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A new formulation of effective states of “atoms in compounds”. application to study hyperfine structures and chemical shifts of x-ray emission lines.

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Concepts of oxidation number state of an atom in a molecule and related theories are extremely useful in chemistry. At the same time, a good (clear and unambiguous) definition of the state of an atom in a molecule does not exist. Various methods of determining it from calculations lead to different results [1]. Each of known definitions has its drawbacks. The methods based on the use of one-electron density matrices (Mulliken or Löwdin populations analyses, etc.) are basis set dependent. The methods that use the electron densities (Bader or Hirschfield charges, Voronoi cells), suggest introduction of some complementary (artificial) notions or partitioning a molecule (solid) on regions in a manner that is not arising from any of physical principles.
There is a number of experimentally observed properties of compounds, depending on a distribution of the valence electron densities or their changes in the atomic core regions. They include chemical shifts of X-ray emission spectra [2], hyperfine structure constants, isotope (volume) shifts, etc. Earlier our group has developed a two-step method to calculate these properties through first-principle based electronic structure calculations within the generalized relativistic pseudopotential approximation followed by a posteriori restoration of the information on the wave functions in the atomic core regions that is missed in the results of pseudopotential calculations [3]. On the basis of this two-step method one can formulate an approach for determining the state of an atom in a molecule (compound). A radius Rc of the core region is determined by the smallness of interaction of valence electrons located within a sphere (r < Rc) with the external (chemical) environment (r > Rc) compared to their interaction with the nucleus and core electrons of a considered atom.

Using the properties of proportionality of valence spinors in the atomic core region with the radius Rc [4], one introduce some new terms: “charges of partial waves” for valence electrons in the core region, “reduced population numbers” and one-center density matrices “reduced on the radial quantum number nr”. It is shown that the above-discussed properties characterized by the state of an atom in a compound rather than by chemical bonds are well described by only these terms. Results of calculations of the properties of atoms and molecules are presented.
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Primary authors: Prof. TITOV, Anatoly (Petersburg Nuclear Physics Institute, Gatchina, Russia; Dept. of Physics, St. Petersburg State University, Petrodvoretz, Russia); LOMACHUK, Yuriy (Petersburg Nuclear Physics Institute, Gatchina, Russia; Dept. of Physics, St. Petersburg State University, Petrodvoretz, Russia)

Co-authors: SKRIPNIKOV, Leonid (Petersburg Nuclear Physics Institute, Gatchina, Russia; Dept. of Physics, St. Petersburg State University, Petrodvoretz, Russia); MOSYAGIN, Nikolay (Petersburg Nuclear Physics Institute, Gatchina, Russia; Dept. of Physics, St. Petersburg State University, Petrodvoretz, Russia)

Presenter: LOMACHUK, Yuriy (Petersburg Nuclear Physics Institute, Gatchina, Russia; Dept. of Physics, St. Petersburg State University, Petrodvoretz, Russia)

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