natural atomic orbital (NAO)

A valence-shell atomic orbital whose derivation involves diagonalising the localized block of the full density matrix of a given molecule associated with basis functions $\chi_i(A)$ on that atom. A distinguishing feature of NAOs is that they meet the simultaneous requirement of orthonormality and maximum occupancy. For isolated atoms, NAOs coincide with natural orbitals. In a polyatomic molecule the NAOs (in contrast to natural orbitals that become delocalised over all nuclear centres) mostly retain one-centre character, and thus are optimal for describing the molecular electron density around each atomic centre.

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