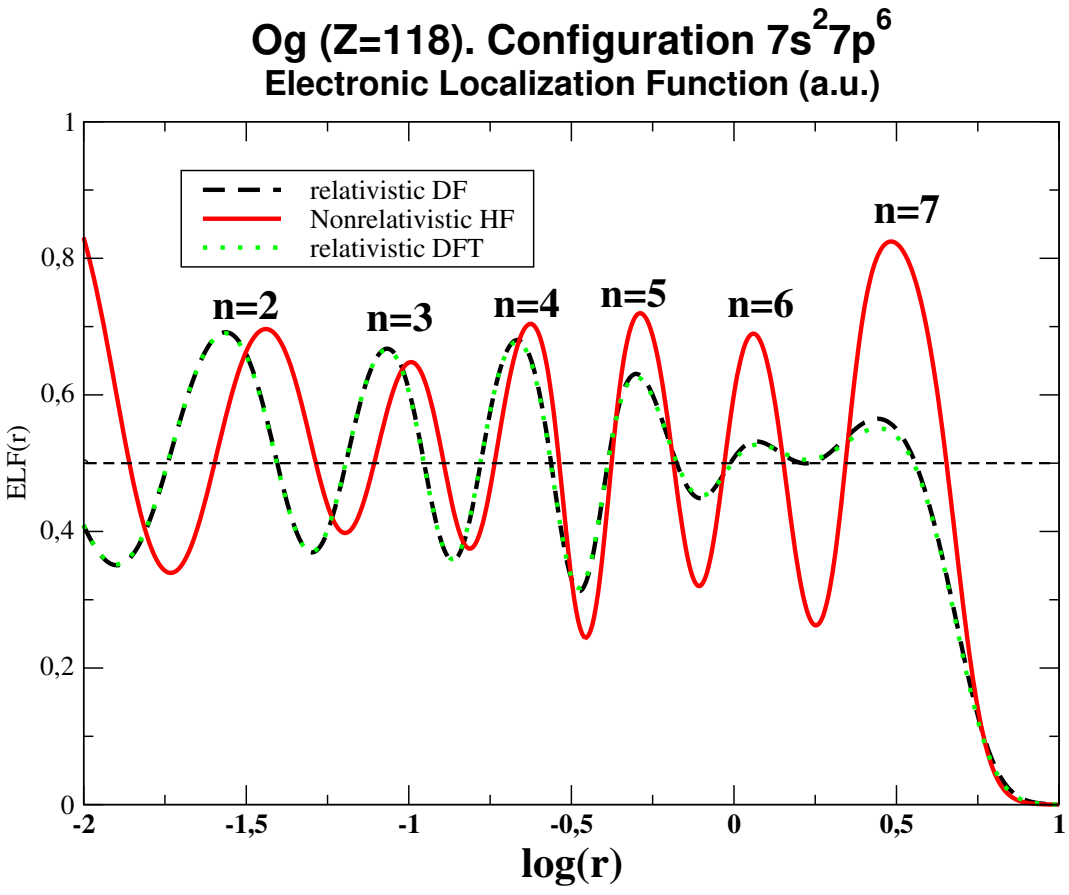
$T^{\lambda}(\boldsymbol{r})$ in formula (8) is the relativistic analogue of the non-relativistic kinetic energy density

