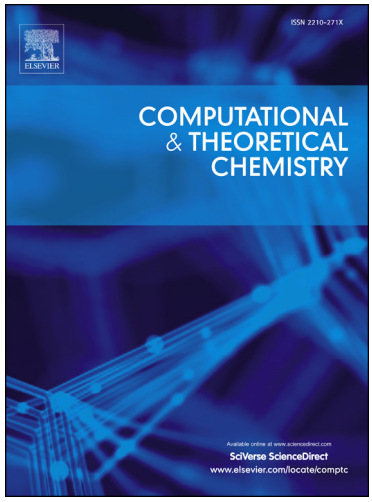

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Spin contamination analogy, Kramers pairs symmetry and spin density representations at the 2-component unrestricted Hartree-Fock level of theory

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Abstract

"Kramers pairs symmetry breaking" is evaluated at the 2-component (2c) Kramers unrestricted and/or general complex Hartree-Fock (GCHF) level of theory, and its analogy with "spin contamination" at the 1-component (1c) unrestricted Hartree-Fock (UHF) level of theory is emphasized. The GCHF "Kramers pairs symmetry breaking" evaluation is using the square of overlaps between the set of occupied spinorbitals with the projected set of Kramers pairs. In the same fashion, overlaps between α and β orbitals are used in the evaluation of "spin contamination" at the UHF level of theory. In this manner, UHF $\hat{S}^2$ expectation value is made formally extended to the GCHF case. The directly evaluated GCHF expectation value of the $\hat{S}^2$ operator is considered for completeness. It is found that the 2c GCHF Kramers pairs symmetry breaking has a very similar extent in comparison to the 1c UHF spin contamination. Thus higher excited states contributions to the 1c so 2c unrestricted wave functions of open shell systems have almost the same extent and physical consequences. Moreover, it is formally shown that a single determinant wave function in the restricted open shell Kramers case has the expectation value of $\hat{K}^2$ operator equal to the negative number of open shell electrons, while the eigenvalue of $\hat{K}^2$ for the series of simple systems (H, He, He*-triplet, Li and Li*-quartet) are found to be equal to minus the square of the number of open shell electrons. The concept of unpaired electron density is extended to the GCHF regime and compared to UHF and restricted open shell Hartree-Fock spin density. The "collinear" and "non-collinear" analogs of spin density at the GCHF level of theory are considered as well. Spin contamination and/or Kramers pairs symmetry breaking, spin

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