A new two-step Uncontracted Determinantal SO-CI method

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The main question about SO-CI methods is the leadership between electrostatic and magnetic interactions. If the spin-orbit interaction can be considered as a perturbation compared to the electronic correlation contributions, it is well founded to treat it after the CI process. This is generally the case for light atoms for which a "two-step" method, where the spin-orbit coupling is handled after the CI process in a scalar relativistic approximation with usual efficient CI codes, is naturally well adapted and gives accurate results. The question of the leading contribution (electrostatic or magnetic) can be eluded with a simultaneous treatment of electronic correlation and spin-orbit coupling, defining here a "one-step" method. When spin-orbit terms are included in the Hamiltonian, we have to deal with a Double Group Configuration Interaction (DGCI) process, with in general a complex representation of the Hamiltonian on the basis of determinants or double group adapted functions. The breakdown of the non relativistic symmetries in the CI process makes high correlated treatments very difficult and expensive, increasing the limitations of such methods.

We propose a new SO-CI treatment taking advantage of both "two-step" and "one-step" methods. We keep the "two-step" efficiency for correlation, where usual sophisticated configuration interaction calculations are carried out in the first step, within a scalar relativistic approximation. The energies of these high correlated states are then used in the second step, in a Bloch-type effective Hamiltonian. In the second step, unlike the usual "two-step" methods using a contracted wavefunction, we propose an uncontracted treatment taking into account the repolarisation of the correlated wavefunction by the spin-orbit operator, which is the main characteristic of "one-step" methods. The most important feature of this approach being the inclusion of polarisation effects, all the excited configurations which have a non-zero spin-orbit interaction with a pre-defined small set of generators are created. The main contributions are kept for a diagonalisation procedure, and the remaining configurations can be treated up to the second order of perturbation.

Atomic and molecular tests calculations involving heavy atoms are presented, and compared with usual SO-CI treatments.