

# Nuclear-Electronic Hartree–Fock Density Matrix Renormalization Group

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We introduced the Nuclear-Electronic Hartree–Fock Density Matrix Renormalization Group (NEHF-DMRG) method, designed to solve the molecular time-independent Schrödinger equation without relying on the Born–Oppenheimer approximation. By considering nuclei and electrons equally, NEHF-DMRG accurately accounts for nuclear quantum, anharmonic, and non-adiabatic effects. The convergence of NEHF is always slower than its electronic counterpart. We addressed this problem by developing a comprehensive framework for exact and approximate Newton self-consistent field (SCF) orbital optimization, utilizing concepts from differential geometry. This framework can be applied to both nuclear-electronic and electronic calculations. We have expanded the Augmented Roothaan–Hall (ARH) algorithm for unrestricted electronic and nuclear-electronic calculations, and we showed that the method offers an optimal balance between stability and computational cost for SCF problems with challenging convergence characteristics. In electronic cases, we exhibit ARH’s ability to overcome slow orbital convergence in highly-correlated molecules, as illustrated by various iron-sulfur clusters. The ARH algorithm substantially improves convergence even in small molecules for nuclear-electronic calculations, as evidenced by a series of protonated water clusters.

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