Cusp conditions and explicitly correlated wavefunctions

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The electron-electron cusp conditions\(^1,2,3\) suggest that the leading terms of the partial wave expansion of atomic correlation errors scale as \((L+1)^{-3}\) and \((L+1)^{-5}\) for singlet and triplet pairs, respectively. The corresponding \(s\) and \(p\) wave cusp conditions are fulfilled automatically by the use of the rational generator with a permutation operator over electronic positions,\(^4\) and the slow convergence can be overcome as \((L+1)^{-7}\). There has been a rapid development for the last 5 years in F12 explicitly correlated electronic structure theory\(^5\) especially with a short-range correlation factor like the Slater-type geminal.\(^6,7\) Correlation energies of near basis set limit can be obtained by using the CCSD(T)-F12 method with orbital basis sets of triple zeta quality only.\(^8,9\) We will also demonstrate the importance of the spin-flipped geminal basis, which is needed for the exact satisfaction of the cusp conditions\(^10\) for open shell molecules, at the MP2 with UHF references.\(^11\)

\(^{10}\) D. Bokhan, S. Ten-no, J. Noga, 10, 3320 (2008).