Relativistic Many-Body Electronic Structure Theory: Approaching the Limit of Dirac Equation

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The fully correlated frequency-independent Dirac-Coulomb-Breit Hamiltonian provides the most accurate description of electron-electron interaction before going to a genuine relativistic quantum electrodynamics theory of many-electron systems. We introduced a Pauli quaternion representation with an optimal spin- and component-separation algorithm that results in a minimal floating-point count algorithm for building the Dirac-Coulomb-Breit Hamiltonian (Fig. 1).[1, 2] The reduced computational cost of the four-component density-integral contraction allows for the development of fully correlated Dirac-Coulomb-Breit many-body methods. In this talk, we introduce the fully correlated Dirac-Coulomb-Breit many-body theory in the variational 4-component multiconfigurational self-consistent-field (4C-MCSCF) framework.[3] We will place a special emphasis on the importance of positive-negative-energy orbital rotation in the 4C-MCSCF procedure and the contribution of the Breit correlation beyond the Dirac-Coulomb operator. A distributed active space (DAS) computational framework is developed to support the massive parallelization of 4C-MCSCF that allows for approaching the theoretical limit of the Dirac many-body theory.

$$g^{\text{Breit}} = g^{\text{Coulomb}} + \frac{1}{2}g^{\text{Gaunt}} + \frac{1}{2}g^{\text{gauge}}$$
$$= \frac{1}{r_{12}} - \frac{1}{2}\left(\frac{\boldsymbol{\alpha}_i \cdot \boldsymbol{\alpha}_j}{r_{ij}} + \frac{\boldsymbol{\alpha}_i \cdot \mathbf{r}_{ij}\boldsymbol{\alpha}_j \cdot \mathbf{r}_{ij}}{r_{ij}^3}\right)$$

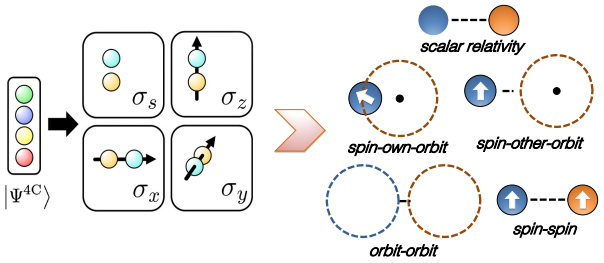

Figure 1: Relativistic two-electron operators can be separated into spin- and orbit-couplings using the Pauli quaternion representation.

[1] S. Sun, T. F. Stetina, T. Zhang, H. Hu, E. F. Valeev, Q. Sun and X. Li, "Efficient Four-Component Dirac–Coulomb–Gaunt Hartree–Fock in the Pauli Spinor Representation", *Journal of Chemical Theory and Computation*, **2021**, *17*, 3388–3402.

[2] S. Sun, J. N. Ehrman, Q. Sun and X. Li, "Efficient Evaluation of the Breit Operator in the Pauli Spinor Basis", *Journal of Chemical Physics*, **2022**, *157*, 064112.

[3] C. E. Hoyer, L. Lu, H. Hu, K. D. Shumilov, S. Sun, S. Knecht and X. Li, "Correlated Dirac–Coulomb–Breit Multiconfigurational Self-Consistent-Field Methods", *Journal of Chemical Physics*, **2023**, *158*, 044101.