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Are MCDF calculations 101% correct in the superheavy elements range?

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Abstract We explore QED and many-body effects in superheavy 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[1]. We confirm that QED corrections are of the order of 1% on ionization energies. We show that the atomic number at which the $1s$ shell dives into the negative energy continuum is 173, and is not affected by the approximation employed to evaluate the electron-electron interaction.

Keywords Superheavy elements · MCDF · Electronic Correlation · relativistic effets

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1 Introduction

Superheavy elements have been subject of an intense experimental activity over the past few decades[2–4]. Elements 108 (Hs)[5–7], 109 (Mt)[8–10],

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110 (Ds)[11], 111 (Rg)[12], 112[13–15], 113[16], 114[17–20], 115[3], 116[21–23], 117[24] and 118[25,23] 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., [26] for a review). The chemical characterization of element 112 was also done recently[15].

In a recent paper [1], 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[27]. The new periodic table constitutes an update of the one by Fricke, Greiner and Waber[28], which was obtained using the Dirac-Hartree-Slater approximation. More recently, Nefedov and coll. proposed similar results, taking into account relativistic effects [29,30].

The objectives of the present paper are as follows. We investigated the electron correlation effects on the ground states of a few selected superheavy 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[31] 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 superheavy elements and studied QED corrections. Finally, we investigated the 1s 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 1s 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 [1].

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., [32–37]. 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

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

$$- \frac{\boldsymbol{\alpha}_i \cdot \boldsymbol{\alpha}_j}{r_{ij}} \tag{3b}$$

$$- \frac{\boldsymbol{\alpha}_i \cdot \boldsymbol{\alpha}_j}{r_{ij}} [\cos\left(\frac{\omega_{ij} r_{ij}}{c}\right) - 1]$$

$$+ c^2 (\boldsymbol{\alpha}_i \cdot \boldsymbol{\nabla}_i)(\boldsymbol{\alpha}_j \cdot \boldsymbol{\nabla}_j) \frac{\cos\left(\frac{\omega_{ij} r_{ij}}{c}\right) - 1}{\omega_{ij}^2 r_{ij}}, \tag{3c}$$

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, $\boldsymbol{\alpha}_i$ 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 [38, 39].

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 $\boldsymbol{\nabla}$ 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[40]. More recently, it has been used for calculation of properties of superheavy elements like Landé g-factors, ionic radii and energies with QED corrections for $Z \leq 108$ [41]. 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 [42]. For element 140, (4) gives R =6.7717 fm, and R =7.3189 fm for element 170.

One of the difficulties in evaluating energies of neutral or quasi-neutral superheavy 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 [32,33]

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

Two recent examples of average level calculations have appeared in the papers by P. Pyykkö [1] and Nefedov and al. [30], who tried to establish new periodic classifications in the super-heavy domain.

In the present paper we used the "optimal level" (OL) energy functional[43] which 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 [44], and Soff et al. [45]. Vacuum polarization for the 1s shell was evaluated for supercritical atoms by Neghabian [46], 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 [47–51], 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 $n = 1$ to 4 shells [52–57], including d states [58]. Only a few works have been performed for outer s shells of neutral super-heavy elements, by P. Pyykkö, L. Labzowsky and collaborators [59,60]. The one-electron self-energy is given by

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

In the 2010 version of *mcdfgme* we interpolate between known values of $F_{1s}(Z\alpha)$ for the 1s shell, which are known for $1 \leq Z \leq 170$ [61,44,45], 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 [62,63]. 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 $-2m_e c^2$. 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., [64].)

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 [28] was made in the Dirac-Slater approximation. More recent works [30,1] 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. [30], the ground state of element 140 was attributed the configuration $8s^2 8p^2 7d 6f^3 5g^{14}$. We confirmed this assignment in AL mode, but the J-dependent OL calculations give binding energies $\approx$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 which include only the relativistic configurations contributing to a single LS parent. In the OL mode, the lowest configuration is $8s^2 8p^4 6f 5g^{15}$ $J = 8$. We could not evaluate the $8s^2 8p^2 7d 6f^3 5g^{14}$ configurations in OL mode, since the calculation could not fit into any computer we have access to (32GB RAM). Therefore the $8s^2 8p^2 7d 6f^3 5g^{14}$ 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 on Fig. 2. The changes in the ground state structure for element 140 isoelectronic sequence are presented on Fig. 3 . The most tightly bound configuration as a function of Z is presented in Table 1. The ground configuration becomes $8s^2 8p^2 5g^{18}$, $J = 0$ at $Z = 143$. The 142^{2+} ion has two configurations with identical energies, $8s^2 8p^3 5g^{17}$, $J = 3$ 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 on Fig. 4 as a function of configuration. The maximum numbers of integrals, obtained for the $8s^2 8p^4 6f 5g^{15}$, $J = 5$ configurations are of 8.6, 29.7 and 25.7 million for the Coulomb, Magnetic and Retardation interaction, respectively. They correspond to 1.67GB 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 20638 determinants, 3898 configurations which yield 44, 151 and 117 millions angular integrals, respectively. They would require 8.2GB 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 $-2m_e c^2$. 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 $Z = 172$.

