Theor Chem Acc (2011) 129:495–505
DOI 10.1007/s00214-010-0887-3

REGULAR ARTICLE

Are MCDF calculations 101% correct in the super-heavy elements range?

Paul Indelicato · Jacek Bieroń · Per Jönsson

Received: 29 December 2010 / Accepted: 31 December 2010 / Published online: 26 January 2011
© Springer-Verlag 2011

Abstract We explore QED and many-body effects in super-heavy elements up to $Z = 173$ using the multiconfiguration Dirac–Fock method. We study the effect of going beyond the average level approximation on the determination of the ground state of element 140 and compare with the recent work of Pekka Pyykkö on the periodic table for super-heavy elements (Pyykkö, in Phys Chem Chem Phys, 13:161, 2011). We confirm that QED corrections are of the order of 1% on ionization energies. We show that the atomic number at which the 1*s* shell dives into the negative energy continuum is 173 and is not affected by the approximation employed to evaluate the electron–electron interaction.

Keywords Super-heavy elements · MCDF · Electronic correlation · Relativistic effects

---

Dedicated to Professor Pekka Pyykkö on the occasion of his 70th birthday and published as part of the Pyykkö Festschrift Issue.

P. Indelicato (✉)
Laboratoire Kastler Brossel, École Normale Supérieure,
CNRS, Université Pierre et Marie Curie—UPMC, Case 74,
4, place Jussieu, 75252 Paris CEDEX 05, France
e-mail: paul.indelicato@lkb.ens.fr

J. Bieroń
Instytut Fizyki imienia Mariana Smoluchowskiego,
Uniwersytet Jagielloński, Reymonta 4, 30-059 Kraków, Poland
e-mail: Bieron@uj.edu.pl

P. Jönsson
Nature, Environment, Society Malmö University,
205 06 Malmö, Sweden

1 Introduction

Super-heavy elements have been subject of an intense experimental activity over the past few decades [1–3]. Elements 108 (Hs) [4–6], 109 (Mt) [7–9], 110 (Ds) [10], 111 (Rg) [11], 112 [12–14], 113 [15], 114 [16–19], 115 [2], 116 [20–22], 117 [23], and 118 [22, 24] have been observed in a series of experiments in Berkeley, GSI, Dubna, and RIKEN. Chemistry of transactinide elements 104 (Rf) to 108 has been performed one atom at a time (see, e.g., [25] for a review). The chemical characterization of element 112 was also done recently [14].

Relativistic calculation of X-ray transition energies and binding energies have a long history. As early as 1958, Werner and Wheeler investigated the stability of elements of atomic numbers $Z^{\perp}$ 13 [26]. In 1968, Tucker et al. performed Relativistic Hartree-Fock-Slater calculations of elements 114, 126 and 140. Progress has been steady since then. In a recent paper [27], Pekka Pyykkö proposed an extended version of the periodic table, based on average level (AL) Dirac–Fock calculations, up to $Z = 172$, for which he used the 2005 version of the Desclaux and Indelicato MCDF code [28]. The new periodic table constitutes an update of the one by Fricke et al. [29], which was obtained using the Dirac–Hartree–Slater approximation. More recently, Nefedov and coll. proposed similar results, taking into account relativistic effects [30, 31]. The objectives of the present paper are as follows. We investigated the electron correlation effects on the ground states of a few selected super0heavy elements. We made an attempt to investigate at a very high-*Z* the well-known statement by Pekka Pyykkö, concerning the introduction of Dirac–Fock methods in chemistry: 'relativistic theory of atoms and molecules is 101% correct', attributing the surplus 1% to the (missing) QED effects. We used the 2010 development version of the *mcdfgme* code [32] to make full Dirac–Fock calculations for the ground level of element 140 and its isoelectronic sequence to evaluate the effect of the Breit interaction, an order of magnitude of QED corrections and to find the most likely candidate for the ground configuration. We also performed correlation contributions to the ground configuration of a number of super-heavy elements and studied QED corrections. Finally, we investigated the 1*s* shell binding energy for neutral atoms as a function of Z and tried to identify the most likely 'end' of the periodic table, which occurs when the 1*s* electron binding energy dives below $-2mc^2$. The *last but not least* objective of the present paper is a birthday contribution to the extended version of the periodic table, produced recently by Pekka Pyykkö [27].

2 Calculations

2.1 Dirac–Fock calculations

The MCDF method is well known, and we will here only recall its main features. More details can be found in, e.g., [33–38]. The total wavefunction is calculated with the help of the variational principle. The total energy of the atomic system is the eigenvalue of the equation

$$\mathcal{H}^{\text{no pair}}\Psi_{\Pi,J,M}(\ldots,\boldsymbol{r}_i,\ldots)=E_{\Pi,J,M}\Psi_{\Pi,J,M}(\ldots,\boldsymbol{r}_i,\ldots), \tag{1}$$

where Π is the parity, J is the total angular momentum eigenvalue, and M is the eigenvalue of its projection on the z axis J_z. Here,

$$\mathcal{H}^{\text{no pair}}=\sum_{i=1}^{N}\mathcal{H}_D(r_i)+\sum_{i<j}\mathcal{V}(|\boldsymbol{r}_i-\boldsymbol{r}_j|), \tag{2}$$

where $\mathcal{H}_D$ is the one electron Dirac operator and $\mathcal{V}$ is an operator representing the electron–electron interaction of order one in α. The expression of V_{ij} in Coulomb gauge, and in atomic units, is

$$V_{ij}=\frac{1}{r_{ij}} \tag{3a}$$

$$-\frac{\alpha_i\cdot\alpha_j}{r_{ij}} \\ -\frac{\alpha_i\cdot\alpha_j}{r_{ij}}\left[\cos\left(\frac{\omega_{ij}r_{ij}}{c}\right)-1\right] \tag{3b}$$

$$+c^2(\alpha_i\cdot\nabla_i)(\alpha_j\cdot\nabla_j)\frac{\cos\left(\frac{\omega_{ij}r_{ij}}{c}\right)-1}{\omega_{ij}^2 r_{ij}}, \tag{3c}$$

where $r_{ij}=\left|\boldsymbol{r}_i-\boldsymbol{r}_j\right|$ is the inter-electronic distance, ω_{ij} is the energy of the exchanged photon between the two electrons, α_i are the Dirac matrices, and c is the speed of light. We use the Coulomb gauge as it has been demonstrated that it provides energies free from spurious contributions at the ladder approximation level and must be used in many-body atomic structure calculations [39, 40].

The term (3a) represents the Coulomb interaction, the term (3b) is the Gaunt (magnetic) interaction, and the last two terms (3c) stand for the retardation operator. In this expression, the ∇ operators act only on r_{ij} and not on the following wavefunctions. The *mcdfgme* code can include as an option, the full Breit operator in the self-consistent field process, i.e., in both the Dirac–Fock differential equations for the orbitals and in the Hamiltonian matrix.

The *mcdfgme* code has been adapted to work with elements with $Z\geq 137$ a long time ago [41]. More recently, it has been used for calculation of properties of super-heavy elements like Landé g-factors, ionic radii, and energies with QED corrections for $Z\leq 108$ [42]. Elements with $Z\geq 137$ can only be calculated in the case of finite nuclear charge distribution, as the *s*-state Dirac binding energy for point nuclei contains a $\sqrt{1-(Z\alpha)^2}$ factor. Here, we use a Fermi model to represent the nucleus charge distribution, with a thickness parameter $c=2.3$ fm and a mean-square radius provided by

$$R=\left(r_0+\frac{r_1}{A^{2/3}}+\frac{r_2}{A^{4/3}}\right)\times A^{1/3}, \tag{4}$$

which has been fitted to all available experimental data [43]. For element 140, (4) gives $R=6.7717\,\text{fm}$, and $R=7.3189\,\text{fm}$ for element 170.

