An analysis method to compare two similar molecules using natural orbitals of the difference density matrix

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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 virtually impossible to use the conventional MO-analysis i.e. investigating the subtle difference between two sets of MOs for huge molecules. To overcome this situation, we propose 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. In this method, non-interacting and inactive NOs can be excluded from the analysis by using the eigenvalues (See Fig. 1). As a simple example, we applied the method to the nitro-substituent effect on the benzene ring, namely, comparison of a nitrobenzene molecule with a benzene molecule. Our analysis successfully detected the inductive and resonance effects of the substituent effects by investigating a few orbital-sets (See Fig. 2).

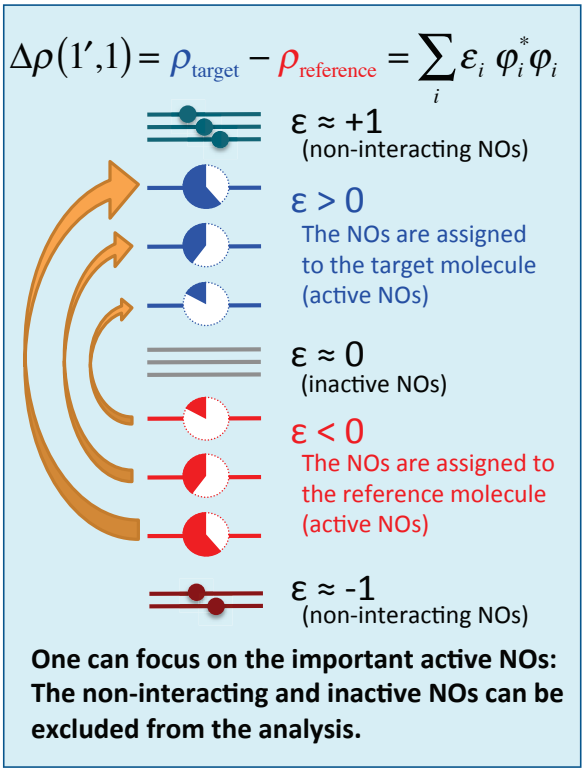

Fig. 1 Eigenvalues (ε) and natural orbitals of the difference density matrix (Δρ)

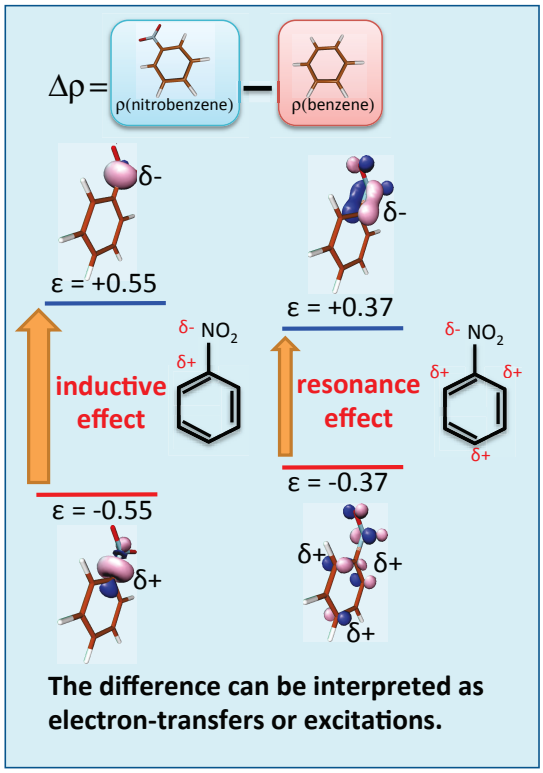

Fig. 2 Analysis of the nitro-substituent effects on the benzene ring