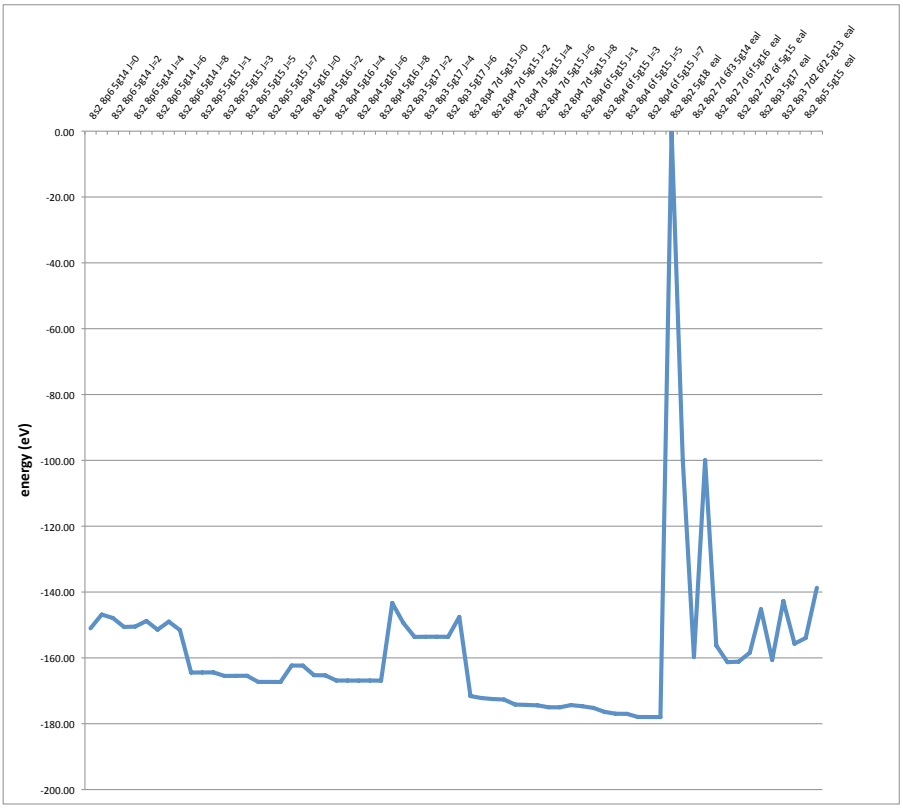

Fig. 1 Comparison between the AL calculations and fully optimized, J dependent total biding energies for element $Z = 140$ relative to the $8s^2 8p^2 5g^{18}$ AL binding energy $E = -2538277.59$ eV set as 0. The AL calculations are plotted to the right of the $8s^2 8p^2 5g^{18}$ AL configuration.

Table 1 Ground configuration for the isoelectronic sequence of $Z = 140$. All contributions in eV.