One of the difficulties in evaluating energies of neutral or quasi-neutral super-heavy systems arises from their complex outer shell structure, with several open shells of high angular momenta. They often lead to very large numbers of configurations, even at the Dirac–Fock level, which require several tens of gigabytes of memory, as well as storage requirements for the angular coefficients, if calculations take into account the full Breit operator. For that reason, previous calculations have been often limited to the so-called "average level" (AL) mode, where the energy functional is of the form [33, 34]

$$E_{\text{av}}=\frac{\sum_J(2J+1)E_{\Pi,J}}{\sum_J(2J+1)}. \tag{5}$$

Two recent examples of average level calculations have appeared in the papers by Pyykkö [27] and Nefedov et al. [31], who tried to establish new periodic classifications in the super-heavy domain.

In the present paper, we used the "optimal level" (OL) energy functional [44] that allows to optimize wavefunctions separately for each individual J value. The (OL) functional provides a better approximation of the true energy for each specific atomic level, at the cost of a very complex energy expression, with many angular integrals beyond the one involved in the average energy.

2.2 QED corrections

The self-energy for a super-heavy element is only known for the 1s shell from the papers of Cheng and Johnson [45], and Soff et al. [46]. Vacuum polarization for the 1s shell was evaluated for supercritical atoms by Neghabian [47], who found that the dive in the negative energy continuum of the 1s shell occurs at $Z = 174$. For shells other than 1s, accurate, all-orders calculations of self-energy have been also performed [48–52], but they are limited to one-electron states for point nuclei and $Z \leq 110$. Two-electron corrections (also called self-energy screening) have been calculated in few-electron ions, mostly for ions involving n = 1–4 shells [53–58], including d states [59]. Only a few works have been performed for outer s shells of neutral super-heavy elements, by Pyykkö et al. [60, 61]. Very recently Thierfelder and Schwerdtfeger have published an extensive Dirac-Fock calculation of ionization energies with QED corrections for group 1 (alkali), 2, 11, 12, 13 and 18 (rare gases) elements that goes up to Z = 120 [62]. This work also include Li-like, Na-like and Cu-like ions. These results are in good agreement with the one from Labzowsky and Pyykkö cited above. QED effects in ionization energies of element Z = 112 [63] and group 11 and 12 superheavy elements have also been studied recently [64].

Atoms with one K or L hole have been the subject of intense experimental and theoretical studies up to Z = 100 (see for example Ref. [65, 66] and reference therein), but the calculations have been very scarce for super-heavy elements. One can however cite Gaston et al. [67, 68], who have performed Dirac-Hartree-Fock calculations for atoms of Z = 112, 114, 116, and 118, with a 1s or 2s hole with QED and finite nuclear size corrections. A calculation of K and L shell ionization energies in $^{268}_{109}$Mt was performed by the same group [69]. Such calculations are important for experiments aiming at detecting X-rays from super-heavy elements formed in nuclear collisions like TASCA and TASISPec (see, e.g., [25, 68, 70]).

The one-electron self-energy is given by

$$\Delta E^{\mathrm{SE}}_{nlj} = \frac{\alpha}{\pi}\frac{(Z\alpha)^4}{n^3}F_{nlj}(Z\alpha) \qquad (6)$$

In the 2010 version of *mcdfgme*, we interpolate between known values of $F_{1s}(Z\alpha)$ for the 1s shell, which are known for $1 \leq Z \leq 170$ [45, 46, 71], corrected for finite size for the lower Z. For the other shells, when no one-electron value is known, we simply use the value of $F_{nlj}(Z\alpha)$ for highest known Z, as this function is very slowly varying. For the screening, we use the Welton approximation [72, 73]. This approximation, which involves evaluating the hydrogenic wavefunction of the screened electron for finite nucleus, fails for the 1s shell and $Z \geq 169$, since one-electron energy becomes smaller than $-2m_ec^2$. In that case, we used 100% screening. The vacuum polarization is included as the average of the Uehling, Wichmann and Kroll, and Källen and Sabry potentials. The Uehling potential can be included in the Dirac equation, allowing for an all-order calculation of the Loop-after-Loop contribution to vacuum polarization (see, eg., [74]).

3 Study of the ground state of a few super-heavy elements

3.1 The structure of the ground state of element 140

The pioneering work on the periodic classification for super-heavy elements [29] was made in the Dirac–Slater approximation. More recent works [27, 31] used the AL approximation. We have performed fully relaxed calculations for a number of configurations, in the OL approximation. The Breit interaction was treated self-consistently in both the OL and AL modes. In Ref. [31], the ground state of element 140 was attributed to the configuration $8s^28p^27d6f^35g^{14}$. We confirmed this assignment in AL mode, but the J-dependent OL calculations give binding energies ≈ 20 eV lower than AL ones, as can be seen on Fig. 1. Due to the large number of open shells with large j values, the number of configurations becomes very large, even in simple Dirac–Fock calculations that include only the relativistic configurations contributing to a single LS parent. In the OL mode, the lowest configuration is $8s^28p^46f5g^{15}J = 8$. We could not evaluate the $8s^28p^27d6f^35g^{14}$ configurations in OL mode, since the calculation could not fit into any computer we have access to (32GB RAM). Therefore, the $8s^28p^27d6f^35g^{14}$ configuration could still hold lower energy level. Obviously, finding the real minimum would require mixing several configurations of identical parity. The main contributions to the total binding energies in the OL calculations are shown in Fig. 2. The changes in the ground state structure for element 140 isoelectronic sequence are presented in Fig. 3. The most tightly bound configuration as a function of Z is presented in Table 1. The ground configuration becomes $8s^28p^25g^{18}, J = 0$ at $Z = 143$. The 142^{2+} ion has two configurations with identical energies, $8s^28p^35g^{17}, J = 3$ and $J = 6$. Only a fully correlated calculation would allow to decide which one is the ground configuration. To illustrate the complexity of the calculation, the numbers of extra Coulomb, magnetic, and retardation integrals are shown in Fig. 4 as a function of configuration. The maximum numbers of integrals, obtained for the $8s^28p^46f5g^{15}, J = 5$

Fig. 1 Comparison between the AL calculations and fully optimized, J dependent total biding energies for element $Z = 140$ relative to the $8s^2 8p^2 5g^{18}$ AL binding energy $E = -2538277.59$ eV set as 0. The AL calculations are plotted to the right of the $8s^2 8p^2 5g^{18}$ AL configuration

