Necessary N-representability constraints from time-reversal symmetry for extended systems

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Abstract

The variational two-electron reduced density matrix method is formulated for systems with periodic boundaries. We derive the structure of approximate N-representability constraints based on 2-positivity for systems with translational symmetry and time-reversal symmetry. The enforcement of time-reversal symmetry augments the normal 2-positivity constraints with equalities between Kramers pairs of one- and two-particle density matrices when treating systems built from crystalline orbital theory. The extra constraints naturally arise for complex valued Hamiltonians in a momentum-space basis because spin-symmetry adapting no longer implicitly preserves time-reversal symmetry. The necessity of the extra equality constraints to accurately capture the ground state energy and occupation numbers of strongly correlated systems is demonstrated through an examination of the binding curves for an infinite Hydrogen chain and infinite Lithium Hydride chain with and without the time-reversal equality constraints.