Challenges for variational reduced-density-matrix theory: Total angular momentum constraints

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The variational two-electron reduced density matrix (v2RDM) method is generalized for the description of total angular momentum (J) and projection of total angular momentum (M_J) states in atomic systems described by non-relativistic Hamiltonians, and it is shown that the approach exhibits serious deficiencies. Under ensemble N-representability constraints, v2RDM theory fails to retain the appropriate degeneracies among various J states for fixed spin (S) and orbital angular momentum (L), and, for fixed L, S, and J, the manifold of M_J states are not necessarily degenerate. Moreover, a substantial energy error is observed for a system for which the two-electron reduced density matrix is exactly ensemble N-representable; in this case, the error stems from violations in pure-state N-representability conditions. Unfortunately, such violations do not appear to be good indicators of the reliability of energies from v2RDM theory in general. Several states are identified for which energy errors are near zero and yet pure-state conditions are clearly violated.