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Local Relativistic Exact Decoupling

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We present a systematic hierarchy of approximations for {\it local} exact-decoupling of four-component quantum chemical Hamiltonians based on the Dirac equation. Our ansatz reaches beyond the trivial local approximation that is based on a unitary transformation of only the atomic block-diagonal part of the Hamiltonian. Systematically, off-diagonal Hamiltonian matrix blocks can be subjected to a unitary transformation to yield relativistically corrected matrix elements. The full hierarchy is investigated with respect to the accuracy reached for the electronic energy and molecular properties on a balanced test molecule set that comprises molecules with heavy elements in different bonding situations. Our atomic (local) assembly of the unitary transformation needed for exact decoupling provides an excellent local approximation for any relativistic exact-decoupling approach. Its order-N^2 scaling can be further reduced to linear scaling by employing the neighboring-atomic-blocks approximation. Therefore, it is an efficient relativistic method perfectly well suited for relativistic calculations on large molecules. If a large molecule contains many light atoms (typically hydrogen atoms), the computational costs can be further reduced by employing a well-defined non-relativistic approximation for these light atoms without significant loss of accuracy.

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