Contribution ID: **1653**   Type: **Oral**

Towards a software ecosystem for high-precision multi-scale ab initio relativistic quantum modeling of atoms, molecules, and materials

Wednesday 30 October 2024 15:20 (15 minutes)

Heavy-element-containing compounds and materials are among the most challenging objects for ab initio electronic structure modeling due to the interference of strong relativistic effects, typically multi-configuration nature of electronic states, and high density of levels in their spectra. A thorough modeling of these objects aimed at reliable predictions of their structure and optical, magnetic, and thermodynamical properties clearly requires a set of theoretical methods and software tools implementing them. We present a project of a software ecosystem for multi-scale ab initio modeling of quantum systems from atoms to cluster models of solid-state materials designed at NRC "Kurchatov Institute" –PNPI and Moscow Institute of Physics and Technology. It will include a set of programs focused on objects of different levels of complexity.

The most precise calculations are available within the relativistic multireference coupled cluster (CC) methodology. Its Fock-space version, including up to triple excitations (the FS CCSDT model) was implemented within the EXP-T program package [1]. The manifold of available extensions of the Fock-space coupled cluster method currently also includes its formulations for systems with three unpaired electrons, a special version of the intermediate Hamiltonian technique to resolve numerical stability issues, and finite-field and finite-order approaches to calculate one-electron properties (including transition ones) [2]. Since the coupled cluster method is relatively computationally demanding, its equations were reformulated using the tensor-train decomposition to reduce their formal scaling and implemented as a part of EXP-T. The relativistic CC method was successfully applied recently to predict localized f-d excitations on the Ce^{3+} and Th^{3+} impurity ions embedded into the xenotime (yttrium orthophosphate YPO_4) crystal matrix [3].

To simulate much larger objects (up to several dozens of atoms), a set of programs implementing the second-order multi-partitioning perturbation theory (MPPT) [4] is currently being developed. Being a genuine multi-state method, MPPT is perfectly suitable to predict excited electronic states and spectra of systems with a pronounced multireference character, including those possessing several unpaired electrons, like materials containing atoms of d- and f-elements (lanthanides and actinides).

Both the CC and MPPT methods employ many-electron Hamiltonian integrals over molecular orbitals / spinors; thus, it seems reasonable to design an efficient relativistic Hartree-Fock and density functional program to produce the latter entities. Moreover, it is also necessary to perform preliminary calculations, e.g., geometry optimization, before applying more sophisticated methods. For this purpose, we started the work on the BUFO program, implementing both non-relativistic and two-component relativistic versions [5] of the Hartree-Fock method. It heavily relies on a generalized relativistic pseudopotential (GRPP) concept. It employs the LIBGRPP library to evaluate integrals over the GRPP operator based on atomic Gaussian functions [6]. The GRPP approach, especially its latest versions which account for quantum electrodynamic and Breit effects, is also a cornerstone for modeling of d- and f-element compounds with unprecedented accuracy using the MPPT and CC methods.

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Session Classification: Condensed Matter Physics

Track Classification: Condensed Matter Physics