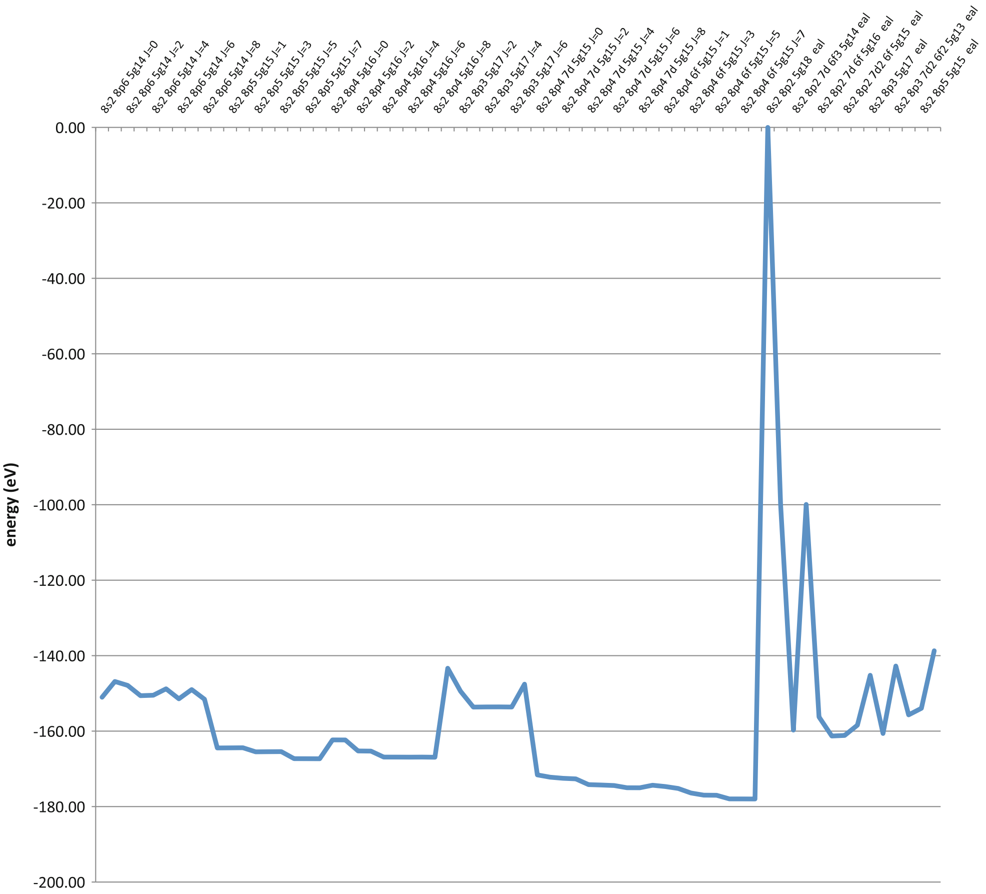
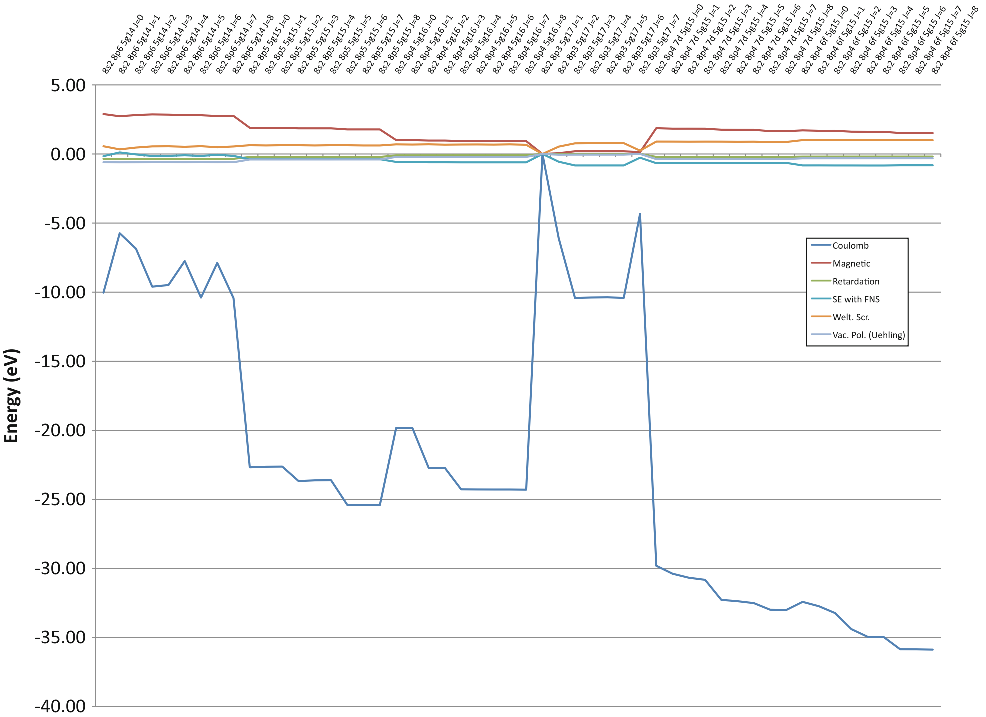


Fig. 2 Contributions to the binding energy of element $Z = 140$ relative to the $8s^2 8p^3 5g^{17}$, $J = 1$ configuration



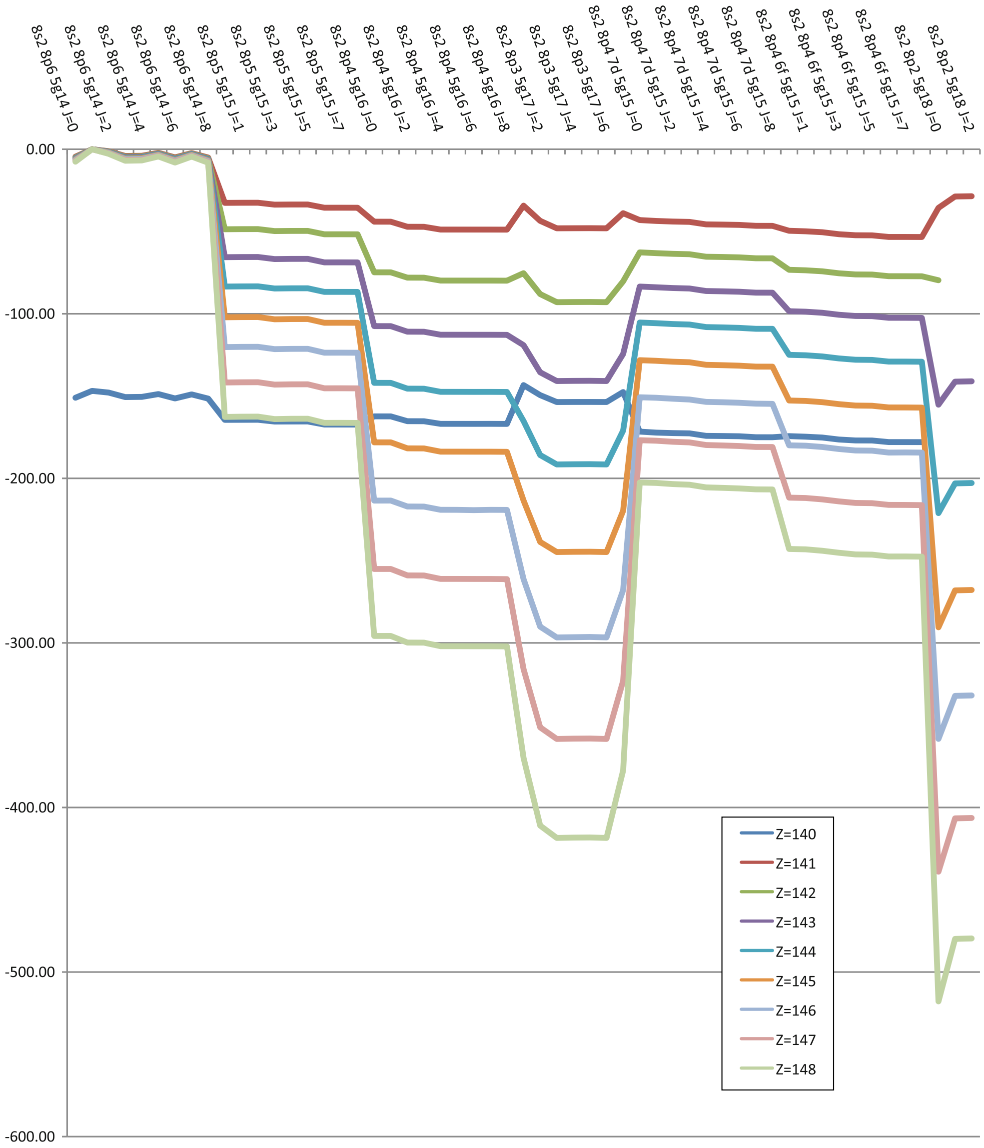


Fig. 3 Ground state configuration determination for the elements in the $Z = 140$ isoelectronic sequence

configurations are of 8.6, 29.7, and 25.7 million for the Coulomb, magnetic and retardation interaction, respectively. They correspond to 1.67 GB of angular integrals. In order to evaluate the external electron biding energy, one needs to determine the ground state of the 140^+ ion. In the case of the $8s^2 8p^4 7d 5g^{14}, J = 11/2$ level, one gets 20,638 determinants, 3,898 configurations which yield 44, 151 and 117 millions angular integrals, respectively. They would require 8.2 GB for storage. Adding an extra open shell is not possible even with the most powerful computers.

