Beyond Hartree-Fock

The Hartree-Fock approximation does not include any correlation in the position of electrons with opposite spins and only limited correlation for electrons with same spin (the exchange-correlation, which comes from the anti-symmetrization and results in the Fermi hole). This is because of the single Slater determinant form of the trial function which does not properly take into account the $1/r_{12}$ Coulomb interaction between the electrons. The Hartree-Fock approximation is a mean-field approximation and does not take into account simultaneous position of two or more electrons. It is possible to approach the 'exact' solution, i.e., the solution of the Schrödinger equation with the H^{exact} Hamiltonian, by adding corrections to the Hartree-Fock approximation. Note that this 'exact' solution is still approximate because it involves the non-relativistic approximation and the Born-Oppenheimer approximation.

It is possible to evaluate systematically corrections to the Hartree-Fock approximation to obtain a more accurate solution. This is the *ab initio* approach where no information about chemical bonds is used in the development of the methodology. Two such approaches are described below, the *configuration interaction* method and the *perturbation* method. But, before discussing these, a different approach, the *semi-empirical* approach is first briefly described.

A. Semi-empirical approaches

The Hartree-Fock calculation is based on a mean field approximation in that each electron is only subject to the average influence of the other electrons. This is a crude approximation. The results of such calculations of molecular properties shows that the structure of molecules is, nevertheless, quite well reproduced but the energy of bonds and activation energy of transitions are not in good agreement with experimental measurements or higher level calculations. The frequency of vibrational modes is typically about 10% too high.

There are several approaches to improve on the Hartree-Fock approximation. One is the semi-empirical approach. There, the goal is to both reduce the computational effort and obtain at the same time better agreement with experimental results. The most computationally demanding integrals are approximated by simple expressions that have parameters adjusted by comparison with some set of experimental data. The two electron, four center integrals are particularly demanding with computational effort scaling as the number of basis functions, K, to the fourth power. By approximating these integrals, the semi-empirical methods can be applied to much larger molecules than Hartree-Fock calculations.

When applied to molecules that are similar to the molecules included in the data set that is fitted, the results can be good, often significantly better than Hartree-Fock. But, when applied to molecules that are significantly different from those included in the data set, the results can be worse and even unphysical. It is, therefore, important to know the range of validity of a given semi-empirical approximation. Since the computational effort is smaller than for Hartree-Fock, it can be useful to start a computational study by doing semi-empirical calculations and get a first estimate of the molecular structure, and then turn to more accurate methods. This can save computer time if the structure is not well known and the molecule is within the range of validity for the semi-empirical method. The most commonly used semi-empirical methods are MNDO, AM1 and PM3. Many calculations of large biomolecules are based on semi-empirical approximations because higher level calculations are not feasible.

B. Configuration Interaction

The orbitals generated in the Hartree-Fock procedure can be used to form an infinite number of orthogonal Slater determinants which then form a complete set. When K spatial basis functions are used to expand the orbitals, $2K$ spin-orbitals can be generated. The best estimate of the Hartree-Fock ground state is a single Slater determinant generated from the N spin-orbitals with the lowest energy:

$$|\psi_0 >= |\chi_1\chi_2\cdots\chi_a\chi_b\cdots\chi_N > .$$

It is also possible to form Slater determinants with one or more of the higher energy orbitals, the virtual orbitals. A *singly excited* determinant is one with an electron in a virtual orbital, for example χ_r rather than χ_a:

$$|\psi_a^r >= |\chi_1\chi_2\cdots\chi_r\chi_b\cdots\chi_N >$$

and a *doubly excited* determinant is, similarly:

$$|\psi_{ab}^{rs} >= |\chi_1\chi_2\cdots\chi_r\chi_s\cdots\chi_N > .$$

A total of

$$\binom{2K}{N} = \frac{(2K)!}{N!(2K-N)!}$$

determinants can be formed.

Each determinant is a valid N-electron wave function. Determinants differing by one or more orbital are orthogonal since the orbitals are orthogonal. In the limit of infinite number of basis functions, $K \to \infty$, the set of all these Slater determinants must form a complete set for N-electron wave functions. The exact wave function, Φ, can, therefore, be expanded in this basis set

$$|\Phi >= C_0|\psi_0 > + \sum_r \sum_a C_a^r|\psi_a^r > + \sum_a \sum_{b>a} \sum_r \sum_{s>r} C_{ab}^{rs}|\psi_{ab}^{rs} > + \ldots .$$

