

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 φ , the electron density function, ρ , is of the form:

$$\rho = \sum_i \sum_j a_{ij} \varphi_i^* \varphi_j$$

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

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

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.

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