Available online at www.sciencedirect.com

ScienceDirect

Nuclear Physics A 944 (2015) 551–577

NUCLEAR PHYSICS A

www.elsevier.com/locate/nuclphysa

Relativistic and quantum electrodynamic effects in superheavy elements

Peter Schwerdtfeger [a,*], Lukáš F. Pašteka [a,b], Andrew Punnett [c], Patrick O. Bowman [c]

[a] *Centre of Theoretical Chemistry and Physics, The New Zealand Institute for Advanced Study, Massey University Auckland, 0745 Auckland, New Zealand*

[b] *Department of Physical and Theoretical Chemistry, Faculty of Natural Sciences, Comenius University, Mlynská Dolina, 841 04 Bratislava, Slovakia*

[c] *Centre of Theoretical Chemistry and Physics, Institute for Natural and Mathematical Sciences, Massey University Auckland, 0745 Auckland, New Zealand*

Received 27 December 2014; received in revised form 12 February 2015; accepted 13 February 2015

Available online 27 February 2015

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

* Corresponding author.
E-mail address: p.a.schwerdtfeger@massey.ac.nz (P. Schwerdtfeger).

http://dx.doi.org/10.1016/j.nuclphysa.2015.02.005
0375-9474/

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 7*s* contraction (giving Cn an atomic radius smaller than Cd), Fl because of the strong spin–orbit splitting of the 7*p* 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

[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].