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

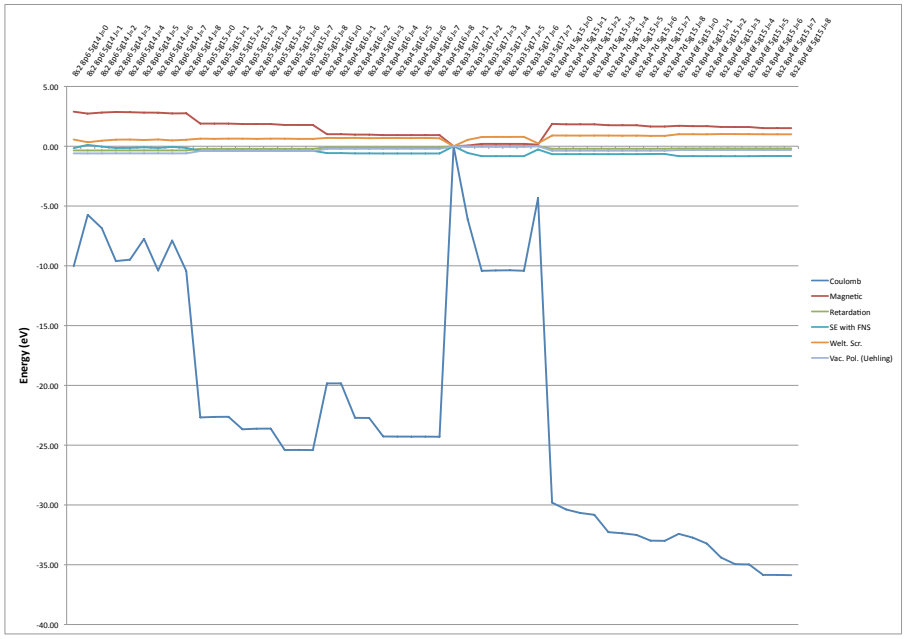

Fig. 2 Contributions to the binding energy of element $Z = 140$ relative to the $8s^2 8p^3 5g^{17}$, $J = 1$ configuration

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 $-2m_e c^2$. The $1s$ shell binding energy within different approximations is plotted on Fig. 6. An extrapolation of a cubic polynomial fit to the data crosses $-2m_e c^2$ 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 [65, 66]. The contributions to the total biding energy and to the ionization energy of the elements with $Z = 171$ to 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).

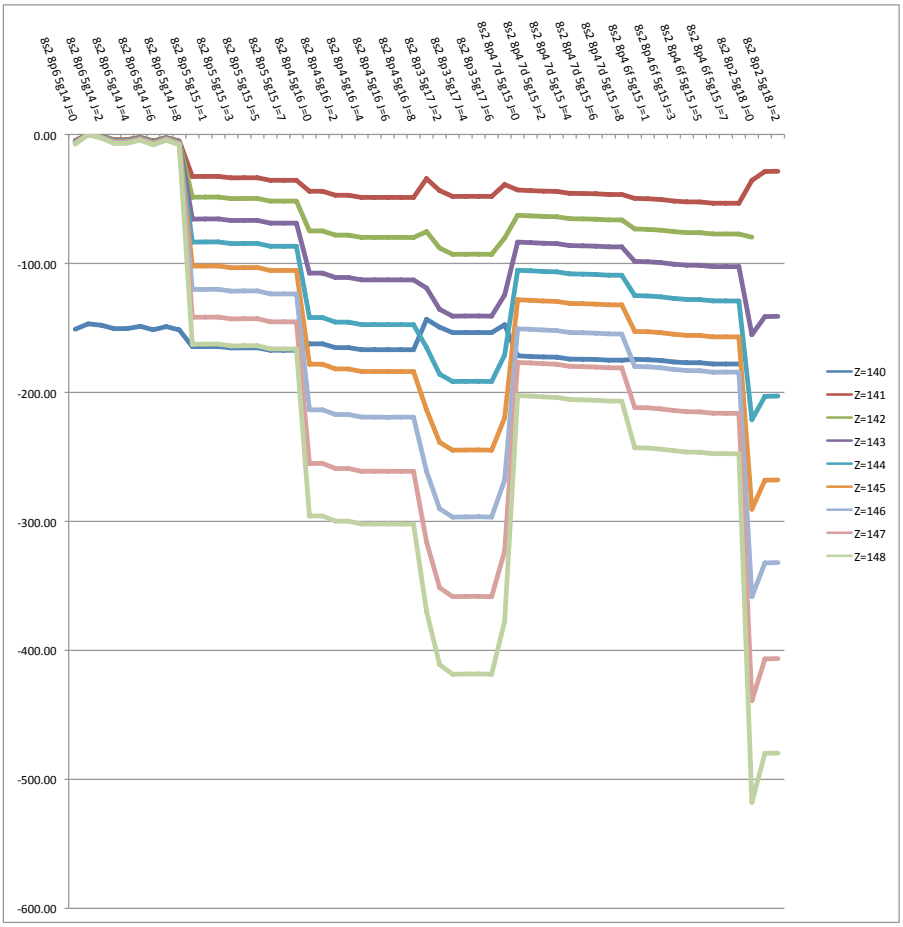

Fig. 3 Ground state configuration determination for the elements in the $Z = 140$ isoelectronic sequence

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.