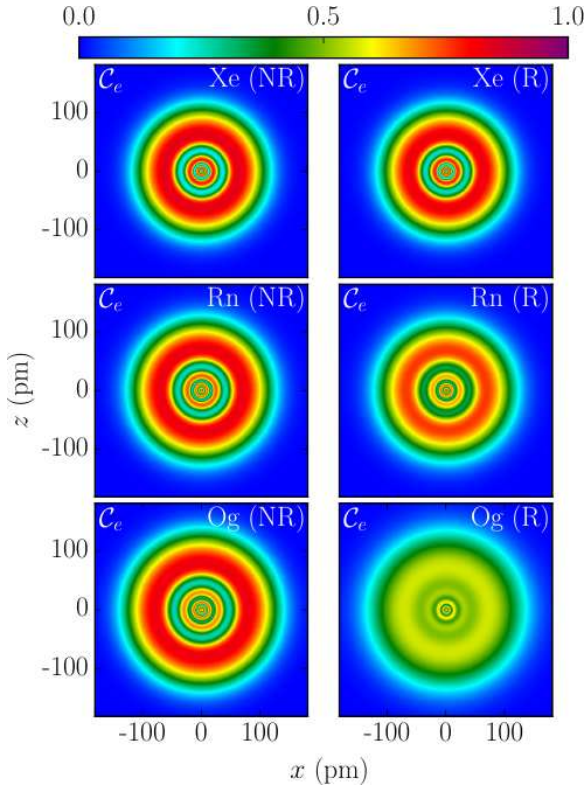
$$T^{\lambda}(\boldsymbol{r}) = \sum_a q_a\, t_a^{\lambda}(\boldsymbol{r})\,, \qquad t_a^{\lambda}(\boldsymbol{r}) = \frac{1}{2}\, \frac{1}{2j_a+1} \sum_{\mu_a,\sigma} \left|\boldsymbol{\nabla}\phi^{\lambda}_{a\mu_a}(\boldsymbol{r},\sigma)\right|^2 \tag{10}$$

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

$$W^{\lambda}(r) = \frac{\rho^{\lambda}(r)}{\rho(r)}\,. \tag{11}$$

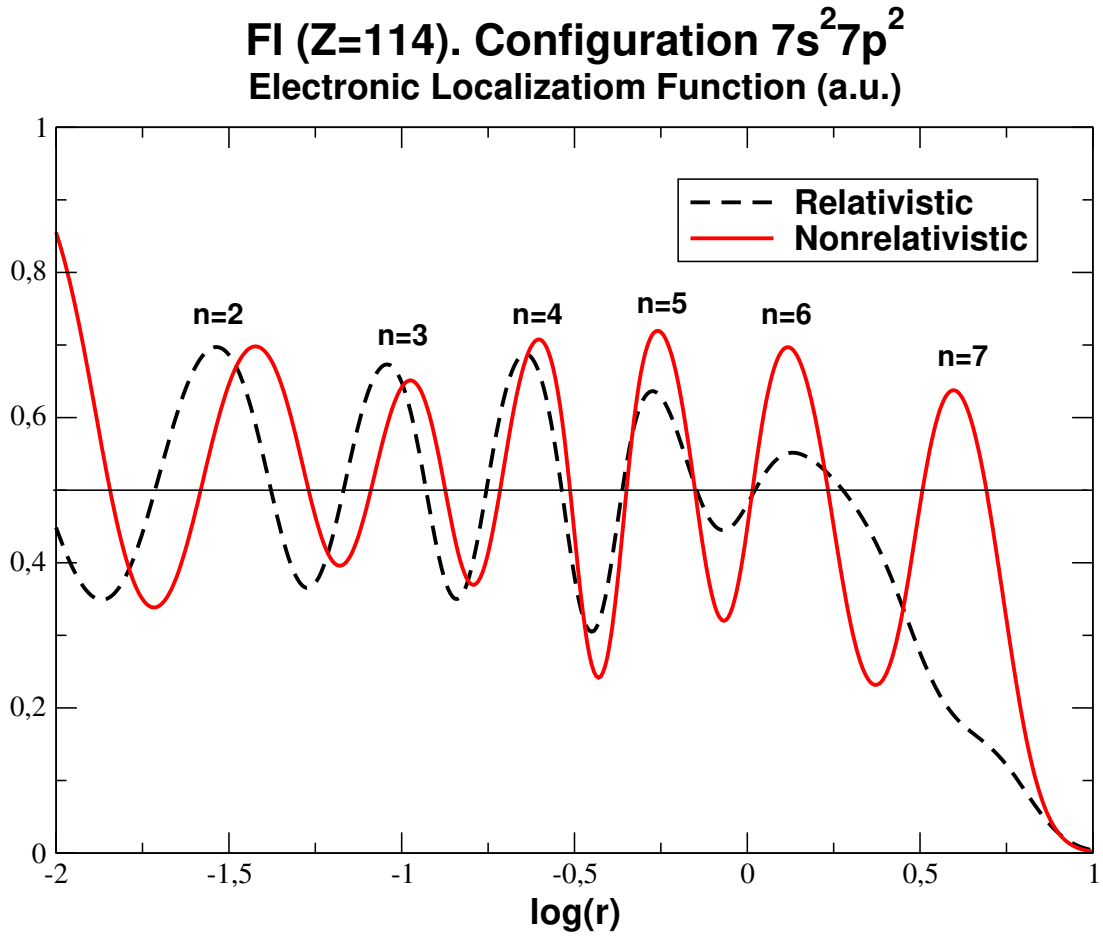
I.I Tupitsyn et al., Optics and Spectroscopy, 130, 1022 (2022)

