Relativistic effective configurations of heaviest atoms in compounds: local and global approaches

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The concept of effective states (effective electronic configurations) of atoms in compounds plays a key role both in representing the results of electronic structure modelling in conventional "chemical" language and in the interpretation of the data obtained by experimental techniques. Strong spin-dependent relativistic effects in heavy element compounds require the description of effective atomic states in terms of relativistic configurations, discerning the fractional populations of valence subshells with the same orbital angular momentum l and different total angular momenta j. There are at least two main general approaches to determine such configurations of heavy atoms in compounds. The most widely used and popularized approach (projection analysis technique, [1] and references therein) is based on the analysis of global molecular one-electron density matrices, using some pre-chosen reference atom-centered spinors to separate the atomic contributions to these entities. An alternative strategy is the recently proposed Atoms-in-Compounds (AiC) theory [2], which is based on the idea of the core restoration and consists in the local analysis the molecular density matrices in the vicinities of heavy nuclei through simulating their basic features in the fractional-occupancy calculations of the corresponding free (or confined in a spherical cavity) heavy atoms. In contrast with the case of common global analysis, the resulting effective configurations are directly related to certain measurable (spectral) characteristics of the compounds associated with core properties of heavy atoms. Both "local" (AiC-based) and "global" methods were applied to simple molecular compounds of Cn, Nh, Fl and their lighter homologues Hg, Tl and Pb. In order to avoid the dependence on the reference atomic configurations we have modified the conventional projection analysis technique. In both approaches density matrices were obtained using the two-component noncollinear density functional theory [3] and the relativistic pseudopotential model. The results of "global" and "local" effective configuration analysis were qualitatively consistent. The simple semi-quantitative model was proposed to make conclusions about strength and features of chemical bonds formed by superheavy atoms. d-orbitals are shown to be active in bond formation in Cn compounds, otherwise, Nh and Fl manifest themselves as typical p-elements. The difference in populations of valence subshells with the same l and different j is demonstrated to be essential for understanding the peculiarities of chemical bonding in superheavy elements compounds.

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