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

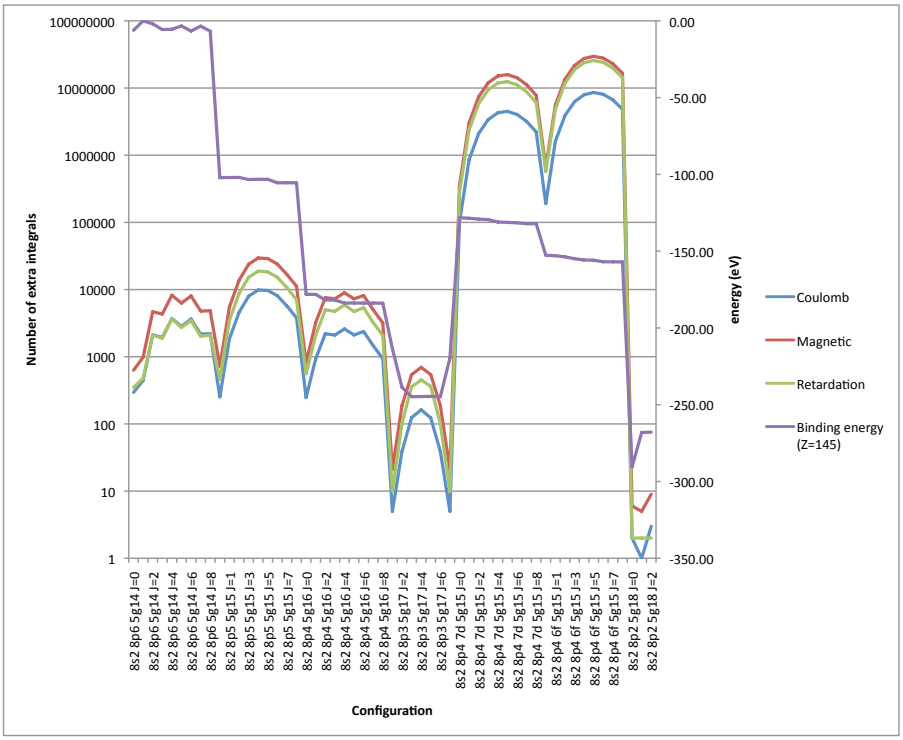

Fig. 4 Number of extra Coulomb, Magnetic and Retardation integrals as a function of the configuration (left vertical axis). The biding energy for $Z = 145$ in the isoelectronic sequence of element 140, respective to the $8s^2 8p^6 5g^{14}$ configuration is also plotted (right vertical axis)

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 [56] 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 superheavy 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 superheavy atom, calculated in the Dirac-Fock approximation. To this end, several calculations have been performed for super-heavy elements, most of them in

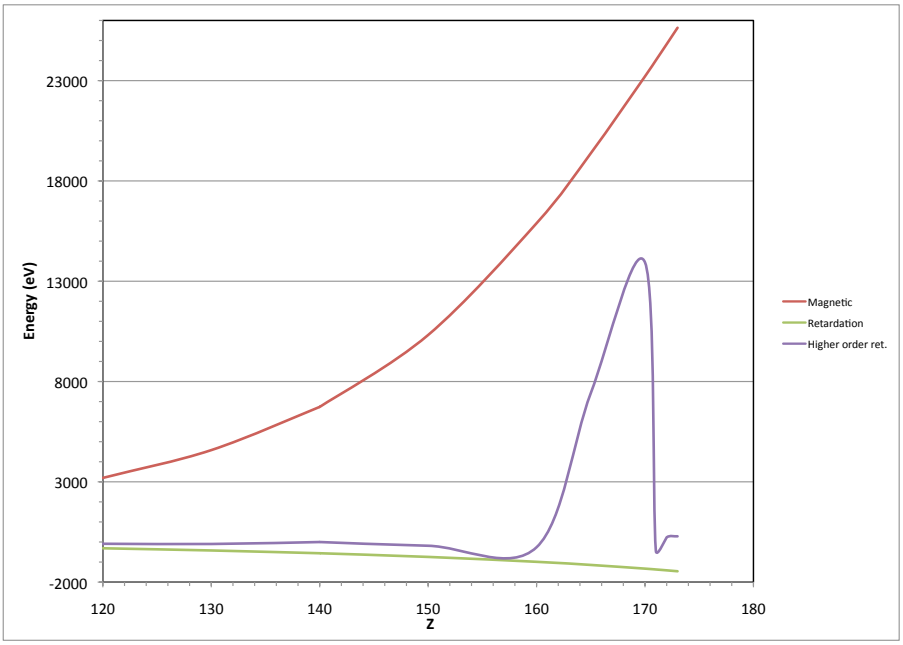

Fig. 5 Unexpected non-monotonic behavior in the variation of higher-order retardation as a function of Z.

