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ОТЗЫВ

члена диссертационного совета Сафроновой Марианны Святославны на диссертацию Олейниченко Александра Витальевича на тему: «Развитие релятивистского метода связанных кластеров для электронных состояний молекул с несколькими открытыми оболочками», представленную на соискание ученой степени кандидата физико-математических наук по специальности 1.3.3. Теоретическая физика.

Precision calculation of atomic and molecular properties is very important for many modern applications in physics and chemistry, including studies of fundamental symmetries, tests of physics postulates, quantum information and simulation, studies of degenerate quantum gases, development of atomic and molecular clocks, searches for the variation of fundamental constants, extraction of nuclear moments from laser spectroscopy, quantum control of chemical reactions, interstellar chemistry, and many others. Two examples of such applications of particular relevance to the work described in the thesis of Alexander Oleynichenko is the search for the electric dipole moment of electron (eEDM) with molecules and photoassociation of ultracold molecules with alkali-metal atoms. ACME experiment in Harvard with ThO molecules has improved the limits on the eEDM by two orders of magnitude in the last decade. Future experiments will use laser-cooled YbF and YbOH (in Imperial College, UK, and Caltech, USA, respectively), requiring precise knowledge of these systems. An eEDM experiment with laser-cooled polyatomic molecules trapped in an optical lattice has the potential to improve eEDM precision by several orders of magnitude. A discovery of eEDM, predicted by many theories, will be an unambiguous signal of new physics. In addition, extensive experimental efforts are aimed towards the precision measurement of transitions in molecules and simple molecular ions to search for the variation of fundamental constants and related dark matter searches. All these experiments need not only theoretical predictions but also reliable estimates of theoretical uncertainties.

This thesis presents important developments of a relativistic coupled-cluster (CC) theory, specifically full inclusion of triple excitations in various sectors of Fock space as well as extending the applications of the FS-CC methods as discussed below. A detailed study of various approximate schemes for the inclusion of triples excitations is carried out. Extensive method tests are carried out, confirming the validity of the new methodologies. This is novel and important work.

The thesis of Alexander Oleynichenko includes an introduction, four chapters, a conclusion, and five appendixes that include diagrammatic representation of the CC equations, results for La and La ions, and basis sets. The text is clear and well written. Extensive relevant literature is cited, with 220 references. The results are published in seven publications in peer-reviewed journals

and presented at several conferences, including the 13th European Conference on Atoms, Molecules, and Photons (ECAMP13).

The introduction discusses the motivation and main goals of this work, summarizes the present status of the field, outlines the content of the chapters and important results. Chapter 1 presents an excellent review of the development of the Fock-space coupled-cluster method and its numerical implementation. A discussion of methods to deal with intruder states is particularly useful. Implementation of the OpenMP and CUDA parallelization in the codes is important as FS-CCSDT computations are very numerically intensive. Furthermore, as new hardware is becoming available (a large number of CPUs per node, large 1-2TB memories, and fast hardware storage-RAM interfaces), codes must be designed to use such resources for the full realization of theoretical method capabilities.

Chapter 2 presents the development of the FS-CCSDT with either full or partial inclusion of triple excitations. The inclusion of triples excitations is a very complicated and challenging endeavor. This work presents the first full inclusion of triple excitations in relativistic FS-CC method capable of treating both atoms and molecules. I find a detailed investigation of different approaches to the partial treatment of the triple excitation particularly interesting. The inclusion of triples is very computationally demanding, and it is important to understand the advantages and limitations of various restrictions. Limiting the number of computed triple excitations rather than restricting either the number of included diagrams or limiting summations in diagrams by some criteria is particularly interesting. Computations are carried out for Tl, Pb, and TlH molecules. Excellent agreement with the experiment is demonstrated for the FS-CCSDT method, with an improvement shown for low-lying levels over other published theory results.

Chapter 3 considers an extension of the work for higher sectors of space, with results presented for the 0h3p sector. The results are compared with the FCI calculations to test the method on the examples of N, N+, N^{2+}, and CH. Results of full-scale computations are compared with experiments for CH, La, La+, and La^{2+}. A drastic improvement in the results is demonstrated with the inclusion of SDT/SBas compared to CCSD/LBas computations for La. It would have been very interesting to see results for La and its ions for states that include 4f electrons. Much larger differences with experiment for such states were found with the CI+LCCSD method in Phys. Rev. A 91, 022504 (2015), possibly resulting from omitting triples in constructing the effective Hamiltonian.

Chapter 4 presents applications of the finite-field (FF) scheme to the computation of non-diagonal matrix elements. The results are presented and discussed for the potential energy curves of RbCs and KCs, transition dipole moment functions of RbCs, and hyperfine matrix elements of KCs. The estimated accuracy of the resulting transition moments is estimated to be a few percent. Such computations are important for designing a laser-cooling scheme for molecules, as it is essential to know line intensities and branching ratios to ensure a closed laser-cooling cycle. This thesis presents the first adaptation of the FF method for computation of magnetic-dipole hyperfine interaction matrix elements.

This is excellent work, and I have only a few comments:

1) Page 23. The first realization of RCC (linearized CCSD) was implemented in 1989, applied to Li and Be^+ in Phys. Rev. A 40, 223, and Cs in 1991. However, this approach was restricted to monovalent atoms.

2) It would have been useful to have more information about the model space considered in various examples. Further details of computation with pseudopotentials would also be useful (page 38), in particular procedures for calculations of triples in this case.

3) Page 65, Table 2.3, and other tables when compared with FCI. For comparison purposes, it would be useful to state if FCI is complete for this basis, i.e., if all possible excitations have been allowed or if some restrictions were made.

4) Page 67. Ref. [146] for Pb used CI+LCCSD method, not CI+PT.

5) With such detailed consideration of triples excitations, it would have been interesting to also separate contributions of non-linear terms, such as {TT} and higher in Eq. (1.12). Significant cancellations of linear triple terms and non-liner SD terms have been demonstrated in atoms, and the size of non-linear triple contributions is unknown.

These comments are minor and do not affect my very high evaluation of this thesis.

Диссертация Олейниченко Александра Витальевича на тему: «Развитие релятивистского метода связанных кластеров для электронных состояний молекул с несколькими открытыми оболочками» соответствует основным требованиям, установленным Приказом от 01.09.2016 № 6821/1 «О порядке присуждения ученых степеней в Санкт-Петербургском государственном университете», соискатель Олейниченко Александр Витальевич заслуживает присуждения ученой степени кандидата физико-математических наук по специальности 1.3.3. Теоретическая физика. Пункты 9 и 11 указанного Порядка диссертантом не нарушены.

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30.10.2021