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Electronic structure theory of the superheavy elements

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Abstract

High-accuracy calculations of atomic properties of the superheavy elements (SHE) up to element 122 are reviewed. The properties discussed include ionization potentials, electron affinities and excitation energies, which are associated with the spectroscopic and chemical behavior of these elements, and are therefore of considerable interest. Accurate predictions of these quantities require high-order inclusion of relativity and electron correlation, as well as large, converged basis sets. The Dirac–Coulomb–Breit Hamiltonian, which includes all terms up to second order in the fine-structure constant α, serves as the framework for the treatment; higher-order Lamb shift terms are considered in some selected cases. Electron correlation is treated by either the multiconfiguration self-consistent-field approach or by Fock-space coupled cluster theory. The latter is enhanced by the intermediate Hamiltonian scheme, allowing the use of larger model (P) spaces. The quality of the calculations is assessed by applying the same methods to lighter homologs of the SHEs and comparing with available experimental information. Very good agreement is obtained, within a few hundredths of an eV, and similar accuracy is expected for the SHEs. Many of the properties predicted for the SHEs differ significantly from what may be expected by straightforward extrapolation of lighter homologs, demonstrating that the structure and chemistry of SHEs are strongly affected by relativity. The major scientific challenge of the calculations is to find the electronic structure and basic atomic properties of the SHE and assign its proper place in the periodic table. Significant recent developments include joint experimental–computational studies of the excitation spectrum of Fm and the ionization energy of Lr, with excellent agreement of experiment and theory, auguring well for the future of research in the field.

Keywords: Superheavy elements; Relativity; Electron correlation; Coupled cluster methods; Multiconfiguration SCF

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1. Introduction

The term "superheavy elements" (SHE) has been given different meanings over the years. Here we shall follow the suggestion made in the preface to the second edition of "The Chemistry of Superheavy Elements" [1], and refer as SHEs to all elements from Rf (E104) onwards. From the viewpoint of nuclear physics, these elements start showing enhanced stability of some isotopes; Rf has isotopes with half-lives of up to one minute, 16 orders of magnitude longer than expected without extra shell stabilization [1]. From a chemistry viewpoint, Rf is the first transactinide, so that the two terms "superheavy elements" and "transactinides" become synonymous.

The discovery of the last missing transactinide in the seventh period, element E117, has recently been announced [2,3]. Thus, the updated periodic table contains 118 elements in total, including 15 SHEs, from rutherfordium to eka-radon, E118. Furthermore, various attempts to synthesize the elements 119 and 120 have been reported [4], but cross sections smaller than 0.4 pb prevented a clear success so far. All known SHEs were produced artificially. Marinov et al. [5] presented evidence for the existence in nature of a long-lived superheavy element with atomic number $Z = 122$ and mass $A = 292$, with an abundance of about 1×10^{-12} relative to Th, but this has not been confirmed in more recent studies [6,7]. A concise summary of SHE chemistry has appeared recently [8].

Due to the low production rates, the short half-lives and the need for special facilities that are capable of processing one atom at a time, experimental studies on SHEs are currently limited to the measurement of a few atomic properties. Atomic and chemical studies of the heaviest elements shed light on the lower part of the periodic table, revealing trends which may differ from those shown by lighter elements. The properties of SHEs cannot always be estimated by simple extrapolation of the relevant group in the periodic table. One fundamental aim of experiment is, therefore, to reveal the similarities and differences in the chemistry of the SHEs and their lighter homologs. Relativity, and in some cases quantum electrodynamics (QED), are known to strongly affect the SHEs valence electron shells and, hence, their chemical behavior, causing significant deviations from the trends exhibited by the group. In particular, the relative energies of orbitals may be affected, modifying the electron configurations of atomic ground and excited states. While some chemistry of SHEs can be studied in single-atom experiments, spectroscopy usually requires larger amounts of the relevant species. Important atomic properties, such as ionization potentials (IP), electron affinities (EA) and excitation energies (EE), have not yet been measured for SHEs, as the term is defined above, and theoretical investigations are the only source of this information. This situation may be expected to change in the near future, as two joint experimental–theoretical efforts involving the spectroscopy of elements with $Z \geq 100$, just below the SHE range, have been reported in recent years. The excitation spectrum of Fm, using a weighable quantity of an isotope with half life of 20 hr, was measured and calculated in 2003 [9], with very good agreement of the two approaches (see Section 3.2 below). Even more relevant is the very recent measurement of the IP of Lr, the heaviest actinide [10], using an isotope with a half life of 27 s and a production rate of one atom every few seconds. The extraction of the experimental IP from the measured data required in this case the earlier high-precision calculations of the excitation energies [11]; a different set of calculations obtained the IP independently. Excellent agreement between experiment and theory was found (see Section 3.3). Theory can reveal the contributions of electron correlation, relativistic and QED effects to different atomic and chemical properties. These effects are often large and non-additive, and their contributions are complicated by the multireference character of many electronic states, presenting severe challenges to theoretical and computational methodology.

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