3.2 The end of the periodic table

Another interesting question is to study the elements with atomic numbers high enough that the $1s$ shell binding energy is close to $-2\, m_e c^2$. In the work of Fricke et al., the periodic table was extended up to $Z = 172$. Nefedov et al. stopped at $Z = 164$, while Pyykkö went up to $Z = 172$.

In the present paper, we evaluated the self-consistent Breit interaction and vacuum polarization within an OL calculation. The aim was to investigate whether these contributions could change the screening of the $1s$ electron by the rest of the atomic cloud to the point that they would eventually affect the end of the periodic table. We have found that in all cases, the limit is not sensitive to the method of treating the Breit interaction, i.e., whether the Breit interaction is treated as a perturbation or self-consistently.

The limit corresponds to the atomic number where the diagonal Lagrange parameter for the Dirac–Fock differential equation for the $1s$ orbital becomes smaller than

Table 1 Ground configuration for the isoelectronic sequence of $Z = 140$

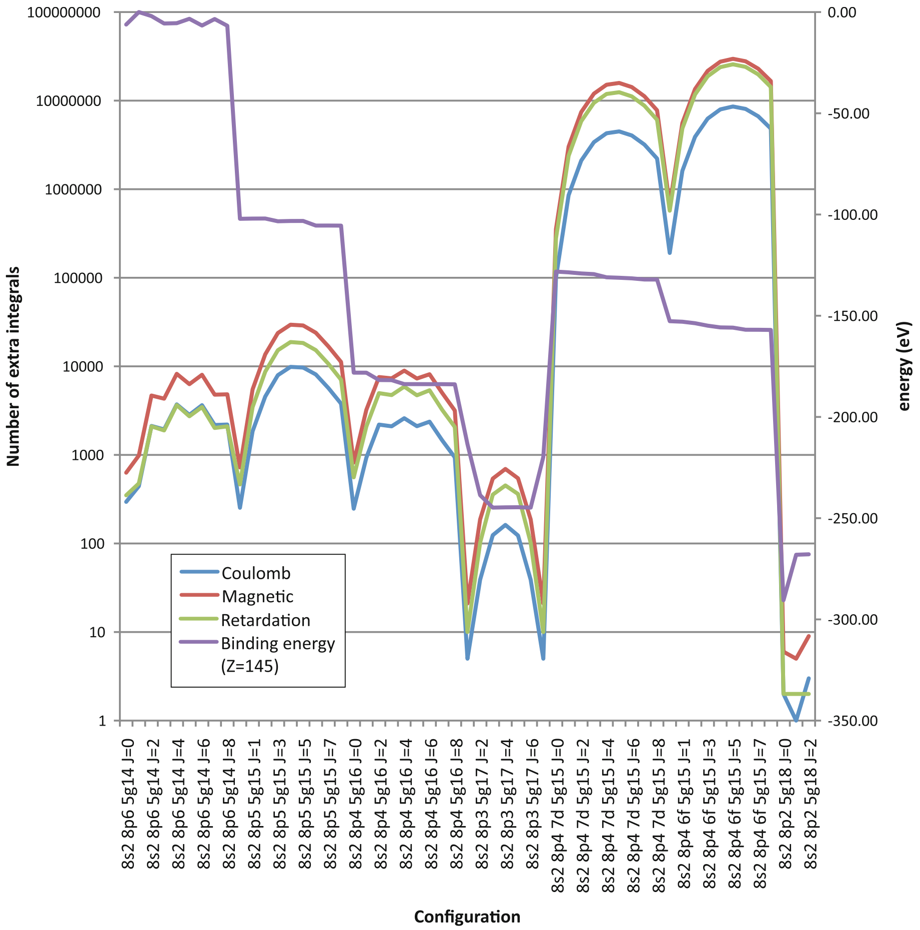
Z	Configuration	J	Total binding energy
140	$8s^2 8p^4 6f 5g^{15}$	8	−2538455.57
141	$8s^2 8p^4 6f 5g^{15}$	8	−2603656.93
142	$8s^2 8p^3 5g^{17}$	3	−2671099.87
142	$8s^2 8p^3 5g^{17}$	6	−2671099.87
143	$8s^2 8p^2 5g^{18}$	0	−2740824.19
144	$8s^2 8p^2 5g^{18}$	0	−2812825.12
145	$8s^2 8p^2 5g^{18}$	0	−2887405.73
146	$8s^2 8p^2 5g^{18}$	0	−3023446.23
147	$8s^2 8p^2 5g^{18}$	0	−3044385.17
148	$8s^2 8p^2 5g^{18}$	0	−3126941.02

All contributions in eV

$-2m_ec^2$. The 1*s* shell binding energy within different approximations is plotted on Fig. 6. An extrapolation of a cubic polynomial fit to the data crosses $-2m_ec^2$ mark at $Z_c = 173.17$, which yields the end of the periodic table at $Z = 173$. Diving into the negative continuum was studied, e.g., in [75, 76]. The contributions to the total biding energy and to the ionization energy of the elements with $Z = 171 - 173$ are given in Table 2. All two-loop QED contributions to the binding energy cancel since they are not known for outer shells. We expect them be small against correlation. An interesting feature is the much smaller binding energy of the element 172, compared to the two neighboring elements. There is also an unexpected non-monotonic behavior of the higher-order retardation correction to the total binding energy as a function of the atomic number, which contrasts with the smooth variation of the Coulomb, magnetic, and low-order retardation behavior (Fig. 5).

The sum of one and two-loop QED corrections represents roughly 0.4% of the total binding energy of these elements, slowly increasing from 0.35% ($Z = 171$) to 0.38% ($Z = 173$). Its contribution to the ionization energy varies more. We get 1.7, 0.1, and 1.2% for $Z = 171$, 172, and 173, respectively. The very low value for $Z = 172$ corresponds to both an almost exact screening of the self-energy, as well as an exact cancelation of vacuum polarization in the neutral and singly ionized case.

