LASSI singles and the model space selection problem in multireference quantum chemistry

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Multireference quantum chemistry is infamously bedeviled by the "active space selection problem": how is one to construct an orbital subspace in which to directly diagonalize the molecular Hamiltonian that 1) encompasses the relevant degrees of freedom for the process under investigation 2) in a small enough subspace that Hamiltonian diagonalization is tractable 3) without undermining the predictive quality of the results by problem-specific fine tuning? One tactic to make larger active spaces usable is to factorize or decompose the active-space wave function such that direct diagonalization of the molecular Hamiltonian in the Fock space basis is carried out only for small subspaces to generate a model space, followed by diagonalization in the model space basis – an approach which has been explored by multiple groups of workers under names such as cluster mean-field (cMF), active space decomposition (ASD), rank one basis functions, and localized active space (LAS) methods. However, this two-step diagonalization approach does not *solve* the active space selection problem: it *recontextualizes* it as the question of how to split the active space into fragments and how to build the model space from different selections of fragment wave functions – what we call the "model space selection problem." In the context of localized active space state interaction (LASSI) calculations, we systematically explore the model space selection problem by taxonomizing the model states in terms of three critical concepts: "rootspace," a particular distribution of quantum numbers such as charge and spin among the various fragments; the "trial Hamiltonians," the operator whose eigenstates are the many-electron basis functions of a particular fragment in a particular rootspace; and the "excitation number vector," the address of a particular product state in terms of which eigenstate of each fragment appears in it. Using these concepts, we systematically probe the ability of LASSI calculations to reproduce the corresponding CASCI reference wave functions using various candidate model spaces. By studying results for multiple potential energy curves as well as spin-state energy gaps of bi- and tri-metallic compounds, we develop a general "low-order" model space recipe systematically applicable to any LASSCF reference wave function. This so called "LASSI singles" (LASSIS) method does not present the user with any additional "selection" parameters once the underlying LASSCF wave function is constructed, and tends to exhibit qualitative agreement with corresponding CASCI results despite orders of magnitude fewer electronic degrees of freedom.