Introduction

The concept of electrons in atoms and molecules being described by an atomic or molecular orbital is a cornerstone of chemistry and physics and its difficult to imagine present day science without this. The basic assumption that gives rise to the orbital concept is that one can approximate the solution to the Schrodinger equation for an atom or molecule with a single determinant, the elements of which are atomic or molecular orbitals which are then determined so that the energy calculated using this determinant is as low as possible. The resulting orbitals satisfy the Hartree-Fock equations which where first written down by Douglas Hartree in 1930 and subsequently modified by Fladimir Fock in 1932 to allow for the in-distinguishability of electrons. While the equations describing atoms where solved numerically by Hartree it was not until 1950 that Clemens Roothaan at the University of Chicago developed a general method that allowed for their solution for both atoms and molecules. While many methods have been developed over the years for obtaining more accurate solutions to the Schrodinger equation virtually all begin by solving the HF equations. In what follows we will first derive the equations for a general single determinant wave function and then specialize them to three important cases. The one is for systems with an even number of electrons in which a given spatial orbital is doubly occupied with an $\alpha \& \beta$ spin function. The next one is the unrestricted open shell case where the system has an odd number of electrons and the orbitals hosting an α electron are different from those hosting a β electron. Finally we will consider the restricted open shell case where some orbitals are doubly occupied as in the closed shell case and some are singly occupied as in the unrestricted case.