STUDY OF P,T-ODD INTERACTIONS IN MOLECULES. TWO-STEP METHOD FOR CALCULATION OF ELECTRONIC STRUCTURE OF MOLECULES WITH HEAVY ATOMS

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Modern "shape-consistent" Effective Core Potential (ECP) calculations of electronic Wave Function (WF) of molecules with heavy atoms are rather good for potential curves (or surfaces) of ground and low-lying excited states and other chemical properties [1] because they allow to treat satisfactory the correlation structure and relativistic effects in the valence region of a molecule. However, inaccuracy of the conventional ECP method (where the valence molecular orbitals or spinors are smoothed in the core regions of heavy elements and only valence nodeless pseudoorbitals are used for generation of the ECP components) reaches few per cent for transition and dissociation energies. Calculation of such nonstandard properties as electronic density near heavy nuclei, hyperfine structure and P,T-odd interactions with pseudoorbitals is impossible.

The former circumstance stimulated future development of the ECP approach and Generalized ECP (GRECP) method was proposed both for nonrelativistic [2,3] and for relativistic cases [4] where valence and outercore pseudoorbitals were included in the ECP generation scheme. The latter one had led to methods of restoration of correct shape of orbitals or four-component spinors in the core regions of heavy elements [5,6].

In the paper [2], the widespread conception about necessity of generating the ECP components only for nodeless pseudoorbitals was demonstrated to be wrong, and outermost core pseudoorbitals (nodeless) together with valence pseudoorbitals (with nodes) had been included in the ECP generation scheme. Significant improvement in accuracy (about 10 times) was demonstrated for transition energies as compared with the conventional ECP approach.

However, high accuracy of the GECP and rather singular shapes of components of the Generalized ECP put serious obstacles for approximation of numerical potentials with gaussian functions and we developed a new procedure for this purpose. In the paper [3], our first results of gaussian expansion of the Generalized ECPs for atoms Xe, Pd and Ag are presented in the framework of the nonrelativistic approach.

In the paper [4], a generalization of the Relativistic ECP method was developed for the case of pseudospinors that may have nodes. The numerical potentials had been generated and the calculations of transition energies had been made in order to study quality of treatment of relativistic effects in the scope of the Generalized RECP approach.

For evaluation of matrix elements of singular on nuclei operators, a correct shape of valence molecular orbitals should be restored in the atomic core regions. In the paper [5], a simple method of restoration was applied to HgF, PbF and YbF where the Hamiltonian parameters including terms of the weak interaction that break the symmetry over the space inversion and time-reversal invariance were evaluated. In the work [6], a variational procedure for computation of orbitals or four-component spinors near heavy nuclei is proposed with the help of an one-centre expansion for orbitals and interactions.

The two-step approach for separate calculations of valence and core parts of a molecule gives us a way to join the advantages of nonrelativistic-type ECP molecular calculations in gaussian basis set with a simplicity of relativistic one-centre calculations within the sphere with a radius of atomic core.

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