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Relativistic and quantum electrodynamic effects in superheavy elements

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Abstract

The current status of relativistic electronic structure theory for superheavy elements is reviewed. Recent developments in relativistic quantum theory have made it possible to obtain accurate electronic properties for the trans-actinide elements with the aim to predict their chemical and physical behaviour. The role of quantum electrodynamic effects beyond the no-virtual-pair approximation, which is usually neglected in relativistic molecular calculations, is discussed. Changes in periodic trends due to relativistic effects are outlined for the superheavy elements with nuclear charge $Z = 111$–120. We also analyse the role of the negative energy states for the electronic stability of superheavy elements beyond the critical nuclear charge ($Z_{crit} \approx 170$), where the $1s$ state enters the negative energy continuum at $-2m_e c^2$.

Keywords: Superheavy elements; Electronic structure theory; Relativistic and quantum electrodynamic effects

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1. Introduction

It is now well established that relativistic effects in the electronic structure of heavy elements are important to the extent that they can significantly alter their chemical and physical behaviour [1–5]. Simple extrapolations from the lighter to the heavier elements to deduce the physical or chemical behaviour of the heaviest elements in the periodic table [6] is therefore not always possible. Prime examples are the unusual chemistry and physics of gold [1,7], including the stability of high oxidation states in gold compounds [8,9] and its implications to homogeneous gold catalysis [10,11], or the yellow colour of bulk gold [12]; mercury being a liquid at room temperature [13]; the high superconducting transition temperature of Hg (4.15 K) in comparison to Zn (0.855 K) or Cd (0.52 K) [14]; or the fact that a lead-acid battery owes much of its voltage to relativity [15]. As relativistic effects scale approximately like $\sim (Z\alpha)^2$, even larger relativistic effects are expected for the transactinide elements (also called super-heavy elements, i.e. elements with nuclear charge $Z \geq 104$) [16,17]. As early as 1975 Kenneth S. Pitzer pointed out that $_{112}$Cn, $_{114}$Fl and the element with nuclear charge 118[1] are expected to be volatile and chemically inert as they are of closed-shell character; in the case of Cn as a result of the strong relativistic $7s$ contraction (giving Cn an atomic radius smaller than Cd), Fl because of the strong spin–orbit splitting of the $7p$ shell resulting in a closed $7p_{1/2}^2$ shell, and element 118 as it belongs to the series of rare gas elements (but with a rather diffuse $7p_{3/2}^4$ shell) [18].

The heaviest nuclei on Earth were formed in the so-called r-process of stellar nucleosynthesis before our planetary system was formed,[2] i.e. though rapid neutron capture and subsequent β-decay processes, producing isotopes up to thorium, uranium and plutonium [20] or even beyond [21]. Beside the many uncertainties in modelling stellar nucleosynthesis [22–24], the fact that the transactinide elements are not naturally found on Earth and have to be synthesised by nuclear fusion instead, implies that isotopes of the transactinide elements are rather short-lived compared to the age of our solar system [25]. Despite the recent success in the synthesis of superheavy nuclei up to nuclear charge 118 (with the synthesis of elements 119 and 120 in progress), by cold or hot nuclear fusion processes with cross sections as low as 1 pb [26], we are still many neutrons short from the predicted shell-closure within the island of nuclear stability, which, depending on the nuclear structure model used, is predicted to occur at nuclear charges (proton numbers) $Z = 114, 120,$ or 126 and neutron number $N = 184$ [27–29]. For comparison, the heaviest 114 isotope synthesised has a neutron number of 175 with an estimated half-life of 2.6 seconds [30].

If the nuclear decay half-life is in the second range or above, chemical experiments become feasible to study the properties of such exotic elements and to gain insight into their chemical and physical behaviour compared to the lighter congeners in the Periodic Table [31]. Such one-atom-at-a-time experiments have been carried out so far with transactinide isotopes up to nuclear charge $Z = 108$ (Hs) [17], and more recently with Cn (Z =112) and Fl (Z =114) [32–35]. The design of such difficult experiments relies on predetermined knowledge of the electronic structure and chemical behaviour of these superheavy elements, even more so as strong relativistic effects often do not allow the deduction of properties directly from the chemical knowledge of their lighter congeners within the Periodic Table. For this, one requires accurate relativistic electronic structure calculations. We mention here that Sewtz and co-workers investigated the atomic

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[1] We will abbreviate unnamed elements by their nuclear charge in the following.

[2] Recent research indicates that neutron star collisions are the primary locations of r-process nucleosynthesis [19].

level structure of fermium ($Z = 100$) using a sample of 2.7×10^{10} atoms of the $_{255}$Fm isotope with a half-life of only 20.1 h. Multi-configuration Dirac–Fock calculations gave strong support for electronic transitions from the $5f^{12}7s^2$ (^{3}H$_6$) ground state to the $5f^{12}7s7p$ (^{5}I$_6$) and $5f^{12}7s7p$ (^{5}G$_5$) excited states [36]. Unfortunately, the originally anticipated project to study the electronic spectra of even heavier elements such as No ($Z = 102$) at the GSI in Darmstadt did not continue. More recently, the first ionisation potential of the heaviest actinide element lawrencium $_{103}$Lr has been determined experimentally by surface ionisation to be $4.96^{+0.08}_{-0.07}$ eV [37]. There is, however, the possibility for future single-atom trapped spectroscopy of superheavy elements if the nuclear decay half-life is long enough to carry out such experiments [38].

Great progress in the treatment of heavy elements by relativistic quantum theoretical methods using the Dirac–Coulomb–Breit equation, including electron correlation and quantum electrodynamic effects beyond the no-virtual-pair approximation (NVPA) [39] if required [40], has been made in the past 30 years [41,42]. Suitable boundary conditions [43,44] (e.g. kinetic balance [45]) and the use of prolapse-free basis sets for solving the Dirac equation have made it possible to obtain variationally stable solutions for both atoms and molecules [46]. However, the treatment of molecular two-electron integrals in the Dirac–Hartree–Fock procedure including the large and small Dirac components is computationally still a formidable task. More computer efficient approximations (without loosing too much accuracy) can be obtained by transformation of the Dirac equation into a two-component (or even relativistic scalar) form [47,48], for example by using the exact two-component Hamiltonian (X2C) [49], or a two-component effective core potential approach (ECP) [50,51]. In the past, these methods have been successfully applied to the treatment of heavy and superheavy element compounds [52]. The major bottle-neck in such calculations no longer lies in the relativistic treatment of the atomic or molecular electronic structure, but in capturing most of the electron correlation at the relativistic level of theory.

In the past decade it has become clear that quantum electrodynamic (QED) effects cannot be neglected for the accurate treatment of superheavy elements. While the vacuum polarisation, electron self-energy and the frequency dependent part of the Breit equation are known to be important for the core-like s- and $p_{1/2}$ electrons in strong Coulomb fields [53–55], for superheavy elements they become quite sizeable even for valence orbitals [4,56–62]. The exact treatment of QED effects order by order using Feynman diagrams in bound state QED together with electron correlation for many-electron systems is still a formidable and challenging task [63–65], and recent progress in constructing accurate model Hamiltonians opens the way for treating QED effects efficiently and accurately for molecules [4,62,66–68]. In this article we review the current status of relativistic electronic structure theory for superheavy elements and its implications to superheavy element research.

