Analysis of relativistic effects by using the difference of density matrices

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The sizes of systems calculated by molecular orbital (MO) theories are becoming huge with the development of computation power and algorithms. To compare between a system with huge numbers of orbitals and another similar reference system is difficult, because it is practically impossible to use the conventional MO-analysis scheme that investigates the subtle difference between two sets of orbitals. To overcome this situation, previously, we proposed analysis methods that use natural orbitals (NOs) of the difference density matrix between a target system and a reference system, which may have different numbers of electrons and basis-sets [1].

In this paper, we focus on relativistic effects and analyze detailed changes in the electronic states due to them. By using our method, we compare relativistic results calculated by such as Dirac–Fock method with non-relativistic one.

[1] D. Yamaki, Mol. Phys. **113**, 342 (2015). (DOI: http://dx.doi.org/10.1080/00268976.2014.951702)