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Developments for a Relativistic Four-Component Many-1/2-Fermion Theory BENJAMIN SIMMEN, ETH - Zürich, EDIT MÁTYUS, ELTE - Budapest, MARKUS REIHER, ETH - Zürich — Explicitly correlated configuration interaction methods have proven to be highly successful in the study of non-relativistic many-electron systems. They are also suited for pre-Born–Oppenheimer calculations where nuclei and electrons are treated on equal footing. Relativistic quantum chemistry is based on the no-pair approximation and provides a four-component Hamiltonian capturing the essential aspects of special relativity for molecular systems. Two fundamental issues arise when aiming at four-component pre-Born–Oppenheimer calculations. The concept of a center of mass cannot be exploited for the Dirac–Coulomb Hamiltonian: It is not possible to separate the overall motion of the system through a linear transformation of the one-particle Cartesian coordinates [1]. Second, a finite number of basis functions leads to an artificial decrease of the bound state energies since the Dirac–Coulomb Hamiltonian is not bounded from below [2]. Kinetic balance solves this for Slater determinants, but its explicitly correlated variant is considerably more involved.

[1] B. Simmen, E. Mátyus, M. Reiher; Mol. Phys. 111; 2086 (2013)
[2] B. Simmen, M. Reiher; In: Many-Electron Approaches in Physics, Chemistry and Mathematics; Eds.: V. Blum, L. Delle Site; Springer (in press); (2014)

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