Introduction

Wave functions for atoms and molecules constructed with modern methods often consist of thousands or more terms and are very difficult to interpret in terms of chemical concepts like orbitals or electron densities. One of the most important tools for analyzing these functions is the density matrix associated with it and subsequently the natural orbitals that are the eigenfunctions of the one-particle density matrix. These natural orbitals take the place of atomic and molecular orbitals when the effects of electron correlation are included in the wave-function. Interestingly the natural orbitals often resemble the atomic and molecular orbitals of the system except that they can have non-integer occupation numbers. The sum of the squares of the natural orbitals weighted by their occupancy is the electron or spin density. The natural orbitals are also very useful in defining and discussing the concept electron correlation. In what follows we will outline the methods of determining the density matrix and after that we will discuss the natural orbitals.