Generalization of the Non-Redundant Fockian for N>2 electronic systems: Application to Excited States of Be Atom

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A recently developed technique of the non-redundant Fock operator for calculation of excited states of He atom [1,2] has been generalized also for N-electron systems where N>2 [3]. The method generates a set of virtual orbitals that more properly describe electronic excitations than the standard Hartree-Fock orbitals.

Recently, we used this one-electron approach to develop an exponentially-tempered Gaussian basis set scheme (ExTG), which more properly describe atomic excited states than other Gaussian sets. Such a basis set scheme proved particularly suitable for complex scaling calculations, so far being tested on helium Rydberg states, Feshbach resonances [1], and dynamical simulations of the helium atom in strong XUV laser field [2].

Here, the generalized non-redundant Fockian technique has been applied to excited states of Be atom. We compare electronic spectra obtained by employing either the regular or the non-redundant Fockian for generating virtual orbitals. The spectra are calculated at CIS level and for truncated MO space also by FullCI. Several standard quantum chemistry basis sets are compared to the ExTG basis.

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