Decomposition of Deformation Density into Orbital Components

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Introduction

The natural orbital picture provided by diagonalization of density matrix is one of the most used methods in the analysis of inter-orbital interactions. The natural orbitals provide optimal orbitals with respect to the convergence of first-order reduced density expansion (Eq. 1).

\[ q = \sum_i n_i |0_i|^2 \]  

(1)

In the above equation, \[ q \], \[ 0_i \] and \[ n_i \] are first-order reduced density, natural orbitals and their corresponding occupancies, respectively. One may consider “density difference” or “deformation density” instead of the electron density. The deformation density is defined as the difference between electron density of the complex and the fragments as Eq. 2.

\[ Oq = q_{\text{complex}} - \sum q_{\text{fragments}}. \]  

(2)

Topological analysis of the deformation density has been found as a powerful tool to detect fine structure of the electronic density distribution [i]. However, it has not yet been investigated in the Hilbert space as orbital picture of the deformation density. In this research, we are going to express the deformation density analogous to Eq. 1 as:

\[ Oq = \sum_{i, o} n_{o,i} |q_{o,i}|^2. \]  

(3)

where the O subscript for \[ 0_i \] and \[ n_i \] distinguishes them from those of Eq. 1

Theory
The molecular orbitals of fragments and the first order reduced density of each
fragment are related to the AOs as Eqs. 4 and 5, respectively:

\[
z_{\text{frag},i} = 0_{\text{frag},i}C_{\text{frag},i} \quad i = 1, 2, \ldots, n
\]  

(4)

\[
q_{\text{frag},i} = O_{\text{frag},i}P_{\text{frag},i}^{0}O^{\dagger}_{\text{frag},i}
\]  

(5)

where \( z \), \( O \), \( C \), \( P \) and \( q \) are canonical molecular orbital matrix, atomic orbitals (AO) matrix, molecular orbital eigenvectors, density matrix and first-order reduced density, respectively. \( \Delta q \) can now be defined as

\[
O q = q_{\text{comp}} - q_{\text{frags}} = OP_{\text{frags}}^{(0)}O^{\dagger} - OP_{\text{comp}}^{(0)}O^{\dagger} = O(P_{\text{frags}}^{(0)} - P_{\text{comp}}^{(0)})O^{\dagger}
\]  

(6)

where \( P_{\text{frags}}^{(0)} \) and \( P_{\text{comp}}^{(0)} \) are density matrices of fragments and complex in the atomic orbitals basis, respectively. Eq. 6 suggests that we could write the deformation density in terms of \( P_{\Phi}^{(0)} \) as:

\[
O q = OP_{O}^{(0)}O^{\dagger}
\]  

(7)

where \( P_{O}^{(0)} \) is introduced as deformation density matrix and is defined as:

\[
P_{O}^{(0)} = P_{\text{comp}}^{(0)} - P_{\text{frags}}^{(0)}
\]  

(8)

At this point, we can introduce deformation natural orbitals (DNO), \( O_{\Phi}^{(0)} \), and their eigenvalue, \( n_{O} \), which can be obtained by diagonalization of the deformation density matrix.

\[
P_{O}^{(0)}S_{\Phi}^{(0)}C_{\Phi}^{(0)}n_{O} = 0
\]  

(12)

\[
0_{O} = 0C_{(0)}^{(0)}
\]  

(13)

where \( S_{\Phi}^{(0)} \) is overlap matrix of the atomic orbitals. The eigenvalues, \( n_{O} \), reflect the
magnitude of displaced charge in the space defined by $0_o$ as Eq. 13.

Numerical Example: Application to CO$_2$ Planar Dimer

There are two important configurations for CO$_2$ dimer: T-shaped (C$_{2v}$ symmetry) and
The molecular geometry have been optimized at MP2/6-311++G** level of theory with the help of Gaussian 03 package, and the SCF density has been used in order to obtain the DNOs. Fig. 1 shows eight of the most important DNOs for CO$_2$ dimer.

References