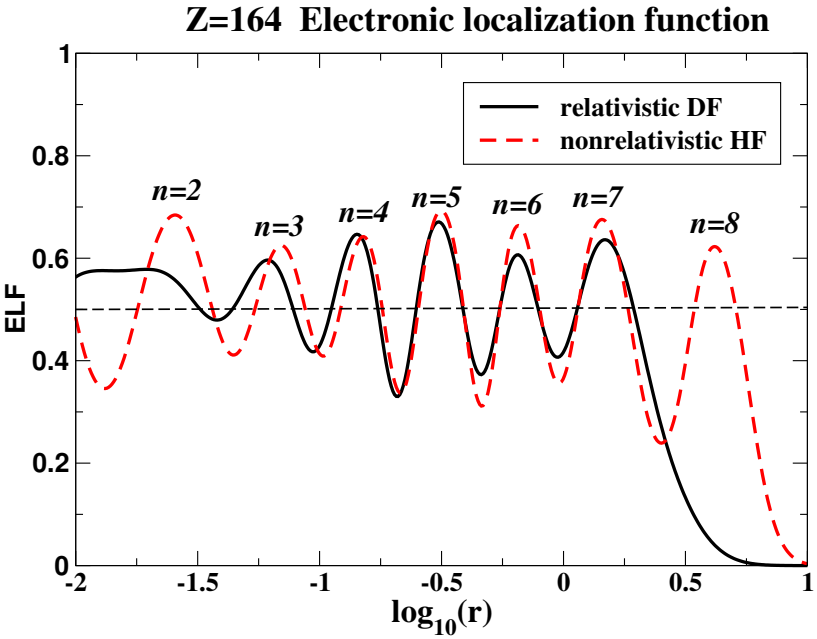


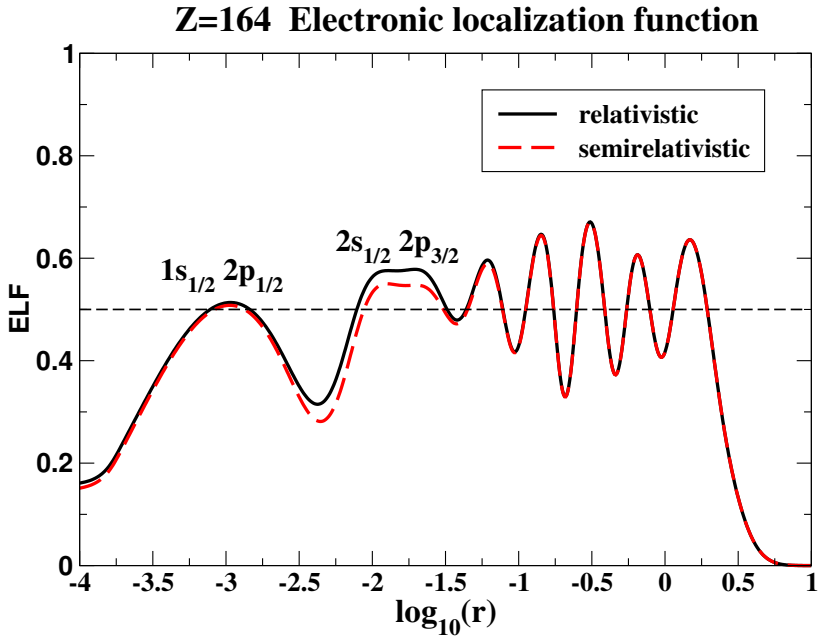


"Spin-orbit splitting in the 7p electronic shell becomes so large (∼10 eV) that Og is expected to show uniform-gas-like behavior in the valence region" [1].

