# Analysis method using natural orbitals of the difference density matrix for comparison of two similar molecules: application to molecular interactions

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The size of molecules calculated by molecular orbital (MO) theory is becoming huge with the development of computation power and algorithms. To compare between a huge molecule and another similar reference molecule is difficult, because it is practically impossible to use the conventional MO-analysis which investigates the subtle difference between two sets of MOs for huge molecules. To overcome this situation, previously, we proposed an analysis method that uses natural orbitals (NOs) of the difference density matrix between a target molecule and a reference molecule, which may have different numbers of electrons [1]. In this presentation, we show an application of this method to analysis of molecular interactions between the water dimer, as an example. To analyze the change of the electronic state induced by the interactions, we use difference of density matrix between the super molecule consisting of the water molecule dimer (the target molecule) and one of the water molecules (the reference molecule), latter of which is calculated as an isolated molecule (as shown in Figure). Our analysis successfully detected the formation of the hydrogen bond and electron-rearrangements. The non-interacting components of the difference density matrix can be excluded from the analysis by using the eigenvalues for the SCF-derived density matrices. We also discuss applicability of our analysis method to calculation results of the post Hartree-Fock methods.

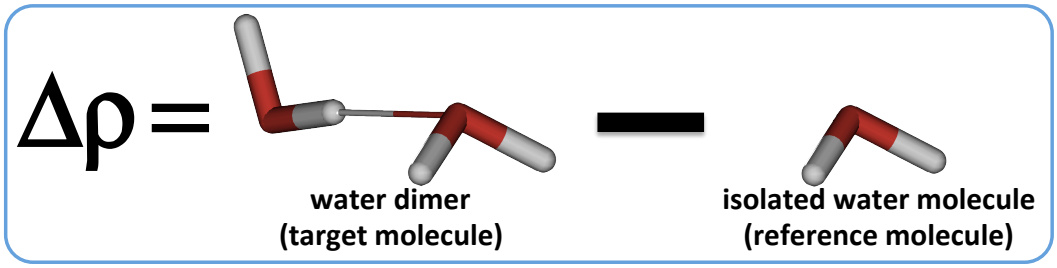


**Figure** **Comparison of a water dimer with the isolated water molecule chosen from the dimer. The change of the electronic states induced by the intermolecular interaction can be extracted.**

[1] D. Yamaki, Mol. Phys., in press. (DOI: http://dx.doi.org/10.1080/00268976.2014.951702)