2. Relativistic electronic structure theory

The Dirac–Coulomb–Breit Hamiltonian for a multi-electron atomic system with finite nuclear charge correct to order c^{-2} is

$$H_0 = \Lambda_+ \left(\sum_i h_i + \sum_{i<j} g_{ij} \right) \Lambda_+ \tag{1}$$

with the one-electron Hamiltonian (in atomic units)

$$h_i = c\vec{\alpha}_i \vec{p}_i + c^2 \beta_i + V_{\text{ext}}(i) I_4 = \begin{pmatrix} \left(V_{\text{ext}}(i) + c^2\right) I_2 & c\vec{\sigma}_i \vec{p}_i \\ c\vec{\sigma}_i \vec{p}_i & \left(V_{\text{ext}}(i) - c^2\right) I_2 \end{pmatrix} \tag{2}$$

and the two-electron part

$$g_{ij} = g_{ij}^{\text{Coulomb}} + g_{ij}^{\text{Breit}} = r_{ij}^{-1} - \frac{1}{2} r_{ij}^{-1} \left[\vec{\alpha}_i \vec{\alpha}_j + r_{ij}^{-2} (\vec{\alpha}_i \vec{r}_{ij})(\vec{\alpha}_j \vec{r}_{ij}) \right] \tag{3}$$

The matrices $\vec{\alpha}$ and β are the Dirac matrices in the standard representation,[3] the $\vec{\sigma}$ are the Pauli matrices, I_n denotes the $n \times n$ unit matrix, and the projection operator Λ_+ makes sure that only positive energy states are occupied (no-virtual pair approximation, NVPA) [69], which also circumvents the Brown–Ravenhall continuum dissolution [39,70,71]. We note that the projection operator Λ_+ depends on the actual potential used, and numerical examples for Hartree–Fock orbital energies using different projections together with a detailed discussion can be found in Ref. [49]. The vector potential $\vec{A}$ can be introduced if required by minimal substitution of the momentum $\vec{p}$. The two-electron part contains the classical Breit interaction in the Coulomb gauge of two relativistic electrons interacting through their electromagnetic fields [41]. In the Feynman gauge the dominant correction is just the Gaunt-term,

$$g_{ij} = g_{ij}^{\text{Coulomb}} + g_{ij}^{\text{Gaunt}} = r_{ij}^{-1} - r_{ij}^{-1} \vec{\alpha}_i \vec{\alpha}_j \tag{4}$$

The external Coulomb potential arising from a positively charged finite nucleus (with charge $+Z$) is,

$$V_{\text{ext}}(i) = -Z \int d\vec{r} \rho_N(\vec{r}) |\vec{r} - \vec{r}_i|^{-1} \tag{5}$$

For a point nucleus we simply have $\rho_N(\vec{r}) = \delta(\vec{r})$. In numerical atomic program packages a spherical 2-parameter Fermi charge distribution for the protons inside the nucleus is usually applied [72],

$$\rho_N(\vec{r}) = \rho_0 \left[1 + e^{(r-R_0)/a} \right]^{-1} \tag{6}$$

where R_0 is the half-density nuclear radius and a is the diffuseness parameter related to the skin thickness t of the nucleus by $t = (4 \ln 3)a$. There is no analytical solution for Eq. (5) using Eq. (6). Therefore, in molecular calculations it is more convenient to choose charge distributions leading to functions which can easily be handled in standard integral packages, such as the Gaussian charge distribution [73],

$$\rho_N(\vec{r}) = \rho_0 e^{-r^2 \xi_G^2} \tag{7}$$

This yields a simple form for the Coulomb potential,

$$V_{\text{ext}}(i) = -Z r_i^{-1} \text{erf}(r_i \xi_G) \tag{8}$$

where $\xi_G^2 = 3/(2\langle R^2 \rangle) \approx 3R_0^{-2}/2$. Hence, ξ_G is very large and $\text{erf}(r_i \xi_G) = 1$ for $r_i >> R_0$ and the finite extension of the nucleus only affects the wave function very close to the nucleus. For an overview of different nuclear models see Andrea [74] or Mårtensson-Pendrill and Gustavsson [75], and for a comparison between different nuclear structure calculations see Visscher and Dyall [76]. Using a finite nuclear charge distribution is important for obtaining accurate values for deep core ionisations in heavy elements [54,77], and to obtain physical solutions from the

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[3] The substitution $\beta \rightarrow (\beta - I_4)$ shifts the spectrum by $-m_e c^2$ to make relativistic electronic energies comparable to non-relativistic ones, which we adopt here.

Dirac equation beyond a critical nuclear charge (we note, however, that different nuclear charge models lead to very similar results in electronic structure calculations [76]). It is well known that the one-electron Dirac equation does not have physical solutions for nuclear charges greater than the inverse of the fine-structure constant[4] (in atomic units $c = 1/\alpha = 137.035999173(35)$),

$$E_{nj} = c^2 \left[1 + \left(\frac{Z/c}{n - |k| + \sqrt{k^2 - (Z/c)^2}} \right)^2 \right]^{-1/2} \tag{9}$$

where k is the (relativistic) angular quantum number defined as $k = \pm(j + 1/2)$ for $j = l \mp 1/2$. While partial screening of the nucleus in multi-electron systems may lead to physical solutions slightly above $Z_{\text{crit}} = 137.036$, it is the finite extension of the nucleus, removing the singularity of the Coulomb potential at the origin, which leads to physical solutions far beyond Z_{crit} (for a recent detailed discussion on the self-adjointness of the Dirac operator in that region see Gitman et al. [78]). However, the lowest energy level for a hydrogen atom enters the negative energy continuum at a critical charge of $Z_{\text{crit}} \approx 170$–$172$, which will be discussed in the last section.

Fock-space coupled-cluster calculations performed by the Kaldor group in Israel have led to very accurate predictions of atomic spectra for heavy element atoms, and for spectroscopic constants of a few diatomic compounds [58,79–87]. However, for larger molecules containing heavy elements it is more convenient to avoid computer-time intensive four-component wave function calculations by eliminating the small Dirac component (which goes to zero in the nonrelativistic limit), or by transforming the Dirac operator to a two component form (either directly by a unitary transformation of the Dirac operator or in its matrix representation) [49,88]. The most widely all-electron two-component methods applied are the exact two-component relativistic Hamiltonian approach (X2C) [89], the closely related normalised elimination of the small component (NESC) [42,90,91], the Douglas–Kroll–Hess Hamiltonian (DKH) [92,93], and the zero-order relativistic approximation (ZORA) and its extensions [94,95] used in various molecular program packages. We only mention the X2C method here implemented in the program package DIRAC, as it is one of the most accurate approximations in use [96].

The idea behind a two-component approach is to obtain a relativistic Hamiltonian h_{++} acting on a two-component ("large") wave function only having a spectrum as close as possible to the four-component Dirac–Coulomb–Breit solution. This can be formally achieved by block-diagonalisation to decouple the larger from the smaller Dirac component [49],

$$H_{BD} = U^\dagger H_D U = U^\dagger \begin{pmatrix} h_{LL} & h_{LS} \\ h_{SL} & h_{SS} \end{pmatrix} U = \begin{pmatrix} h_{++} & 0 \\ 0 & h_{--} \end{pmatrix} \tag{10}$$

If we relate the upper (large) ϕ_L and lower (small) ϕ_S components of the Dirac four-spinor for particle-like solutions by

$$\phi_L = X\phi_S \tag{11}$$

we can find a closed form expression of the exact decoupling transformation in terms the operator X [97],

$$U = (1 + X^\dagger X)^{-1/2} \begin{pmatrix} 1 & X^\dagger \\ -X & 1 \end{pmatrix} \tag{12}$$

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[4] We distinguish between the Dirac matrix $\vec{\alpha}$ and the fine structure constant α, which unfortunately carry the same symbol, by the additional vector sign for the Dirac matrix.

While in operator form the analytical expression for X becomes energy-dependent, in matrix form at the Dirac–Fock level this operator can be expressed in terms of the coefficients of the one-electron basis set expansion of the upper and lower components. This computationally very efficient X2C procedure is perhaps the most elegant way to transform to a two-component form. For more details and how to efficiently treat the two-electron relativistic corrections to the Coulomb operator within a mean-field approach see Ref. [98].