Fig. 4 Number of extra Coulomb, magnetic, and retardation integrals as a function of the configuration (*left vertical axis*). The biding energy for $Z = 145$ in the isoelectronic sequence of element 140, respective to the $8s^2 8p^6 5g^{14}$ configuration is also plotted (*right vertical axis*)



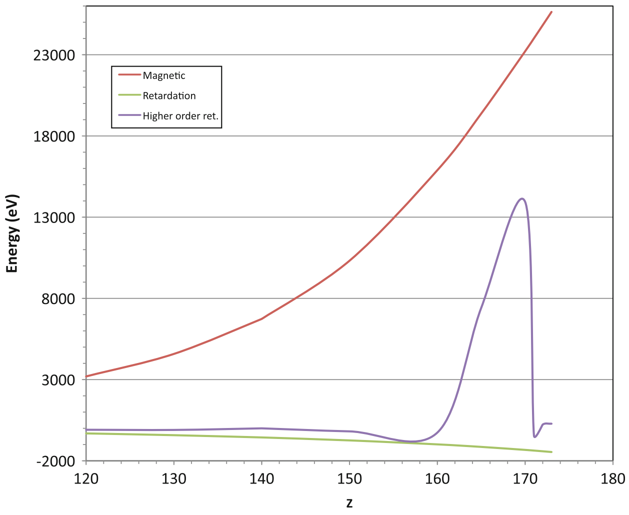


Fig. 5 Unexpected non-monotonic behavior in the variation of higher-order retardation as a function of Z

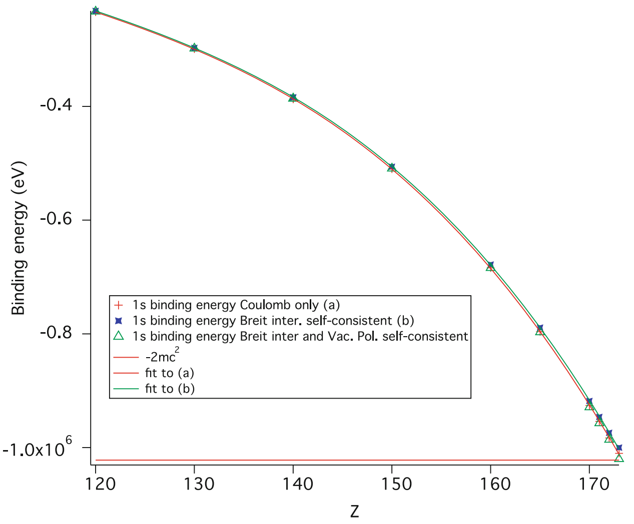


Fig. 6 Behavior of the 1s shell binding energy of a neutral superheavy atom as a function of the atomic number with different approximation

Table 2 Contributions to the ground state total binding energy and ionization energy for elements with $Z > 170$

Z	171	172	173
Total binding energy			
[Rn]$5f^{14}6d^{10}7s^27p^68s^28p^67d^{10}5g^{18}6f^{14}$	$9s^2$ $9p$, $J = 1/2$	$9s^29p^2$, $J = 2$	$9s^29p^3$, $J = 3/2$
Coulomb	−6052798	−6229026	−6409504
Magnetic	24012	24820	25636
Retardation	−1369	−1413	−1459
Higher order ret.	−437	233	284
S.E.&F.N.	28719	29398	30087
Welt. Scr.	−1073	−1093	−1113
Uehling Vac. Pol.	−53303	−55764	−58259
Muon Vac. Pol.	−70	−74	−78
Uelhing corr to elec. Inter.	313	331	350
Wichmann and Kroll VP	4522	4767	5019
Kàllén and Sabry VP	−400	−420	−439
Two-loop SE	−516	−536	−557
SEVP terms	546	579	615
S[VP]E terms	141	150	160
Total	−6051712	−6228047	−6409259
Ionization energy of the outer electron–with respect to the following ion configuration			
[Rn]$5f^{14}6d^{10}7s^27p^68s^28p^67d^{10}5g^{18}6f^{14}$	$9s^2$, $J = 0$	$9s^2$ $9p$, $J = 1/2$	$9s^29p^2$, $J = 2$
Coulomb	−12.399	−2.096	−19.833
Magnetic	0.078	0.002	0.113
Retardation	0.001	−0.001	−0.001
Higher order ret.	0.021	−0.001	0.041
S.E.&F.N.	−0.299	0.591	−0.313
Welt. Scr.	0.239	−0.594	0.282
Uehling Vac. Pol.	−0.166	0.001	−0.222
Uelhing corr to elec. Inter.	0.002	0.000	0.003
Wichmann and Kroll VP	0.014	0.000	0.019
Kàllén and Sabry VP	−0.001	0.000	−0.002
Total	−12.510	−2.097	−19.912

All values in eV

Therefore, one may conclude that neglecting radiative QED in the high-Z range yields a total energy of the order of 101% of the QED-corrected energy, as emphasized by Pekka Pyykkö, yet in specific cases, the ionization energy can be as large as 110% of the energy obtained by neglecting QED. It should be noted, however, that we have employed several approximations, since full QED calculations are not feasible at this level. Firstly, we assumed that the self-energy $F(Z\alpha)$ functions are constant for high-Z. Secondly, the self-energy screening is evaluated in the Welton approximation. Moreover, the vertex correction [57] has not been calculated, except for $n = 1$ and $n = 2$ level. The exchange correction to the SE screening is known only for He-like and Li-like ions. The non-radiative corrections to the electron–electron interaction, due to the negative energy states, are neglected. Finally, two-loop radiative corrections are known only for the $n = 1$ and 2 levels, except for the Kàllén and Sabry, and the Loop-after-Loop vacuum polarization corrections, which can be calculated for any level, using the Kàllén and Sabry potential or including the Uehling potential in the Dirac–Fock equations.

4 Correlation effects on the ground state energy of super-heavy elements

The calculations described in the previous sections did not take electron correlation into account. It is a well-established fact that electron correlation is the largest contribution to the error of the total energy of a heavy or a super-heavy atom, calculated in the Dirac–Fock approximation. To this end, several calculations have been performed for super-heavy elements, most of them in the coupled-cluster approximation. Correlation energy for the ground state of elements with $Z =$ 102 [77], 103 [78, 79], 104 [80], 111 [81], 112 [82], 113 [83], 114 [84, 85], 115 [86], 118 [87, 88], and 122 [89] have been calculated with this approach. More recently a combined configuration interaction and many-body perturbation theory method was used to evaluate accurately transition energies in element 112 [90]. The MCDF method was used for evaluating correlation on transition energies and rates for Fm and No, as well as for the element 118 [42, 91, 92] and 122 [93]. In the present paper, we used the MCDF method for a much more modest goal: an estimate of the effect of the full Breit interaction on the ground state energy of a very high-Z super-heavy element. We have chosen element 162 with configuration $[\mathrm{Rn}]5f^{14}6d^{10}7s^{2}7p^{6}7d^{10}5g^{18}6f^{14}6s^{2}$ and performed a simple calculation with valence shell correlation arising from the interaction with configurations $8s^2 + 8p^2 + 8d^2 + 8f^2$. Such a choice was made because cases with open d, f, and g shells would lead to very large numbers of configurations and integrals, and would have been impossible to handle. The calculations were performed either with Coulomb interaction (3a) or with full Breit interaction (3) in the self-consistent process (both in the differential equations and in the hamiltonian matrix). The results are presented in Table 3 and are quite surprising for such a high-Z element—the changes in the Dirac–Fock energy are very large for the total binding energy. The ionization energy is also calculated. If the same approximation is used for the $8s$, $J = 1/2$ in element 162^+, as for the $8s^2$, $J = 0$ case, the correlation energy of the $8s$, $J = 1/2$ level in element 162^+ is zero. One also notes that the higher-order retardation is much larger than the low-order part. However, the effect on the ionization energy of the $8s$ electron is very small. The total QED correction represents 0.4%, as in the $Z \geq 171$ range, and 1.6% for the ionization energy, which is consistent with what was observed at lower Z.