The expansion coefficients can be found by carrying out a second variational calculation (the first one being the Hartree-Fock calculation). The first term in this expansion is the Hartree-Fock approximation. Since each term can be thought of as a certain configuration of the electrons over the available orbitals, the procedure is called *configuration interaction (CI)*. In practice, a finite number of basis functions is used and the expansion is truncated to include only finite number of Slater determinants. The term *'full CI'* for a basis set of K functions means that all $\binom{2K}{N}$ determinants are used in the approximation to $|\Phi>$. As the basis set is increased, the variational calculation must give the exact solution, and the linear combination of Slater determinants becomes the 'exact' wave function $|\Phi>$ with energy E_0^{exact}. By definition, the correction to the Hartree-Fock energy is called the *correlation energy*, that is

$$E_{corr} \equiv E_0^{exact} - E_0^{HF}.$$

Even for small molecules, the number of configurations in a CI calculation can easily reach many millions. A great deal of effort has been put into the optimization of numerical algorithms for solving large eigenvalue problems and computational chemists have made a large contribution in that area of research.

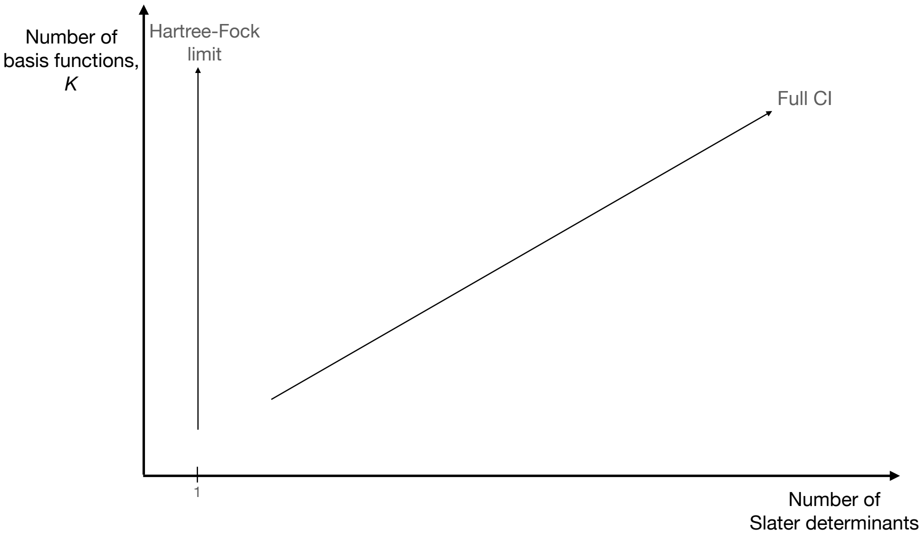

Figure II.4 A diagram illustrating how a calculation of the wave function of a many-electron system converges with respect to the number of basis functions and the number Slater determinants in the configuration interaction calculation, i.e. the level of correlation included in the theoretical method. Only when both the number of basis functions and the number of determinants used in the trial function have reached a sufficient level is convergence reached in the variational calculation. An important aspect of CI calculations is to strike the right balance between basis set and number of Slater determinants.

Except for very small molecules, it is necessary to select just a small subset of the possible Slater determinants in the CI calculation. For example, in CISD approximation, only singly and doubly excited determinants are included. Some of the excited determinants are more important than others. The higher the energy of the determinant, the smaller its contribution is to the ground state solution. Excitations involving the excitation of electrons from HOMO to LUMO are typically most important, while excitations of core electrons are less important and often skipped.

One problem with such truncated CI approximations is that they are not size consistent. That is, by calculating simultaneously two or more replicas of the molecule separated at large distance (so that they do not interact) affects the energy that is obtained per molecule. For example, if a CISD calculation is carried out for a molecule A, then an analogous calculation at the same level of theory for two molecules, 2A, would require quadruple excitations in the CI expansion. Even if the two A molecules are far apart and not interacting, the calculation of 2A would not give an energy corresponding to twice the energy of a single A. Since calculations of binding energy of fragments is an important task in computational chemistry, this is a serious drawback. Approximate schemes have been devised to recover size consistency. One such scheme is QCISD. A frequently used, rather high level aproximation is QCISD(T) where some of the triplet excitations have also been included. The computational effort of such calculations scales as K^7 and is therefore limited to small molecules.

The two variational calculations, the one involved in the Hartree-Fock approximation and the one involved in the CI calculation, can be combined in one variational calculation. The coefficients in the expansion of the orbitals in the basis set are then affected by the higher energy determinants. This can help reduce the number of terms in the CI expansion. This approach is referred to as multi-configuration self-consistent field method (MCSCF). A variant of this approach is the complete active-space SCF method (CASSCF) method where a certain set of occupied and virtual orbitals is labeled as 'active' and all configurations of excitations within the set of these active orbitals is included in the expansion.