

## Spin-Orbit calculations from Spin-Free RASSCF wave functions

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A method is presented, which makes it possible to compute eigenstates of a two-component relativistic Hamiltonian, using spin-free scalar relativistic Restricted Active Space (RAS) SCF wave functions as a basis set. The spin-free basis can comprise hundreds of wave functions, and they may use individually optimized orbital sets. The Hamiltonian matrix is computed by an extension of the Restricted Active Space Interaction (RASSI) method, combined with the Wigner-Eckart theorem. Matrix elements of other operators, over the original basis as well as over the eigenstates, are then computed to give e.g. transition strengths or fluorescence life times.

A computer code has been written, as part of the MOLCAS-5 quantum chemistry package. In this implementation, we use the Douglas-Kroll scalar relativistic Hamiltonian combined with Atomic Mean Field Integrals (AMFI). Tests for atoms and molecules covering the entire periodic system shows that accurate results are obtained. Errors in computed spin-orbit effects on relative energies are normally only a few percent.

**Reference:** P. Å. Malmqvist, B. O. Roos, B. Schimmelpfennig, *The Restricted Active Space (RAS) State Interaction Approach with Spin-Orbit Coupling*, submitted to Chem. Phys Letters.