Going one further level down in the approximation without losing much accuracy in relativistic molecular calculations (compared to the electron correlation error), we may approximate the field originating from the chemically inactive core-electrons by an effective core potential (ECP or pseudopotential) [50,51]. As ECP methods do not treat explicitly the core-levels, it makes no sense to include the negative energy continuum in such calculations [50]. Hence, this approximation is best introduced within a two-component or scalar relativistic approach. The most widely used atomic valence-only two-component model Hamiltonian is in a semi-local form,

$$H_v = \sum_i \left(-\frac{1}{2}\nabla_i^2 + V_{\mathrm{ECP}}(r_i) \right) + \sum_{i<j} \frac{1}{r_{ij}} \tag{13}$$

where the two-component V_{ECP} depends on the total angular momentum j and is given by

$$V_{\mathrm{ECP}}(r_i) = -\frac{Q}{r_i} + \sum_k \sum_{lj} A_{lj}^k r_i^{n_{lj}^k} \exp\left(-a_{lj}^k r_i^2 \right) P_{lj} \tag{14}$$

where Q is the effective core charge ($Q = Z - N_c$, where N_c is the number of core electrons), k an expansion parameter (usually $k = 2$ or 3 is sufficient), and P_{lj} the projection operator onto the Hilbert subspace with total angular momentum $j = l \pm 1/2$,

$$P_{lj} = \sum_{m_j=-j}^{j} |ljm_j\rangle\langle ljm_j| \, . \tag{15}$$

A_{lj}^k and a_{lj}^k are parameters adjusted by a least-squares fit to the valence spectrum of an atom obtained from all-electron multi-configuration Dirac–Fock–Breit calculations, including quantum electrodynamic effects if required [51], and often a simple Gaussian expansion is chosen with $n_{lj}^k = 0$. In this way relativistic ECPs for the superheavy elements from Rg to element 120 have been adjusted [67,68] leading to results in a good agreement with more accurate four-component calculations [99].

The question then arises: what effect the negative energy states have on the electron correlation, especially in strong Coulomb fields at high nuclear charge when the lowest bound states come close to the negative energy continuum. Such effects are not captured in two-component approaches. Watanabe et al. has recently investigated the correlation energy in both a configuration interaction (CI) and Hylleraas procedure for He-like atoms up to nuclear charge $Z = 116$ [40]. The results are shown in Fig. 1. They clearly show what is already well known: For the total electron energy, relativistic effects soon start to dominate over electron correlation (for He-like ions at $Z > 8$), and finite nuclear size contributions become more important than electron correlation at $Z > 41$. The figure also shows that correlating negative energy states has a sizeable effect on the electron correlation. This interesting fact remains relatively unexplored for atomic spectra and molecules in general. However, as the results also show, vacuum polarisation and self-energy contributions cannot be neglected in comparison to electron correlation even for smaller nuclear charges. This will be discussed in detail in the next section.

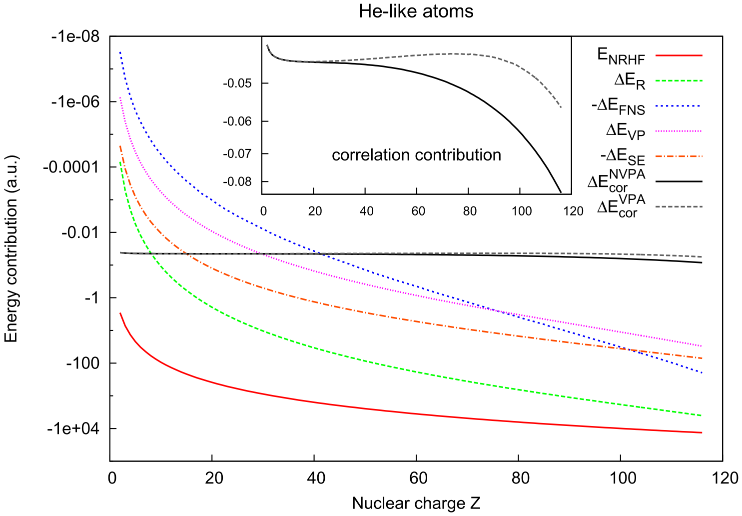

Fig. 1. Energy contributions (logarithmic scale) to $1s^2$ He-like systems up to nuclear charge $Z = 116$. Total nonrelativistic Hartree–Fock energy E_{NRHF}, relativistic effect using a point charge nucleus $\Delta_{\mathrm{R}} E = E_{\mathrm{DHF}} - E_{\mathrm{NRHF}}$, finite nucleus correction ΔE_{FNS} using a 2-parameter Fermi charge distribution and atomic masses from Watanabe et al. [40], vacuum polarisation contribution ΔE_{VP}, electron self-energy contribution ΔE_{SE}, electron correlation using the NVPA $\Delta E_{\mathrm{cor}}^{\mathrm{NVPA}}$ and including the negative energy states $\Delta E_{\mathrm{cor}}^{\mathrm{VPA}}$ (the latter two results from Watanabe et al. [40]). Note the sign definitions for the different contributions. For clarity we show the correlation contributions separately inside the figure.

3. Bound-state quantum electrodynamics

The Dirac equation has certain limitations due to the presence of the negative energy continuum, which are not seen in nonrelativistic theory and clearly point toward the necessity of a quantum field theoretical treatment. Prime examples are the Klein paradox [100,101], the fact that deviating from a Coulomb potential can lead to a completely continuous spectrum of the Dirac operator [102], or the possibility of the $1s$ state diving into the negative energy continuum [101,103]. The appearance of these negative energy states and the consequence that vacuum fluctuation can cause electron–positron pair creation forces us to cope with an indefinite number of particles described by quantum electrodynamics (QED). QED surely is one of the most successful theories in physics. To give an example of this success story the electron g-factor is given by,

$$g = 2(1 + a_e) = 2\left[1 + \sum_{n=1}^{\infty} C_n \left(\frac{\alpha}{\pi}\right)^n\right] \tag{16}$$

where the non-zero anomalous magnetic moment a_e comes purely from QED and can be evaluated order-by-order in this sum through corresponding Feynman diagrams. The latest value for the anomalous magnetic moment is $a_e = 0.00115965218178(77)$ summing over 12 672 Feynman diagrams (up to 10th order) [104–106]. This gives an improved fine-structure constant of α^{-1} of 137.035999173(35).

The situation changes drastically if an electron is bound to a (strong) Coulomb field [53]. Although Dirac–Coulomb–Breit theory is able to explain the fine-structure in atoms to a relatively high accuracy (up to order α^2), Lamb shift separating the degenerate energy levels of equal

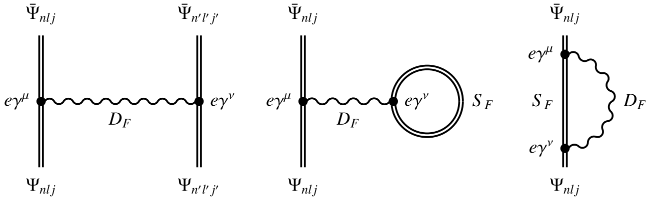

Fig. 2. From the left to the right: lowest order Breit interaction, vacuum polarisation, and electron self-energy with the usual labelling of Feynman diagrams (here we include the elementary charge e for clarity). Double lines indicate bound-state QED, i.e. a charged particle in the Coulomb field of a nucleus. D_F and S_F are the Dyson (photon) and Feynman (electron/positron) propagators respectively.

j-value in hydrogenic atoms, measured by Lamb and Retherford [107] and soon after realised to be due to QED effects, namely electron self-energy [108] and vacuum polarisation [109] (see Fig. 2), grows $\sim Z^4$ and has to be considered in inner-shell transitions of heavy elements as can be seen in Fig. 1. The Lamb shift in hydrogenic atoms[5] is given by [110,111],

$$\Delta E_{nlj}^{QED} \approx \frac{1}{\alpha\pi}\frac{(Z\alpha)^4}{n^3}\left[F_{nlj}^{\mathrm{VP}}(Z\alpha) + F_{nlj}^{\mathrm{SE}}(Z\alpha)\right] + F_{nlj}^{\mathrm{HO}}(Z\alpha) \tag{17}$$

where $F_{nlj}(Z\alpha)$ are expansions in $Z\alpha$ (and α) for the vacuum polarisation (VP), electron self-energy (SE) and all other (e.g. higher-order) contributions (HO). These relatively slowly varying F-functions have been tabulated by Johnson and Soff for the hydrogen-like atoms up to nuclear charge $Z = 100$ [110]. For s-states and small Z-values we have approximately $F^{\mathrm{VP}}(Z\alpha) \approx -4/15$ and $F^{\mathrm{SE}}(Z\alpha) \approx (4/3)\ln(Z\alpha)^{-2} + C_n$. Of course, these F-functions differ for different multi-electron systems as the nucleus is partially screened by the other electrons. Furthermore, such a simple one-particle picture is useful but has its limitations as we shall see.