[1] *Jerabek et al., PRL 120, 053001 (2018).*


Fl (Z=114). Configuration 7s²7p²
Electronic Localizatiom Function (a.u.)
Relativistic
Nonrelativistic
n=2
n=3
n=4
n=5
n=6
n=7
1
0,8
0,6
0,4
0,2
0
-2
-1,5
-1
-0,5
0
0,5
1
log(r)





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

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

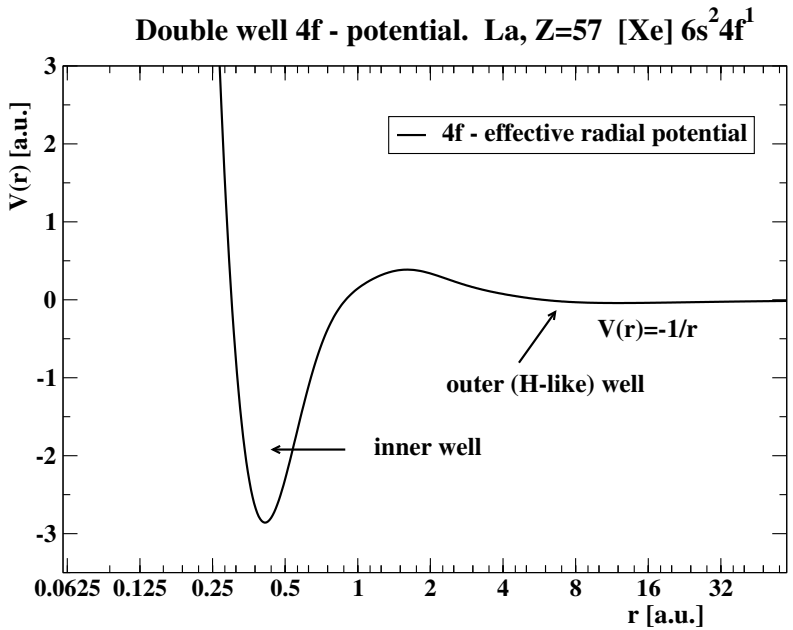
	ε [keV]	<r> [a.u.]
1s 1/2	-770.6	0.0028
2p 1/2	-343.0	0.0038
2s 1/2	-196.3	0.0130
2p 3/2	-66.2	0.0279

mc^2=510.7 keV

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

Moreover, in some cases, it is possible to obtain two different solutions of the Dirac-Fock equations depending on the initial approximation [1,2].

A coexistence of two different states of an atom with the same electronic configuration both for lanthanum ($6s^2 4f_{5/2}$) and for europium ($6s^2 4f^6_{5/2} 4f_{7/2}$) have been obtained in [1].

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, $\varepsilon^{\rm H}_{\rm 4f}$ – nonrelativistic H-like energy for n=4.

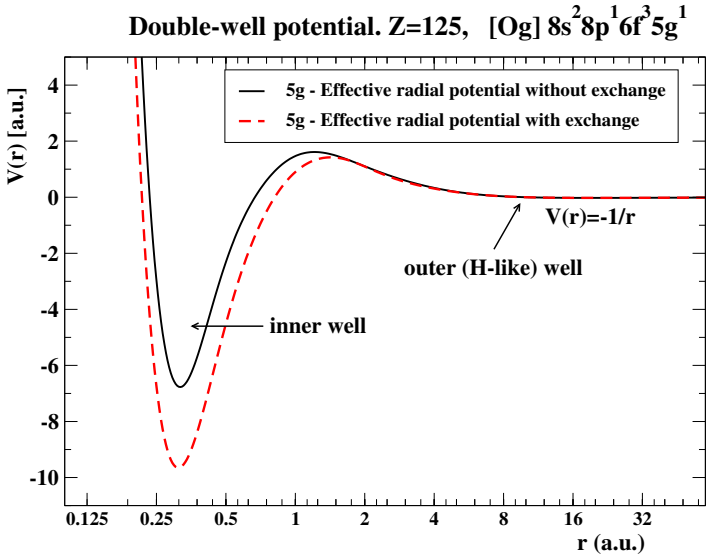
$$\begin{array}{llll} \varepsilon_{\rm 4f} = -0.2304 \text{ a.u.} & & <r>_{\rm 4f} = 1.27452 \text{ a.u.} \\ \varepsilon_{\rm 4f'} = -0.03176 \text{ a.u.} & & <r>_{\rm 4f'} = 17.1653 \text{ a.u.} \\ \varepsilon_{\rm 4f'}[1] = -0.0316 \text{ a.u.} & & -- \\ \varepsilon^{\rm H}_{\rm 4f} = -0.03125 \text{ a.u.} & & <r>^{\rm H}_{\rm 4f} = 17.9999 \text{ a.u.} \end{array} \qquad (12)$$

