ELECTRONIC STRUCTURES CALCULATIONS AT THE EDGE OF PERIODIC TABLE

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High-accuracy calculations of atomic properties of the heaviest elements, are reviewed (see ref.[1] for more details). The properties discussed include electronic structure and energetics (ionization potentials, electron affinities, 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, QED and electron correlation effects, 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 , serves as the framework for the treatment; higher-order Lamb shift terms are considered in selected cases. Electron correlation is treated by the Fock-space coupled cluster method, enhanced by the intermediate Hamiltonian scheme, allowing the use of large, converged model (P) spaces.

The calculations on superheavy elements (SHE) are supported by the very good agreement with experiment obtained for the lighter homologues, usually within a few hundredths of an eV, and similar accuracy is expected for the SHEs, with Z>100, for which experimental values are scarce. Many of the properties predicted for these species 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 and electron correlation.

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 ionization energies of No and Lr, with excellent agreement of experiment and theory. These calculations were required not only for comparison with experiment; the extraction of the ionization potential from experimental data depended on reliable estimates of atomic excitation energies, obtainable from theory.

References:
1. E. Eliav, A.Borschevsky, U.Kaldor, in "Handbook of Relativistic Quantum Chemistry", Ed. W. Liu 2015, Springer-Verlag Berlin Heidelberg, chapter 26, pages 825; in Robert A Scott (Eds.), Encyclopedia of Inorganic and Bioinorganic Chemistry (on-line), 2018