Table 3 Effect on the self-consistent Breit interaction on the ground state total binding energy for element $Z = 162$

Contribution	Total energy	$8s$ binding energy
Coulomb	−4656837.586	−52.956
Magnetic	17331.247	0.276
Retardation	−1051.799	−0.013
Higher order ret.	5741.901	0.159
S.E.&F.N.	21326.870	16.421
Welt. Scr.	−1549.328	−15.593
Uehling Vac. Pol.	−33358.385	−0.686
Muon Vac. Pol.	−37.130	−0.001
Uelhing corr to elec. Inter.	174.757	0.008
Wichmann and Kroll VP	2658.840	0.052
Kàllén and Sabry VP	−293.829	−0.007
Two-loop SE	−355.807	0.000
SEVP terms	313.736	0.000
S[VP]E terms	78.355	0.000
Coul. Intrashell Corr.	−1.858	
Mag. Intrashell Corr.	0.103	
Ret. Intrashell Corr.	−0.005	
Higher order IS ret. Corr.	0.256	
SC Breit (DF) on Coul.	47.744	0.002
SC Breit (DF) on Mag.	−101.041	−0.003
SC Breit (DF) on Ret.	5.488	0.000
SC Breit (DF) on HO ret.	−153.323	−0.007
SC Breit on Coul. Corr.	0.004	
SC Breit on Mag. Corr.	−0.009	
SC Breit on Ret. Corr.	0.000	
SC Breit on HO Corr.	−0.028	
Total	−4646060.83	−52.35

All values are in eV

5 Conclusion

We have studied in detail the structure of the ground state of several super-heavy elements. We have investigated the influence of taking into account the total angular momentum for determining the ground configuration. Determination of the ground state, even at the Dirac–Fock level, is very difficult, due to a very large number of open shells arising from large angular momenta which have to be considered, leading to thousands of determinants and configurations, and very large number of Coulomb and Breit integrals. An attempt to include even relatively simple correlation contributions, which may be necessary to confidently identify the ground state, would lead to configuration expansions beyond the capabilities of today's computers. We also found that convergence of the calculation was often problematic, in particular for $8p$, $9p$, and $5g$ electrons, even at the DF level. The inclusion of the Breit interaction in the SCF process usually makes things worse. Development of stable numerical strategies for diffuse orbitals and Dirac–Fock potentials with several minima is a pre-requisite for more systematic calculations. Very often, the JJ coupling limit is the cause of problems, as for example, the configurations with an $np_{3/2}$ orbital have a very small weight, compared to the ones with $np_{1/2} (n = 8 \mathrm{or} 9)$. This point was already emphasized for highly charged super-heavy elements and $2p$ shells in Ref. [42]. We have studied the influence of QED on the total binding energy in the very high-Z range, finding that on average it represents $\approx 0.4\%$, a fitting extrapolation of the well-known estimate by Pekka Pyykkö: 'relativistic theory of atoms and molecules is 101% correct'.

On the other hand, the QED correction can be as large as 10% for $Z = 172$, due to a strong decrease in the Coulomb DF contribution. A survey of the literature shows that there are no direct QED calculations in the range of super-heavy elements, except for the $1s$ shell. Many QED contributions have never been calculated for neutral super-heavy elements, except for a very limited number of cases, notably in [42, 61, 88]. A systematic evaluation of all necessary contributions to order α^2 would represent a daunting task. Another question, which requires a completely fresh approach, is whether perturbation theory still works in QED for elements close to $Z = 173$. Such an approach is required if one wants to understand what would an atom do when the $1s$ shell has dived into the negative energy continuum. Finally, we are delighted to join the other contributors to this volume in wishing Pekka Pyykkö a 101% sunshine on his birthday.

Acknowledgments PI acknowledges partial support by the Helmholtz Alliance HA216/EMMI for this research. Laboratoire Kastler Brossel is "Unité Mixte de Recherche n° 8552" of École Normale Supérieure, CNRS and Université Pierre et Marie Curie. PI wishes to thank Jean-Paul Desclaux with whom the *mcdfgme* 2010 version is being developed, and Valeria Pershina for interesting discussions and for bringing to his attention Refs. [30, 31]. All authors wish to thank Pekka Pyykkö for many years of fruitful collaboration. We should mention that both the subject and the title of the present paper were inspired by an entangled influence of Pekka.

References

1. Hofmann S, Münzenberg G (2000) Rev Mod Phys 72(3):733
2. Oganessian YT, Utyonkoy VK, Lobanov YV, Abdullin FS, Polyakov AN, Shirokovsky IV, Tsyganov YS, Gulbekian GG, Bogomolov SL, Mezentsev AN, Iliev S, Subbotin VG, Sukhov AM, Voinov AA, Buklanov GV, Subotic K, Zagrebaev VI, Itkis MG, Patin JB, Moody KJ, Wild JF, Stoyer MA, Stoyer NJ, Shaughnessy DA, Kenneally JM, Lougheed RW (2004) Phys Rev C 69(2):021601 (R)
3. Hofmann S (2009) In: The euroschool lectures on physics with exotic beams, vol III. Lecture Notes in Physics, vol 764. Springer, Berlin/Heidelberg, pp 203–252
4. Münzenberg G, Armbruster P, Folger H, Heßberger F, Hofmann S, Keller J, Poppensieker K, Reisdorf W, Schmidt KH, Schött HJ, Leino ME, Hingmann R (1984) Zeitschrift für Physik A Hadrons and Nuclei 317(2):235
5. Münzenberg G, Armbruster P, Berthes G, Folger H, Heßberger FP, Hofmann S, Poppensieker K, Reisdorf W, Quint B, Schmidt KH, Schött HJ, Sümmerer K, Zychor I, Leino ME, Gollerthan U, Hanelt E (1986) Zeitschrift für Physik A Hadrons and Nuclei 324(4):489
6. Münzenberg G, Armbruster P, Berthes G, Folger H, Heßberger FP, Hofmann S, Keller J, Poppensieker K, Quint AB, Reisdorf W, Schmidt KH, Schött HJ, Sümmerer K, Zychor I, Leino ME, Hingmann R, Gollerthan U, Hanelt E (1987) Zeitschrift für Physik A Hadrons and Nuclei 328(1):49
7. Münzenberg G, Armbruster P, Heßberger FP, Hofmann S, Poppensieker K, Reisdorf W, Schneider JHR, Schneider WFW, Schmidt KH, Sahm CC, Vermeulen D (1982) Zeitschrift für Physik A Hadrons and Nuclei 309(1):89
8. Münzenberg G, Reisdorf W, Hofmann S, Agarwal YK, Heßberger FP, Poppensieker K, Schneider JRH, Schneider WFW, Schmidt KH, Schött HJ, Armbruster P, Sahm CC, Vermeulen D (1984) Zeitschrift für Physik A Hadrons and Nuclei 315(2):145
9. Münzenberg G, Hofmann S, Heßberger FP, Folger H, Ninov V, Poppensieker K, Quint AB, Reisdorf W, Schött HJ, Sümmerer K, Ambruster P, Leino MF, Ackermann D, Gollerthqn U, Hanelt E, Morawek W, Fujita Y, Schwab T, Tüler A (1988) Zeitschrift für Physik A 330:435
10. Hofmann S, Ninov V, Heßberger FP, Armbruster P, Folger H, Münzenberg G, Schött HJ, Popeko AG, Yeremin AV, Andreyev AN, Saro S, Janik R, Leino M (1995) Zeitschrift für Physik A Hadrons and Nuclei 350(4):277
11. Hofmann S, Ninov V, Heßberger FP, Armbruster P, Folger H, Münzenberg G, Schött HJ, Popeko AG, Yeremin AV, Andreyev AN, Saro S, Janik R, Leino M (1995) Zeitschrift für Physik A Hadrons and Nuclei 350(4):281
12. Hofmann S, Ninov V, Heßberger FP, Armbruster P, Folger H, Münzenberg G, Schött HJ, Popeko AG, Yeremin AV, Saro S, Janik R, Leino M (1996) Zeitschrift für Physik A Hadrons and Nuclei 354(3):229
13. Yakushev AB, Zvara I, Oganessian YT, Belozerov AV, Dmitriev SN, Eichler B, Hubener S, Sokol EA, Turler A, Yeremin AV, Buklanov GV, Chelnokov ML, Chepigin VI, Gorshkov VA, Gulyaev AV, Lebedev VY, Malyshev ON, Popeko AG, Soverna