Bound state QED is formulated in the Furry picture working with the exact propagators but treating the nucleus classically assuming an infinite mass. Beside the standard *S-matrix theory* [53], using the Gell-Mann Low theorem for evaluating the QED energy shift, with all its known problems in terms or renormalisation and treating quasi-degenerate states, there are currently two further approaches to many-body QED: the *two-time Green's functions* developed by the Shabaev group [112], and the *covariant-evolution-operator method* developed by the Lindgren group [113]. Nuclear recoil effects beyond the Furry picture can also been considered as done for example by Shabaev [114]. Even though bound-state QED can lead to precise electronic data for few-electron atomic systems, in a good agreement with experimental data – for example for U^{90+} [115] – it is fair to say that such accuracies are currently very difficult to achieve for many-electron systems such as for neutral high-Z atoms. Here, electron correlation and QED effects should be treated at the same level [64,116]. The data in Table 1 for the gold ionisation potential and electron affinity illustrate the current problem [117]. Even if QED contributions are included, which is required to reach experimental accuracy, deviations to experimental data are still too large demonstrating that the bottle-neck in such elaborate calculations is in the accurate treatment of electron correlation. Moreover, one may have to include even the negative energy states in the active correlation space as the results by Watanabe et al. suggest [40], see also Liu and Lindgren [65]. For a recent discussion on the accuracy of valence-shell calculations for heavy and superheavy elements see the paper by Fritzsche [118].

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[5] We use atomic units where $\alpha^{-1} = c$.

Table 1
Ionisation potential ${}^2\mathrm{S}_{1/2}(\mathrm{Au}) \to {}^1\mathrm{S}_0(\mathrm{Au}^+)$ and electron affinity ${}^1\mathrm{S}_0(\mathrm{Au}^-) \to {}^2\mathrm{S}_{1/2}(\mathrm{Au})$ of gold (in eV). HFNR: nonrelativistic Hartree–Fock; HF–DCB: Hartree–Fock Dirac–Coulomb–Breit; FSCC-NR: nonrelativisitc Fock-space coupled cluster [117]; FSCC-DCB: Fock-space coupled cluster Dirac–Coulomb–Breit [117]; QED: QED contribution including lowest-order self-energy, vacuum polarisation and frequency contribution to the Breit term all treated perturbatively at the HF-DC level of theory (see Ref. [55] for details); total: total theory; exp.: experimental data from Refs. [119, 120]; Δ (theory-exp.): difference between theory and experiment.

Property	HF-NR	HF-DCB	FSCC-NR	FSCC-DCB	QED	Total	exp.	Δ (theory-exp.)
IP	5.9159	7.6769	7.057	9.197	−0.0216	9.175	9.22554(2)	−0.050
EA	0.0990	0.6638	1.283	2.295	−0.0093	2.286	2.30861(3)	−0.023

The three major QED contributions (of lowest order) are the frequency dependent Breit interaction, the electron self-energy and the vacuum polarisation with the corresponding Feynman diagrams shown in Fig. 2. The classical (or instantaneous) Breit interaction arises from the electrodynamic interaction of two relativistic electrons and is usually not termed a QED effect. However, the Breit interaction can be derived more rigorously from QED including the frequency of the exchange photon between the two electrons. In the Coulomb gauge, the frequency dependent (also called transverse or retarted) Breit interaction between electron 1 and 2 becomes [70],

$$g_{12}^{\mathrm{Breit}}(\omega) = -\frac{\vec{\alpha}_1\vec{\alpha}_2}{r_{12}}\exp(ic^{-1}|\omega_{12}|r_{12}) - (\vec{\alpha}_1\vec{\nabla}_1)(\vec{\alpha}_2\vec{\nabla}_2)\frac{\exp(ic^{-1}|\omega_{12}|r_{12}) - 1}{c^{-2}\omega_{12}^2 r_{12}} \tag{18}$$

where ω_{12} is the frequency of the exchange photon (in the one-particle picture in terms of the difference between orbital energies of electron 1 and 2). In the low frequency limit ($\omega = 0$) we obtain the classical Breit term. The QED part of the Breit interaction is therefore defined as

$$\Delta g_{12}^{\text{QED-Breit}}(\omega) = g_{12}^{\text{QED-Breit}}(\omega) - g_{12}^{\mathrm{Breit}}(\omega = 0) \tag{19}$$

To our knowledge, the frequency-dependent two-particle operator $\Delta g_{12}^{\mathrm{Breit}}(\omega)$ has only been considered in atomic program codes such as GRASP [121].

For the evaluation of the QED energy shift in relativistic QED calculations it is convenient to expand the bound state propagator S_F in terms of $(Z\alpha)$ into free states (here in the usual notation used in QED),

$$S_F = \left(\not{p} - \not{k} - mc - \gamma^0(\alpha V)\right)^{-1} = \left(D - \gamma^0(\alpha V)\right)^{-1} = D^{-1}\sum_{k=0}^{\infty}\left(\gamma^0(\alpha V)D^{-1}\right)^k \tag{20}$$

with D^{-1} being the conventional free electron propagator. In this case we get the Feynman diagrams as shown in Fig. 3, with the dominant term for the vacuum polarisation coming from the Uehling potential [109],

$$V_{\mathrm{U}}^{\mathrm{VP}}(r) = -\frac{2Z\alpha^2}{3mr}\int_0^\infty dr'\, r'\rho_N(r')\int_1^\infty dx\left(1 + \frac{1}{2x^2}\right) \times \frac{\sqrt{x^2-1}}{x^3}\left(e^{-2|r-r'|x\alpha^{-1}} - e^{-2|r+r'|x\alpha^{-1}}\right) \tag{21}$$

where ρ_N is the (spherical) nuclear density normalised to 1. The Uehling potential is a short-range attractive potential that decreases exponentially for distances larger than the Compton

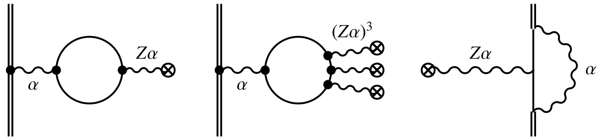

Fig. 3. From the left to the right: vacuum polarisation of order $\alpha(Z\alpha)$ (Uehling) and $\alpha(Z\alpha)^3$ (Wichmann–Kroll), and electron self-energy of order $\alpha(Z\alpha)$. Note that according to Furry's theorem diagrams with a loop containing odd number of vertices vanish [124].

Table 2

Vacuum polarisation and self-energy contributions for the $1s_{1/2}$ level in the hydrogen-like atom with $Z = 110$ (in eV) in comparison to calculations by Johnson and Soff [110], Mohr's parametrisation of Eq. (17), and using the implementation by Thierfelder and Schwerdtfeger [55].

Property	Johnson–Soff	Uehling, Mohr	Uehling, Thierfelder
VP	−281.832	−281.421	−281.421
SE	818.737	806.116	754.146

wavelength ($\sim 2.4 \times 10^{-12}$ m). Higher order terms in $(Z\alpha)$ such as the Wichmann–Kroll terms (see for example Fig. 3) [122] or the Källén–Sabry terms [123] can be evaluated as well.