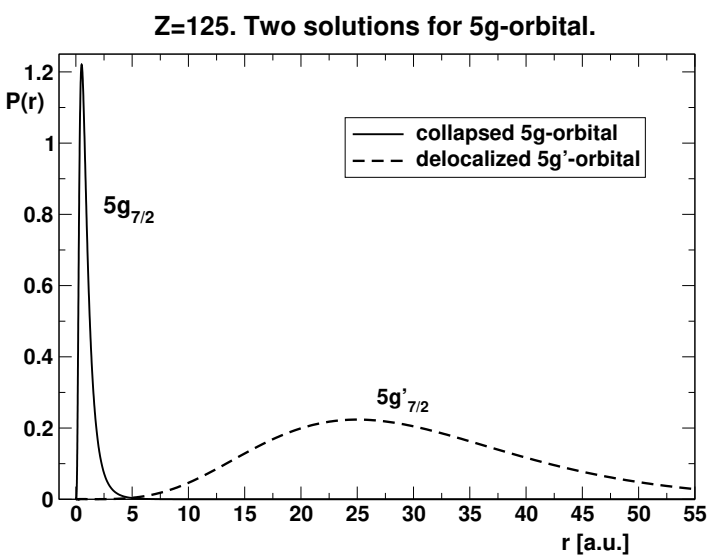
Total Energies (J=0.5):

$$\begin{array}{llll} E_{\rm inner} = -8493.5483 \text{ a.u.} & & E_{\rm inner}[1] = -8493.6247 \text{ a.u.} \\ E_{\rm outer} = -8493.4767 \text{ a.u.} & & E_{\rm outer}[1] = -8493.5512 \text{ a.u.} \end{array} \qquad (13)$$

1. *I.M. Band and V.I. Fomichev, Phys.Letters A,* **75**, *178 (1980)*
2. *J.-R Connerade and R.C. Kamatak, Handbook on the Physics and Chemistry of Rare Earths, v. 28, p. 1 (2000)*

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, $\varepsilon^{\rm H}_{\rm 5g}$ – nonrelativistic H-like energy for n=5.

$$\begin{aligned}
\varepsilon_{\rm 5g} &= -0.51464169 \text{ a.u.} & \langle r \rangle_{\rm 5g} &= 0.71289 \text{ a.u.} \\
\varepsilon_{\rm 5g'} &= -0.02000147 \text{ a.u.} & \langle r \rangle_{\rm 5g'} &= 27.4943 \text{ a.u.} \\
\varepsilon^{\rm H}_{\rm 5g} &= -0.02000001 \text{ a.u.} & \langle r \rangle^{\rm H}_{\rm 5g} &= 27.5000 \text{ a.u.}
\end{aligned} \tag{14}$$

Total Energies (J=0.5):

$$\begin{aligned}
E_{\rm inner} &= -64846.2788 \text{ a.u.} \\
E_{\rm outer} &= -64846.0878 \text{ a.u.}
\end{aligned} \tag{15}$$

One-electron model QED potential

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

$$V^{\rm SE} = V^{\rm SE}_{\rm loc} + \sum_{i,k=1}^{n} |\phi_i\rangle \Delta B_{ik} \langle\phi_k| \,, \tag{16}$$

where

$$\Delta B_{ik} = \sum_{j,l=1}^{n} (D^{-1})_{ji}\, \Delta\Sigma_{jl}\, (D^{-1})_{lk} \,, \tag{17}$$

$\Delta\Sigma_{ik} = \Sigma_{ik} - \langle\psi^{(0)}_i|V^{\rm SE}_{\rm loc}|\psi^{(0)}_k\rangle$ and $\Sigma_{ij} = \langle\psi^{(0)}_i|\hat{\Sigma}|\psi^{(0)}_j\rangle$.

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