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Natural orbitals for electrons and nuclei within the diatomic multiconfiguration time-dependent Hartree-Fock (MCTDHF) method
DANIEL HAXTON, KEITH LAWLER, C. WILLIAM MCCURDY, Lawrence Berkeley National Lab, Chemical Sciences — We discuss natural orbitals in the context of the MCTDHF method for ultrafast dynamics of diatomic molecules with nuclear motion. We show that the natural orbitals for electrons and nuclei, as well as the eigenfunctions of other reduced density operators which could be called natural wavefunctions, are a useful tool for visualization, similar in some respects to a diabatic basis. Furthermore through the Schmidt decomposition, these objects provide the most compact representation of a wavefunction with interacting degrees of freedom. The natural wavefunction electronic state basis is an alternative to the (dressed) Born-Oppenheimer representation and we show the Schmidt decompositions of various diatomic MCTDHF wavefunctions in short laser pulses. We compare the Schmidt decomposition of H_2^+ in prolate spheroidal coordinates (which are parametric) against that in nonparametric coordinates (e.g. cartesian or cylindrical) and discuss the implications for the multielectron problem. These bases may provide an advantageous numerical framework and we outline implementations of various schemes for propagating natural orbitals within our diatomic MCTDHF code.

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