MP2-F12 method for open-shell systems with exact satisfaction of cusp conditions

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Most of the orbital based methods in quantum chemistry exhibit painfully slow convergence of correlation energies towards the CBS limit - the corresponding rate of the error is proportional to $(L_{max} + 1)^{-3}$ [1], where L_{max} is the highest angular momentum of the given one-electron basis. This is caused by the fact that the behavior of the wave function in the vicinity of interelectronic coalescence cannot be described well in terms of products of one-particle basis functions. The introduction of linear-r_{12} terms[2] into the expansion of wave functions improves the convergence behavior to $(L_{max} + 1)^{-7}$ [3] due to the more accurate description of the behavior around the coalescence point [4, 5].

Most of the explicitly correlated methods for open-shell systems, previously described in the literature, are formulated with pair functions as products of the F12 factor and occupied spin orbitals as those in the unitary invariant *Ansatz* [6]. Recently we have suggested that the previous *Ansätze* without the use of the rational generator [7] cannot fully satisfy the cusp conditions[7], but it can be circumvented by the inclusion of a spin-flipped geminal basis[8,9].

An inclusion of the spin-flipped geminals into the computational procedure increases
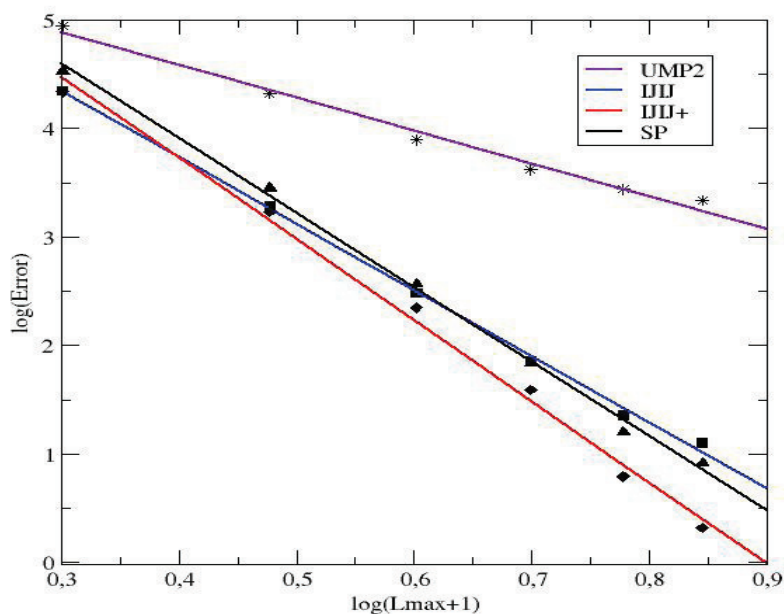

Fig.1. The error in the second-order correlation energy as a function of maximum angular momentum.

the convergence rate for correlation energies. In order to inspect the convergence rate of the correlation energies for *SP, IJIJ* and *IJIJ+ Ansätze* UMP2-F12 correlation energies of N atom was calculated, using the subsets of the near saturated 20s14p11d9f7g5h3i basis [10]. The results are presented in Fig.1.

The atomization energies of a set of 16 molecules were also calculated to assess the effect of spin-flipped geminals. A statistical analysis of errors has shown that the presence becomes more prominent with more extensive basis set. The corresponding error distribution functions are shown in Fig.2.
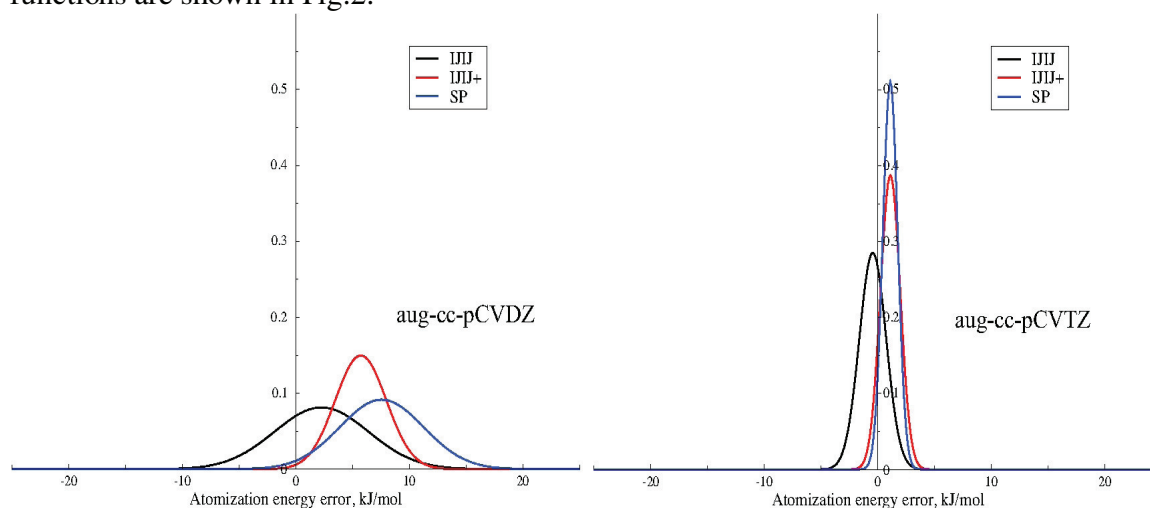

Fig. 2. Normal distribution functions of the the atomization energy errors

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