Precision calculations of atoms with few valence electrons

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The reliable and accurate ab initio methods for atomic calculations are necessary not only for atomic physics itself, but also for application of atomic physics to the investigation of the fundamental interactions. Few years ago the CI+MBPT method was formulated, in which the configuration interaction (CI) calculation for valence electrons is done with the effective Hamiltonian. This Hamiltonian accounts for such effects as core polarization and the screening of the two-electron interaction between valence electrons. It is formed within the Brillouin-Wigner variant of the many-body perturbation theory (MBPT) [1]. In practice most of the calculations were done within the second order MBPT. We used CI+MBPT method for calculations of many atoms with up to 4 valence electrons and with Z from 12 to 82. A full list of references can be found in [2].

The method has several important limitations:
1. The number of valence electrons should not be large. The accuracy of the CI method rapidly decreases when this number exceeds 3 or 4.
2. Only the lower part of the valence spectrum can be described accurately. For the energies above the excitation energy of the core the effective Hamiltonian has poles and results of the CI+MBPT method become unreliable.
3. The accuracy of the calculations is limited because the effective Hamiltonian does not account for the high order core-valence correlations. With the second order effective Hamiltonian the typical accuracy for the transition frequencies is of the order of a percent.

The first two limitations are intrinsic to the method. In order to address the third limitation one has to go beyond the second order MBPT. One obvious way to take is the order-by-order approach. However, it is known that for atoms with one valence electron the third order calculations are often even less accurate than the second order ones. Besides, for atoms with more than one valence electron the third order is already too complicated for practical use. And finally, the convergence of the MBPT series has not been proven.

The arguments given above lead us to one of the variants of the all-order methods. The coupled-cluster method is one of the most widely used. It gives the nonlinear system of equations for cluster amplitudes. In order to truncate this system it is often restricted to the single and double (SD) excitations. The linearized version of the couple-cluster equations in the SD-approximation are also known as pair equations. They were used earlier for the calculations of the atoms with one valence electron and [3] proved to be significantly more accurate than the second order MBPT.

In order to use the pair equation method for the effective Hamiltonian, we developed the Brillouin-Wigner variant of these equations and added equations for the two-electron amplitudes, which were absent in the one-electron atoms. That allowed us to form the effective Hamiltonian for valence electrons in SD-approximation. The first calculations within this CI+SD method for Mg showed that high order corrections were of the order of a fraction of a percent.

References

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