It is often assumed that the Uehling potential has no analytical solutions and has to be evaluated numerically, but Frolov and Wardlaw recently showed a solution for point charge nucleus [125], which could be useful for future implementations into relativistic molecular program packages. They also derived useful formulae for the Wichmann–Kroll term and the Uehling-type two-electron term. Of course, such expansions are only valid if $Z\alpha << 1$, except for diagrams which contain extra factors in α. Nevertheless, these expansions are often used even beyond $Z = \alpha^{-1}$. To give an example, we compare Johnson and Soff's values [110] for the vacuum polarisation and electron self-energy for the $1s_{1/2}$ state of the hydrogen-like atom with nuclear charge $Z = 110$ in Table 2.

From our discussion so far it is clear that effective QED model Hamiltonians are required for the future accurate treatment of multi-electron atoms and molecules, which are applicable to high nuclear charges [66]. This is specially the case for the electron self-energy, which is more difficult to treat than the vacuum polarisation, i.e. the Uehling and Wichmann–Kroll potentials can be easily included in atomic Dirac–Coulomb–Breit calculations. A simple fix would be to reparametrise Eq. (17) for multi-electron systems using data from accurate bound-state QED calculations, but this would be a monumental task and perhaps not very sensible as these F-functions become state dependent. A simple replacement of the bare nuclear charge by the screened nuclear charge already gives qualitatively correct results,

$$\Delta E_{nlj}^{QED} \approx \frac{1}{\alpha\pi} \frac{\left[Z\alpha\left(1 - f_{\mathrm{scr}}\right)\right]^4}{n^3} F_{nlj}(Z\alpha) \tag{22}$$

with f_{scr} being a screening constant (which is zero for hydrogen-like atoms) that can be determined from a scaled effective nuclear charge. A similar scheme has been suggested by Dzuba [126]. Pyykkö suggested a simple local Gaussian model potential for the electron self-energy [66],

$$V^{SE} = B(Z)e^{-\beta(Z)r^2} \tag{23}$$

where $B(Z)$ and $\beta(Z)$ are polynomials in the nuclear charge Z. Dyall analysed the possibility for using a spectral representation of a hypothetical self-energy operator using hydrogen wave functions, but the diagonal representation fails to produce reasonable results, and a rather large matrix presentation is required to achieve convergence [127]. Recently, Shabaev fixed this problem by introducing an extra semi-local operator [62],

$$V_{lj}^{SE} = C_{lj} e^{-\gamma_{lj} r^2} P_{lj} + \sum_{k,l=1}^{m} |k\rangle \tilde{H}_{kl} \langle l| \tag{24}$$

where C_{lj} and γ_{lj} are adjustable parameters and P_{lj} is a projection operator onto the Hilbert subspace with quantum numbers (lj). Shabaev used $\gamma_{lj} = \lambda_C^{-1}$, where λ_C is the Compton wavelength, and the constants C_{lj} were chosen to reproduce the self-energy shift for the lowest energy level at the given (lj) of the corresponding hydrogen-like atom [62]. Routines for such calculations were published recently [128].

The problem of evaluating the self-energy QED term can in principle be divided into two parts, one relating to low-frequency virtual photons and one relating to high-frequency virtual photons [129,130]. Flambaum and Ginges arrived at the following effective Hamiltonian [130],

$$\tilde{H}_{\mathrm{SE}}(r) = V_{\mathrm{low}}^{\mathrm{SE}}(r) + V_{\mathrm{mag}}^{\mathrm{SE}}(r) + V_{\mathrm{el}}^{\mathrm{SE}}(r) \tag{25}$$

The contribution from the magnetic form factor is given by

$$V_{\mathrm{mag}}^{\mathrm{SE}}(r) = \frac{\alpha^2}{4\pi} i\vec{\gamma}\cdot\vec{\nabla}\left[V_{\mathrm{ext}}(r)\left(\int_1^\infty dt\,\frac{e^{-2tr\alpha^{-1}}}{t^2\sqrt{t^2-1}} - 1\right)\right] \tag{26}$$

where $V_{\mathrm{ext}}(r)$ is the electric potential of the nucleus. The first and last terms are contributions from the electric form factor split into a high and a low-frequency part. The low-frequency term is given by

$$\begin{aligned} V_{\mathrm{el}}^{\mathrm{SE}}(r) = {} & A(Z)\frac{\alpha}{\pi} V_{\mathrm{ext}}(r) \int_1^\infty dt\,\frac{e^{-2tr\alpha^{-1}}}{\sqrt{t^2-1}} \\ & \times\left[\left(1-\frac{1}{2t^2}\right)\left\{\log(t^2-1) + 4\log\left(\frac{1}{Z\alpha}+\frac{1}{2}\right)\right\} - \frac{3}{2} + \frac{1}{t^2}\right] \end{aligned} \tag{27}$$

where the function $A(Z)$ is obtained by fitting the total self-energy values to precise data of Mohr for one-electron systems. The (long-range) low-frequency contribution is estimated by

$$V_{\mathrm{low}}^{\mathrm{SE}}(r) = -B(Z) Z^4 \alpha^3 e^{-Zr} \tag{28}$$

where $B(Z) = 0.074 + 0.35 Z\alpha$ is a coefficient adjusted to reproduce the radiative shifts for the high Coulomb p-levels [130]. Thierfelder and Schwerdtfeger modified the function $A(Z)$ to be dependent on the principal quantum number n adjusting it to accurate calculations of for hydrogen-like atoms for ns electrons [55]. Table 3 compares results for the different approximations mentioned for the s-levels of superheavy element gold.

The Uehling potential is of short range as already mentioned. We expect the same for the electron self-energy, but this has never been demonstrated for multi-electron systems. Fig. 4 shows the radial behaviour of the vacuum-polarisation and self-energy expectation values for the ns-orbitals of element 118 according to the formula,

Table 3
VP and SE contributions for the *ns* levels of neutral Au (in atomic units). VP contains the Uehling and Wichmann–Kroll terms. The different approximations to the SE term are as follows: TS – Thierfelder and Schwerdtfeger equations (26), (27), (28) [55], PZ – Pyykkö–Zhao equation (23) [66], B – Blundell screening using hydrogen values [131], M – Mohr screening equation (22), D – Dyall diagonal spectral representation [127].

Orbital	ΔE^{VP}	$\Delta E^{\mathrm{SE}}_{\mathrm{TS}}$	$\Delta E^{\mathrm{SE}}_{\mathrm{PZ}}$	$\Delta E^{\mathrm{SE}}_{\mathrm{B}}$	$\Delta E^{\mathrm{SE}}_{\mathrm{M}}$	$\Delta E^{\mathrm{SE}}_{\mathrm{D}}$
1*s*	−1.529(+0)	7.063(+0)	8.031(+0)	2.120(+1)	7.050(+0)	7.260(+0)
2*s*	−2.167(−1)	1.070(+0)	1.123(+0)	1.077(+0)	1.054(+0)	1.234(+0)
3*s*	−4.923(−2)	2.473(−1)	2.543(−1)	2.482(−1)	2.331(−1)	3.619(−1)
4*s*	−1.226(−2)	6.208(−2)	6.330(−2)	6.211(−2)	5.356(−2)	1.349(−1)
5*s*	−2.284(−3)	1.163(−2)	1.179(−2)	1.159(−2)	8.981(−3)	5.039(−2)
6*s*	−1.718(−4)	8.777(−4)	8.877(−4)	9.476(−4)	7.084(−4)	1.082(−2)