the coupled-cluster approximation. Correlation energy for the ground state of elements with $Z = 102$[67], 103[68,69], 104[70], 111 [71], 112[72], 113 [73], 114 [74,75], 115 [76], 118 [77,78], 122 [79] have been calculated with this approach. The MCDF method was used for evaluating correlation on transition energies and rates for Fm and No, as well as for the element 118[80,81,41] and 122[82]. 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 superheavy element. We have chosen element 162 with configuration $[\mathrm{Rn}]5f^{14}6d^{10}7s^27p^67d^{10}5g^{18}6f^{14}6s^2$ 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

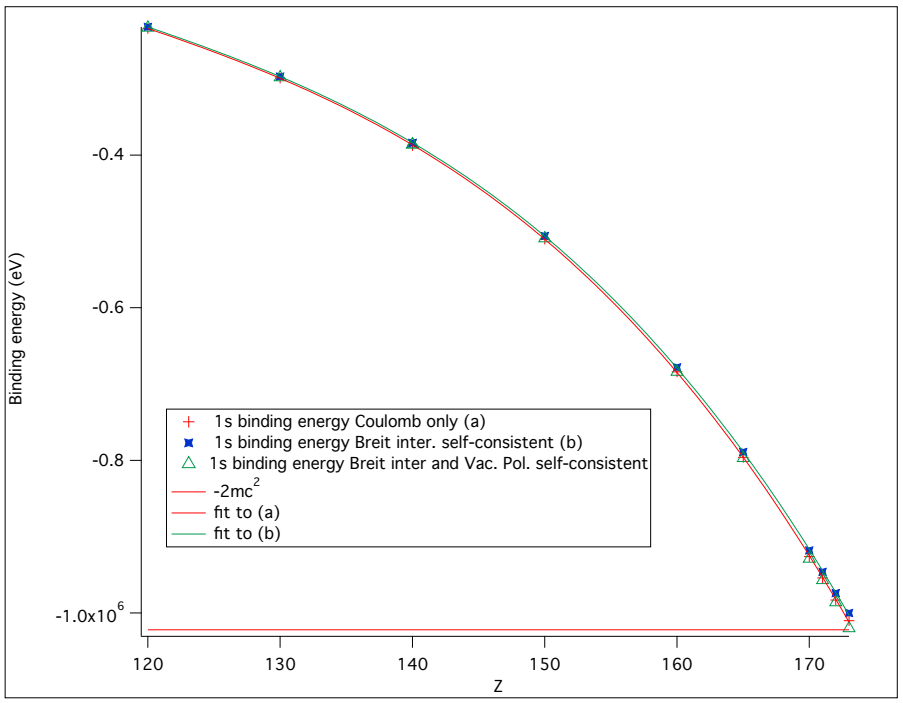

Fig. 6 Behavior of the 1*s* shell binding energy of a neutral super-heavy atom as a function of the atomic number with different approximation.

of the 8*s* 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.

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 8*p*, 9*p* and 5*g* electrons, even at the DF level. The inclusion of the Breit interaction in the SCF process usually makes things worse. Development of stable numerical

Table 2 Contributions to the ground state total binding energy and ionization energy for elements with $Z > 170$. All values in eV.

Z	171	172	173
total binding energy			
[Rn] $5f^{14}6d^{10}7s^27p^68s^28p^67d^{10}5g^{18}6f^{14}$	$9s^29p$, $J = 1/2$	$9s^29p^2$, $J = 2$	$9s^29p^3$, $J = 3/2$
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] $5f^{14}6d^{10}7s^27p^68s^28p^67d^{10}5g^{18}6f^{14}$	$9s^2$, $J = 0$	$9s^29p$, $J = 1/2$	$9s^29p^2$, $J = 2$
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

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 $np_{1/2}$ ($n = 8$ or 9). This point was already emphasized for highly-charged super-heavy elements and $2p$ shells in Ref. [41]. 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 of the Coulomb DF contribution. A survey of the literature shows that there are no direct QED calculations in the range of superheavy elements, except for the $1s$ shell. Many QED contributions have never been calculated for neutral superheavy elements, except for a very limited number of cases, notably in [60,78,41]. A systematic evaluation of all

Table 3 Effect on the self-consistent Breit interaction on the ground state total binding energy for element $Z = 162$. All values are in eV.

Contribution	Total energy	8*s* 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

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 1*s* 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.

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