

## natural orbital

The orbitals defined (P. Lowdin) as the eigenfunctions of the spinless one-particle electron density matrix. For a configuration interaction wave-function constructed from orbitals  $\Phi$ , the electron density function,  $\rho$ , is of the form:

$$\rho = \sum_i \sum_j a_{ij} \Phi_i^* \Phi_j$$

where the coefficients  $a_{ij}$  are a set of numbers which form the density matrix. The NOs reduce the density matrix  $\rho$  to a diagonal form:

$$\rho = \sum_k b_k \Phi_k^* \Phi_k$$

where the coefficients  $b_k$  are occupation numbers of each orbital. The importance of natural orbitals is in the fact that CI expansions based on these orbitals have generally the fastest convergence. If a CI calculation was carried out in terms of an arbitrary basis set and the subsequent diagonalisation of the density matrix  $a_{ij}$  gave the natural orbitals, the same calculation repeated in terms of the natural orbitals thus obtained would lead to the wave-function for which only those configurations built up from natural orbitals with large occupation numbers were important.

**Source:**

PAC, 1999, 71, 1919 (*Glossary of terms used in theoretical organic chemistry*) on page 1954