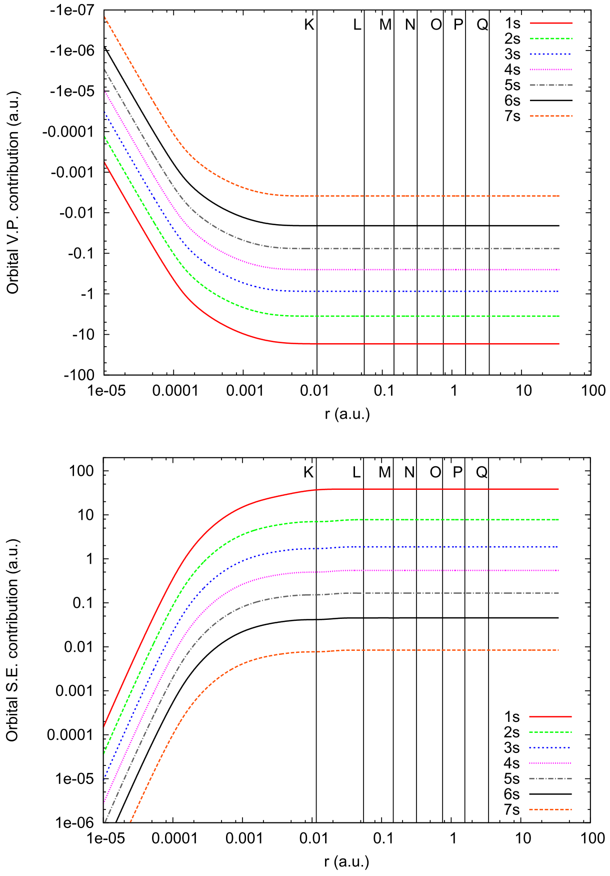

Fig. 4. Radially integrated contributions to the vacuum polarisation and electron self-energy for the *ns*-orbitals of element 118 on a logarithmic scale according to Eq. (29). The shell regions have been determined from the turning points of the valence densities of a particular shell.

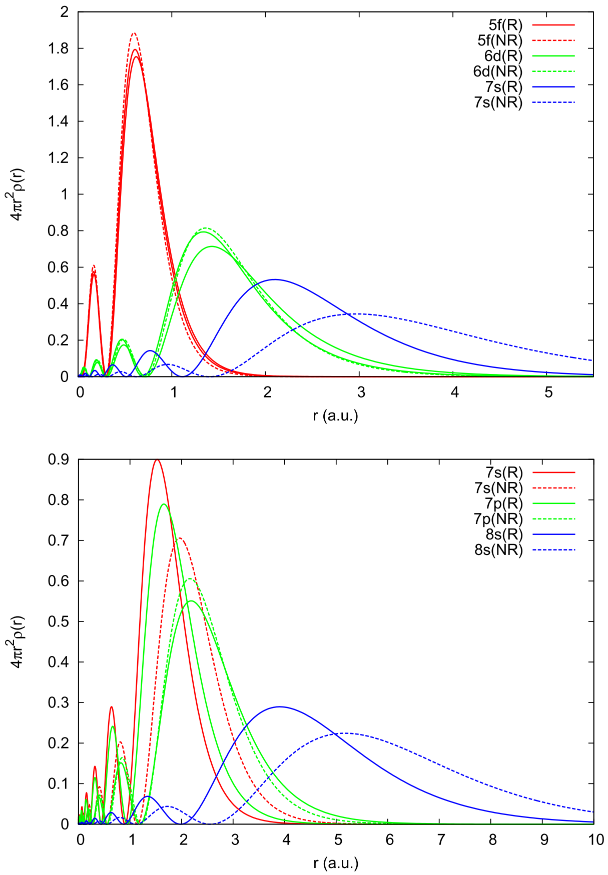

Fig. 5. Relativistic (solid lines) and nonrelativistic (dashed lines) radial orbital densities ($4\pi r^2\rho(r)$) for element Cn ($5f$, $6d$, $7s$ orbitals) and element 120 ($7s$, $7p$ and $8s$).

$$V_\mu(R) = \int_0^R \left(\int \phi_\mu^*(\vec{r}) V(\vec{r}) \phi_\mu(\vec{r}) d\Omega \right) r^2 \, dr \qquad (29)$$

in analogy of what has been used for discussing relativistic perturbation operators [132]. It clearly shows that QED operators are indeed short-range with most of the contributions coming from the K-shell region. The plots also nicely demonstrate that the QED contributions strongly diminish with increasing principal quantum number n. This is in accordance with the n^{-3} behaviour of the electron self-energy shown in Eq. (22).

4. Relativistic and quantum electrodynamic effects in superheavy elements and periodic trends

Fig. 5 shows relativistic and nonrelativistic radial orbital plots for superheavy elements Cn and 120. We see what is already well known: a) a strong relativistic contraction and stabilisation of the $7s$ and $8s$ orbitals (for the neutral elements $\langle r\rangle_{7s}^{R}/\langle r\rangle_{7s}^{NR} = 0.6983$ for Rg, 0.6857 for Cn, and $\langle r\rangle_{8s}^{R}/\langle r\rangle_{8s}^{NR} = 0.7618$ for element 120), such that the $7s$ shell is located close to the $6d_{5/2}$ shell, and the $8s$ shell close to the $7p_{3/2}$ shell; b) a large spin–orbit splitting of the $6d$ orbitals (by 5.38 eV between $6d_{3/2}$ and $6d_{5/2}$ for Cn at the DHF level); c) large spin–orbit splitting between the $7p_{1/2}$ and $7p_{3/2}$ orbitals (for element 117 the $^2P_{3/2}/^2P_{1/2}$ energy difference is ∼7.5 eV [133], which is of a similar magnitude compared to a typical bond dissociation energy); d) a relativistic $7p_{1/2}$ and $8p_{1/2}$ contraction and stabilisation. This clearly has consequences for the chemical and physical behaviour of the superheavy elements. We only discuss a few of these here as several competent review articles on this subject can be found in the literature, see for example Refs. [17, 134–137].

Because of the strong relativistic $7s$ shell contraction/stabilisation, this shell remains filled for the ground states of all elements in the periodic table from radium ($Z = 88$) onwards towards higher nuclear charges [134]. As a consequence, Rg ($Z = 111$) has a ground state configuration of $6d^9 7s^2$ ($^2D_{5/2}$) in contrast to the nonrelativistic configuration which is $6d^{10} 7s^1$ ($^2S_{1/2}$) [79]. The close location of the $7s$ and $6d_{5/2}$ orbitals in Rg and Cn makes these elements true transition elements. This stabilises the higher oxidation states +III and +V in the Röntgenium halides, e.g. $RgF_4^- \rightarrow RgF_2^- + F_2 + 4.73$ eV (2.13 eV) using relativistic (nonrelativistic) coupled cluster theory [138]. A comparison of bond distances along the group 11 hydrides shows comparable values between RgH (1.522 Å) and the lightest group 11 hydride CuH (1.463 Å) due to the relativistic $7s$ contraction in Rg [99,139–141].

Pitzer speculated that both Cn ($Z = 112$) and Fl ($Z = 114$) could be gases in elemental form or at least very volatile liquids [18]. Remember that mercury is a liquid metal at room temperature because of relativistic effects, and simulating the melting accurately is a notoriously difficult problem because of the many-body effects involved [13]. For example, the dimer Cn_2, has the highest dissociation energy (0.079 eV) [142] of all group 12 dimers (Zn_2 0.028 eV, Cd_2 0.040 eV, Hg_2 0.049 eV) [143]. This does not translate so easily into the cohesive energies for the bulk phases as it follows exactly the reverse trend, i.e. from zinc to mercury we have (in eV) Zn 1.35, Cd 1.16, and Hg 0.67. This is clearly a manifestation of strong many-body effects (beyond a simple 2-body interaction), which is known to be very important for mercury, and in fact for metallic systems in general [143–145]. Solid-state calculations for Cn put the cohesive energy of 1.13 eV above the value of Hg [146]. As the $7s$ orbital lies energetically and spatially within the $6d$ range, the higher oxidation state +IV becomes thermodynamically stable even more than in the case of Hg [147–149].