S, Szeglowski Z, Timokhin SN, Tretyakova SP, Vasko VM, Itkis MG (2004) Nucl Phys A 734:204

14. Eichler R, Aksenov NV, Belozerov AV, Bozhikov GA, Chepigin VI, Dmitriev SN, Dressler R, Gaggeler HW, Gorshkov VA, Haenssler F, Itkis MG, Laube A, Lebedev VY, Malyshev ON, Oganessian YT, Petrushkin OV, Piguet D, Rasmussen P, Shishkin SV, Shutov AV, Svirikhin AI, Tereshatov EE, Vostokin GK, Wegrzecki M, Yeremin AV (2007) Nat Biotechnol 447(7140):72
15. Morita K, Morimoto K, Kaji D, Akiyama T, Goto Si, Haba H, Ideguchi E, Kanungo R, Katori K, Koura H, Kudo H, Ohnishi T, Ozawa A, Suda T, Sueki K, Xu H, Yamaguchi T, Yoneda A, Yoshida A, Zhao Y (2004) J Phys Soc Japan 73:2593
16. Oganessian YT, Yeremin AV, Popeko AG, Bogomolov SL, Buklanov GV, Chelnokov ML, Chepigin VI, Gikal BN, Gorshkov VA, Gulbekian GG, Itkis MG, Kabachenko AP, Lavrentev AY, Malyshev ON, Rohac J, Sagaidak RN, Hofmann S, Saro S, Giardina G, Morita K (1999) Nat Biotechnol 400(6741):242
17. Oganessian YT, Utyonkov VK, Lobanov YV, Abdullin FS, Polyakov AN, Shirokovsky IV, Tsyganov YS, Gulbekian GG, Bogomolov SL, Gikal BN, Mezentsev AN, Iliev S, Subbotin VG, Sukhov AM, Buklanov GV, Subotic K, Itkis MG, Moody KJ, Wild JF, Stoyer NJ, Stoyer MA, Lougheed RW (1999) Phys Rev Lett 83(16):3154
18. Oganessian YT, Utyonkov VK, Lobanov YV, Abdullin FS, Polyakov AN, Shirokovsky IV, Tsyganov YS, Gulbekian GG, Bogomolov SL, Gikal BN, Mezentsev AN, Iliev S, Subbotin VG, Sukhov AM, Ivanov OV, Buklanov GV, Subotic K, Itkis MG, Moody KJ, Wild JF, Stoyer NJ, Stoyer MA, Lougheed RW (2000) Phys Rev C 62(4):041604
19. Düllmann CE, Schädel M, Yakushev A, Türler A, Eberhardt K, Kratz JV, Ackermann D, Andersson LL, Block M, Brüchle W, Dvorak J, Essel HG, Ellison PA, Even J, Gates JM, Gorshkov A, Graeger R, Gregorich KE, Hartmann W, Herzberg RD, Heßberger FP, Hild D, Hübner A, Jäger E, Khuyagbaatar J, Kindler B, Krier J (2010) Phys Rev Lett 104(25):252701
20. Oganessian YT, Utyonkov VK, Lobanov YV, Abdullin FS, Polyakov AN, Shirokovsky IV, Tsyganov YS, Gulbekian GG, Bogomolov SL, Gikal BN, Mezentsev AN, Iliev S, Subbotin VG, Sukhov AM, Ivanov OV, Buklanov GV, Subotic K, Itkis MG, Moody KJ, Wild JF, Stoyer NJ, Stoyer MA, Lougheed RW, Laue CA, Karelin YA, Tatarinov AN (2001) Phys Rev C 63(1):011301
21. Oganessian YT, Utyonkov VK, Lobanov YV, Abdullin FS, Polyakov AN, Shirokovsky IV, Tsyganov YS, Gulbekian GG, Bogomolov SL, Gikal BN, Mezentsev AN, Iliev S, Subbotin VG, Sukhov AM, Voinov AA, Buklanov GV, Subotic K, Zagrebaev VI, Itkis MG, Patin JB, Moody KJ, Wild JF, Stoyer MA, Stoyer NJ, Shaughnessy DA, Kenneally JM, Lougheed RW (2004) Phys Rev C (Nucl Phys) 69(5):054607
22. Oganessian YT, Utyonkov VK, Yu VL, Abdullin VL, Polyakov AN, Sagaidak RN, Shirokovsky IV, Yu ST, Voinov AA, Gulbekian GG, Bogomolov SL, Gikal BN, Mezentsev AN, Iliev S, Subbotin VG, Sukhov AM, Subotic K, Zagrebaev VI, Vostokin GK, Itkis MG, Moody KJ, Patin JB, Shaughnessy DA, Stoyer MA, Stoyer NJ, Wilk PA, Kenneally JM, Landrum JH, Wild JF, Lougheed RW (2006) Phys Rev C (Nucl Phys) 74(4):044602
23. Oganessian YT, Abdullin FS, Bailey PD, Benker DE, Bennett ME, Dmitriev SN, Ezold JG, Hamilton JH, Henderson RA, Itkis MG, Lobanov YV, Mezentsev AN, Moody KJ, Nelson SL, Polyakov AN, Porter CE, Ramayya AV, Riley FD, Roberto JB, Ryabinin MA, Rykaczewski KP, Sagaidak RN, Shaughnessy DA, Shirokovsky IV, Stoyer MA, Subbotin VG, Sudowe R (2010) Phys Rev Lett 104(14):142502
24. Oganessian YT, Utyonkov VK, Lobanov YV, Abdullin FS, Polyakov AN, Shirokovsky IV, Tsyganov YS, Gulbekian GG, Bogomolov SL, Gikal BN, Mezentsev AN, Iliev S, Subbotin VG, Sukhov AM, Voinov AA, Buklanov GV, Subotic K, Zagrebaev VI, Itkis MG, Patin JB, Moody KJ, Wild JF, Stoyer MA, Stoyer NJ, Shaughnessy DA, Kenneally JM, Lougheed RW (2004) Nucl Phys A 734:109
25. Schädel M (2007) Eur Phys J D 45(1):67
26. Werner FG, Wheeler JA (1958) Phys Rev 109(1):126
27. Pyykkö P (2011) Phys Chem Chem Phys 13:161
28. Indelicato P, Desclaux J (2005) Mcdfgme, a multiconfiguration dirac fock and general matrix elements program (release 2005). http://dirac.spectro.jussieu.fr/mcdf
29. Fricke B, Greiner W, Waber JT (1971) Theor Chem Acc: Theory Comput Model (Theoretica Chimica Acta) 21(3):235
30. Nefedov VI, Yarzhemcky VG, Trzhaskovskaya MB (2004) Russ J Inorg Chem 49(12):1871
31. Nefedov VI, Trzhaskovskaya MB, Yarzhemskii VG (2006) Doklady Phys Chem 408(2):149
32. Indelicato P, Desclaux JP (2010) The mcdfgme multiconfiguration dirac-fock program. V2010
33. Grant IP (1970) Adv Phys 19(82):747
34. Desclaux JP (1975) Comput Phys Commun 9:31
35. Desclaux JP (1993) Small systems. In: Clementi E (eds) Methods and techniques in computational chemistry, METTEC, vol A. STEF, Cagliary, p 253
36. Desclaux JP, Dolbeault J, Esteban MJ, Indelicato P, Séré E (2003) In: Le Bris C, De Franceschi M (eds) Computational chemistry, handbook of numerical analysis, vol X. Elsevier, Amsterdam, p 1032
37. Grant IP (2007) Relativistic quantum theory of atoms and molecules: theory and computation. Springer, New York
38. Grant IP (2010) J Phys B: At Mol Opt Phys 43(7):074033
39. Gorceix O, Indelicato P (1988) Phys Rev A 37:1087
40. Lindroth E, Mårtensson-Pendrill AM (1989) Phys Rev A 39(8):3794
41. Indelicato P (1986) J Phys B: At Mol Opt Phys 19:1719
42. Indelicato P, Santos JP, Boucard S, Desclaux JP (2007) Eur Phys J D 45(1):155
43. Angeli I (2004) At Data Nucl Data Table 87(2):185
44. Dyall KG, Grant IP, Johnson CT, Parpia FA, Plummer EP (1989) Comp Phys Commun 55:425
45. Cheng KT, Johnson WR (1976) Phys Rev A 14(6):1943
46. Soff G, Schlüter P, Müller B, Greiner W (1982) Phys Rev Lett 48(21):1465
47. Neghabian AR (1983) Phys Rev A 27(5):2311
48. Mohr PJ (1982) Phys Rev A 26(5):2338
49. Mohr PJ, Kim YK (1992) Phys Rev A 45(5):2727
50. Indelicato P, Mohr PJ (1998) Phys Rev A 58(1):165
51. Indelicato P, Mohr PJ (1998) Hyperfine Interact 114(1–4):147
52. LeBigot É O, Indelicato P, Mohr PJ (2001) Phys Rev A 64(5):052508 (14)
53. Cheng KT, Johnson WR, Sapirstein J (1991) Phys Rev Lett 66(23):2960
54. Blundell SA (1992) Phys Rev A 46(7):3762
55. Blundell SA (1993) Phys Rev A 47(3):1790
56. Cheng KT, Chen MH, Sapirstein J (2000) Phys Rev A 62(3):054501
57. Indelicato P, Mohr PJ (2001) Phys Rev A 63(4):052507
58. Chen MH, Cheng KT, Beiersdorfer P, Sapirstein J (2003) Phys Rev A 68(2):022507
59. Sapirstein J, Cheng KT (2006) Phys Rev A 73(1):012503
60. Pyykkö P, Tokman M, Labzowsky LN (1998) Phys Rev A 57(2):R689
61. Labzowsky L, Goidenko I, Tokman M, Pyykkö P (1999) Phys Rev A 59(4):2707
62. Thierfelder C, Schwerdtfeger P (2010) Phys Rev A 82(6):062503
63. Goidenko I, Tupitsyn I, Plunien G (2007) Eur Phys J D 45(1):171
64. Goidenko IA (2009) Eur Phys J D 55(1):35
65. Indelicato P, Boucard S, Lindroth E (1998) Eur Phys J D 3(1):29