As copernicium is a rather inert closed-shell group 12 element with a half-life of ∼3.8 s for the experimentally detected ^{283}Cn isotope, the possible chemistry for such an element at the one-atom-at-a-time timescale is rather limited. Recent experiments on Cn adsorption on gold gave an estimate for the adsorption enthalpy of -52^{+20}_{-4} kJ/mol [150,151]. From this they estimate a boiling point of 357^{+112}_{-108} K, hence the error bars still allow Cn to be a gas at room temperature. However, one has to be careful with such estimates as already mentioned. Furthermore, the data in Fig. 6 show that the current theoretical (density functional) value for the cohesive energy of Cn does not correlate well with the adsorption enthalpy on a gold surface, which requires further investigation. For a detailed discussion on Cn, Fl and 118 adsorption on surfaces see Pershina et al. [152–154] and Gäggeler and Türler [35].

Element 113 and Fl occupy the spin–orbit stabilised $7p_{1/2}$ states with the spin–orbit destabilised $7p_{3/2}$ being several electron volts higher in energy [82,85]. Including the very strong relativistic $7s$ contractions this makes the higher oxidation states +III for element 113 and +IV for Fl rather inaccessible. Indeed, calculations showed rather large relativistic destabilisations for the higher oxidation states [160,161], e.g. we have $(113)F_3 \rightarrow (113)F + F_2 + 0.33$ eV (+5.32 eV) [160] and $FlF_4 \rightarrow FlF_2 + F_2 - 0.16$ eV (+6.06 eV) [161] using relativistic (nonrelativistic) level

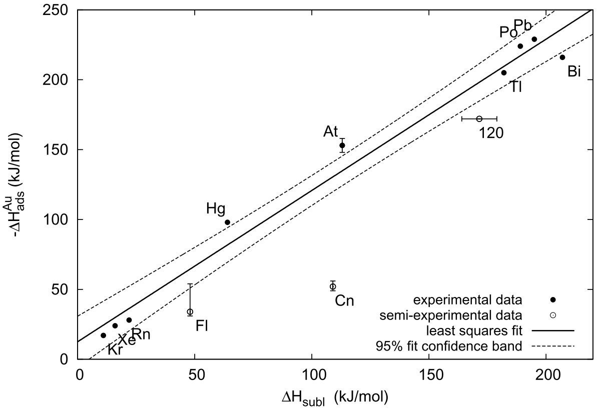

Fig. 6. Correlation between experimental adsorption enthalpies on gold surfaces of homologues of elements Cn through 118 and their respective sublimation enthalpies compared with recent data for Cn, Fl and 120 coming from one-atom-at-a-time experiments [150,155], experimental estimates [6], and computational (DFT) predictions [146,156,157]. Experimental data for Bi, Hg, Kr, Pb, Po, Rn, Tl, and Xe are taken from Ref. [158], and data for At taken from Ref. [159].

of theory. The other halides and the hydrides are all thermodynamically unstable in the high oxidation states [162]. As Fl has a closed shell $7s7p_{1/2}^2$ configuration it may be as much chemically inert as Cn. First experiments (two events) on Fl adsorption on gold surfaces suggest a lower limit for the adsorption enthalpy of ~ 0.5 eV [163]. As Fig. 6 shows, this value correlates better with the calculated cohesive energy of Fl compared to the case of Cn. Again, all solid-state calculations were done by relativistic density functional theory as it is currently very difficult to describe electron correlation for (near) metallic systems. Another interesting feature of the relativistic $7p_{1/2}^2$ stabilisation is that element 113 has the highest electron affinity (0.68 eV [82]) of all group 13 elements in the periodic table, similar to an s-block element such as Li.

The chemistry of elements 115 to 118 will depend on the loosely bound $7p_{3/2}$ electrons with probably little participation of the $7p_{1/2}^2$ closed shell. For example, $(117)F_3$ has been investigated recently by Lee and co-workers who found a perfect D_{3h} symmetry for this molecule,[6] while the AtF_3 shows a second-order Jahn–Teller distortion into the C_{2v} symmetry [164]. Element 118 is notable as it is the first rare gas element with a non-zero electronegativity of 0.064 eV due to the relativistic $8s$ stabilisation [58,83]. QED effects lower this value by 0.006 eV (9% of the total value) [58]. Otherwise 118 is expected to behave just like the other rare gases. First estimates for the adsorption energy of 118 on gold shows that it fits roughly into the series of the rare gas elements [153,165]. However, the dissociation energy of the 118 dimer is predicted to be by a factor of four higher than for Rn_2, and therefore has the highest dissociation energy within the rare-gas group [166,167]. All attempts to synthesise elements beyond nuclear charge 118 have been unsuccessful so far, and the question of the nuclear stability of elements beyond nuclear charge 118 remains open [168]. However, Eichler and co-workers already studied the possible adsorption of element 120 on a gold surface by using relativistic density functional theory (see Fig. 6) [169]. Beyond nuclear charge 126 there is so far no prediction of another island of nuclear stability. While element 119 and 120 clearly fit into the group 1 or 2 element series of the periodic table, and element 121 fills the next $8p_{1/2}$ shell ($^2P_{1/2}$) [170], the filling of the shells

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[6] 113^{3+} is a closed-shell system and in a complete ionic model we would not predict a Jahn–Teller distortion.

from element 122 onwards [171] becomes more complicated as many electronic states involving configurations from occupying $5g$, $6f$, $7d$, $8p_{3/2}$, $9s$, $9p_{1/2}$ levels become rather close in energy requiring more sophisticated electron correlation procedures within a relativistic treatment including QED effects. Thus, for the heavier elements the periodic table of placing elements into certain groups somewhat loses its importance despite several attempts to complete the periodic table to high nuclear charges [4,134,172,173]. This is understandable from the simple fact that the energy spectrum becomes more dense moving to higher principal quantum numbers and angular momentum states, just as this is the case for the simple hydrogen atom.

QED effects will most likely not alter the chemistry of superheavy elements [4,174,175] even up to very high nuclear charges (see discussion in the next chapter), but will be important for future high-resolution spectroscopy experiments on transactinides. As mentioned before, the last experiment using electronic spectroscopy was carried out by Sewtz et al. on ^{255}Fm [36]. For a recent detailed discussion on QED effects in superheavy elements see the paper by Indelicato et al. [59]. Moreover, QED effects are orders of magnitude higher in the core region close to the nucleus where the classical Coulomb potential comes close to $-2m_ec^2$. This is clearly seen in Fig. 4. Indeed, QED effects can be in the 1 keV region for the K-shell ionisation in the superheavy elements Cn to 118, and cannot be neglected anymore [54]. As an example we mention that ^{272}Rg undergoes α-decay into ^{268}Mt with a measured signal of (155.0 ± 0.8) keV energy in the Ge detector [176]. In order to distinguish between a possible nuclear transition and a K-inversion event, QED effects had to be included in the relativistic atomic structure calculations [55].

5. The end of the periodic table?

Fig. 7 shows that at a certain critical charge, $Z_{\rm crit}$, the (nlj) levels of a one-electron Dirac atom dive into the negative energy continuum (set here at $-2m_ec^2$) [177]. In the original paper by Greiner and co-workers, where the dissolution of the $1s_{1/2}$ shell into the negative energy continuum was discussed, the critical charge was estimated to be $Z_{\rm crit} = 173 \pm 1$ for hydrogen-like atoms [178], but later determined to be at $Z_{\rm crit} = 164$ [179]. We note that Greiner predicts an electronic closed-shell structure for the element with $Z = 172$ ([Cn]$5g6f7pd8sp9sp_{1/2}$), close to this critical charge [180]. Indelicato recently determined $Z_{\rm crit} = 173.17$ for the $1s_{1/2}$ shell, only slightly influenced by QED effects [175]. We predict (including QED effects) $Z_{\rm crit} = 170.02$ for the $1s_{1/2}$ shell for hydrogen-like atoms, and $Z_{\rm crit} = 172.16$ for the $1s_{1/2}$ shell in Ar-like atoms. We note that $Z_{\rm crit}$ is not too dependent on the nuclear model chosen, but sensitive to the half-density nuclear radius R_0 of the Fermi nucleus (see Eq. (6)). In our case we used a modified volume-mass equivalence formula [181,182],

$$R_0 = r_0 A^{1/3} + b \tag{30}$$

with atomic mass number $A = N + Z$, $r_0 = 0.836$ fm and $b = 0.570$ fm (1 fm $= 10^{-15}$ m) [110] and an atomic mass obtained through the semi-empirical relation derived from the nuclear liquid-drop model [183],

$$Z = 2A\left(4 + \frac{a_c}{a_a}A^{2/3}\right)^{-1} \tag{31}$$

($a_c = 0.72$ and $a_a = 23$) which for small A-value becomes $Z = A/2$ and therefore $Z = N$.