66. Deslattes RD, Kessler EG Jr, Indelicato P, de Billy L, Lindroth E, Anton J (2003) Rev Mod Phys 75(1):35
67. Gaston N, Schwerdtfeger P, Nazarewicz W (2002) Phys Rev A 66(6):062505
68. Andersson LL, Rudolph D, Golubev P, Herzberg RD, Hoischen R, Merchán E, Ackermann D, Düllmann CE, Eberhardt K, Even J, Gerl J, Heßberger FP, Jäger E, Khuyagbaatar J, Kojouharov I, Kratz JV, Krier J, Kurz N, Prokopowicz W, Schädel M, Schaffner H, Schausten B, Schimpf E, Semchenkov A, Türler A, Wollersheim HJ, Yakushev A, Thörle-Pospiech P, Hartmann W, Hübner A, Lommel B, Kindler B, Steiner J (2010) Nucl Instr Meth Phys Res A: Accelerators, Spectrometers, Detectors and Associated Equipment 622(1):164
69. Thierfelder C, Schwerdtfeger P, Heßberger F, Hofmann S (2008) Eur Phys J A-Hadrons and Nuclei 36(2):227
70. Düllmann CE, Schädel M, Yakushev A, Türler A, Eberhardt K, Kratz JV, Ackermann D, Andersson LL, Block M, Brüchle W, Dvorak J, Essel HG, Ellison PA, Even J, Gates JM, Gorshkov A, Graeger R, Gregorich KE, Hartmann W, Herzberg RD, Heßberger FP, Hild D, Hübner A, Jäger E, Khuyagbaatar J, Kindler B, Krier J (2010) Phys Rev Lett 104(25):252701
71. Mohr PJ (1974) Ann Phys 88(1):52
72. Indelicato P, Gorceix O, Desclaux JP (1987) J Phys B: At Mol Phys 20:651
73. Indelicato P, Desclaux JP (1990) Phys Rev A 42(9):5139
74. Boucard S, Indelicato P (2000) Eur Phys J D 8(1):59
75. Greiner, W (eds) (1983) Quantum electrodynamics of strong fields. Plenum Press, New York
76. Greiner W, Müller B, Rafelski J (1985) Quantum electrodynamics of strong fields. Springer-Verlag, Berlin
77. Borschevsky A, Eliav E, Vilkas MJ, Ishikawa Y, Kaldor U (2007) Phys Rev A 75(4):042514
78. Eliav E, Kaldor U, Ishikawa Y (1995) Phys Rev A 52(1):291
79. Borschevsky A, Eliav E, Vilkas MJ, Ishikawa Y, Kaldor U (2007) Eur Phys J D 45(1):115
80. Eliav E, Kaldor U, Ishikawa Y (1995) Phys Rev Lett 74(7):1079
81. Eliav E, Kaldor U, Schwerdtfeger P, Hess BA, Ishikawa Y (1994) Phys Rev Lett 73(24):3203
82. Eliav E, Kaldor U, Ishikawa Y (1995) Phys Rev A 52(4):2765
83. Eliav E, Kaldor U, Ishikawa Y, Seth M, Pyykkö P (1996) Phys Rev A 53(6):3926
84. Landau A, Eliav E, Ishikawa Y, Kaldor U (2001) J Chem Phys 114(7):2977
85. Borschevsky A, Pershina V, Eliav E, Kaldor U (2009) Chem Phys Lett 480(1–3):49
86. Eliav E, Kaldor U, Ishikawa Y (1998) Mol Phys 94(1):181
87. Eliav E, Kaldor U, Ishikawa Y, Pyykkö P (1996) Phys Rev Lett 77(27):5350–5352
88. Goidenko I, Labzowsky L, Eliav E, Kaldor U, Pyykkö P (2003) Phys Rev A 67(2):020102
89. Eliav E, Landau A, Ishikawa Y, Kaldor U (2002) J Phys B: At Mol Opt Phys 35(7):1693
90. Dinh TH, Dzuba VA, Flambaum VV (2008) Phys Rev A 78(6):062502
91. Backe H, Dretzke A, Fritzsche S, Haire R, Kunz P, Lauth W, Sewtz M, Trautmann N (2005) Hyperfine Interact 162(1–4):3
92. Liu Y, Hutton R, Zou Y (2007) Phys Rev A 76(6):062503
93. Gaigalas G, Gaidamauskas E, Rudzikas Z, Magnani N, Caciuffo R (2010) Phys Rev A 81(2):022508