QED corrections to the $1s$ level for $Z \sim 172$ are rather small compared to $-2m_ec^2$ as VP and SE contributions almost cancel out in such supercritical fields [184]. In Fig. 8 we clearly see the small component of the $1s$ orbital quickly becomes large in the superheavy element region

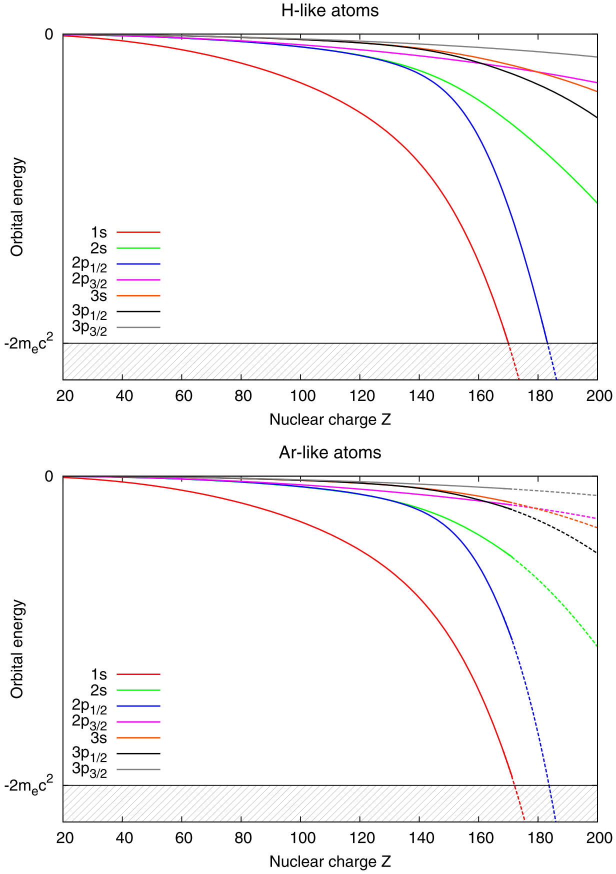

Fig. 7. Orbital energy dependence on nuclear charge Z. $1s_{1/2}$ shell diving into the negative energy continuum ($-2m_ec^2$) at Z_{crit}. Dashed parts of the curves are extrapolations.

and the terms "small" and "large" for the two components are no longer valid. Moreover, in the supercritical region with $Z \sim Z_{\text{crit}}$ the influence of the small component in relativistic procedures cannot be neglected.

There are two related but distinct issues arising from the above discussion: the first is the technical challenge of obtaining reliable results in the supercritical regime; the second is the proper interpretation of what it means for an atomic nucleus to be in a supercritical state. As has already been mentioned, the fact that relativistic quantum mechanics suffers from problematic negative energy states – most famously demonstrated by the Klein paradox – has been known almost since its birth. This and other failings lead to the development of quantum field theory. In any case, it becomes necessary to consider pair creation in order to preserve unitarity.

In the simple case of an electronless ion [177], the vacant $1s$ shell can be filled by the spontaneous production of an electron–positron pair: the electron is bound while the positron goes free. A similar process near the surface of black holes results in Hawking radiation [185]. For a given

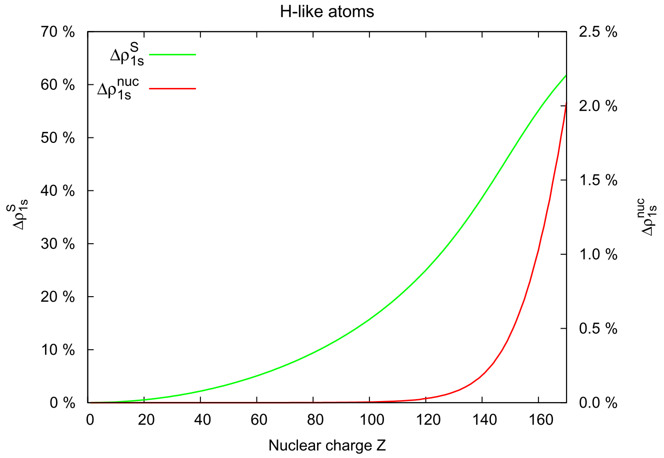

Fig. 8. Dependence of the fraction of the 1*s* electron density due to the small component $\Delta\rho_{1s}^{S}$ and the fraction of the 1*s* electron density contained within the nuclear radius $\Delta\rho_{1s}^{nuc}$ on nuclear charge Z.

barely super-critical nucleus, this can occur twice, then the "vacuum"[7] is stabilised by Pauli pressure. Alternatively, if there is a free electron present, it could occupy the shell, releasing a photon of energy $E \geq 2m_ec^2$. In either case, in the language of Zel'dovich and Popov a supercritical atom is formed [103]. Higher nuclear charges will result in the diving of higher electron orbitals, in turn resulting in further pair production [186,187]. Whatever the physical and practical barriers to creating such nuclei, their supercriticality presents no fundamental problem. But, these processes require a proper QED treatment beyond standard relativistic mean-field theory.

The breakdown of the single-particle picture means that a description using conventional bound state QED with Dirac–Hartree–Fock wave functions as zero-order solutions might not be applicable anymore. At $Z > Z_{\text{crit}}$ one faces serious convergence difficulties in the Dirac self-consistent field procedure. As already mentioned, the screening of the nucleus by the other electrons in a multi-electron system will increase Z_{crit}, which will extend the region of applicability. However, as the 1s density becomes concentrated close to the nucleus – nicely demonstrated in Fig. 8 – K-capture becomes increasingly likely. We might speculate that inverse beta decay therefore represents the most difficult hurdle to the creation of super-heavy elements beside other nuclear decay channels.

The discussion here may seem to be of rather academic value as it seems unlikely that such heavy nuclei will ever be synthesised, and there is no immediate way to test QED in such supercritical fields. However, in collisions of two heavy ions such high charges can be reached for a very short time. For a more detailed discussion see Greiner and co-workers [101,187,188]. We may not expect another "distinct" island of nuclear stability at high nuclear charge as the spectrum of the proton and neutron states become more dense with increasing number of protons and neutrons (just like the case for the electron shells), providing low-energy routes for nuclear decay.

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[7] It is important to note that this charged vacuum is a result of considering the nucleus as an external potential.

6. Conclusions

Considerable progress has been made over the past two decades to correctly account for relativistic and electron-correlation effects in heavy element containing compounds, despite the fact that there are many problems in the correct relativistic treatment of many-electron systems [189–192]. Efficient algorithms are now available to treat atoms and molecules at the four-component Dirac level of theory including approximations to the Breit interaction, and at the two-component level without losing much in accuracy compared to the four-component approach. However, when it comes to spectroscopic accuracy, the interplay between relativistic, quantum electrodynamic and electron correlation effects become important. Some newer developments in this area are encouraging, but it is fair to say that progress is still needed [62,64,116]. The problem of the $1s$ state entering the negative energy continuum at high nuclear charges requires a more rigorous QED treatment going beyond standard many-body perturbation theory. The end of the periodic table is, however, more likely determined by the nuclear instability of highly charged nuclei and low cross section in the fusion process than by its electronic structure. More accurate nuclear structure calculations are required as this area remains rather unexplored for nuclear charges beyond $Z = 120$. K-capture could be a limiting factor as the 1s density resides close to the finite nucleus, which also remains to be explored [193–196].

Acknowledgements

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