Post Hartree-Fock: A. Configuration Interaction

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 antisymmetrization). This is because of the single Slater determinant form of the trial function which does not properly take into account the full effect of the $1/r_{12}$ Coulomb interaction between the electrons. The Hartree-Fock approximation is a mean-field approximation and does not involve knowledge of the 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 *Quantum Chemistry.* Note that no information about chemical bonds is used in the development of the methodology and as a result it is often referred to as *ab initio.* Two such approaches are commonly used, the *configuration interaction* method and the *perturbation* method.

A. 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 in the expansion of the orbitals, $2K$ spin-orbitals can be generated. The best estimate of the ground state when only a single Slater determinant is generated from the N spin-orbitals is the one giving the lowest energy

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

This is the Hartree-Fock approximation. But, it is also possible to form Slater determinants by including one or more of the higher energy orbitals generated by solving the Hartree-Fock equations, the virtual orbitals. A *singly excited* determinant has one electron removed from an occupied orbital to 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 in this way.

Each of these Slater determinants 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 representation of $|\Phi>$. 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. Note that if the basis set is small, a full CI calculation can be far from reaching the exact wave function. Only when both the number of basis functions and the number of determinants have reached a sufficient level can convergence to E_0^{exact} be reached in the CI calculation. An important aspect of practical CI calculations is to strike the right balance between the basis set and the number of Slater determinants.

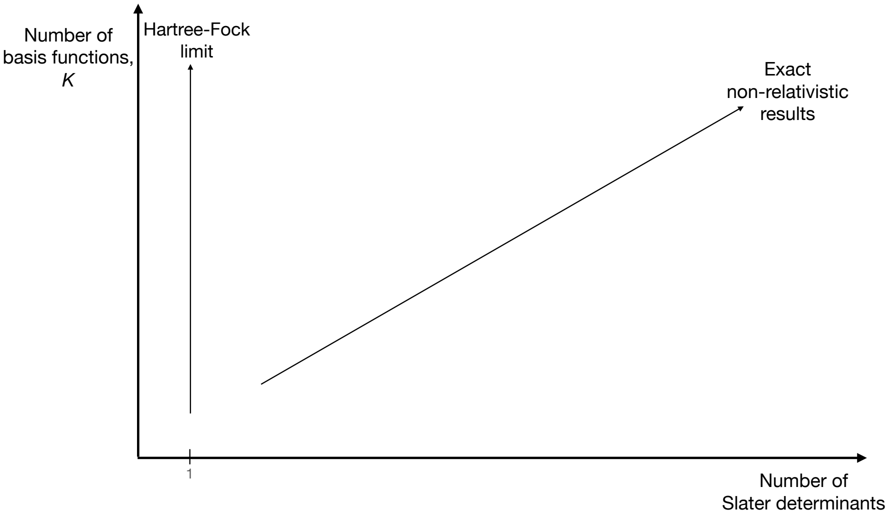

Figure 6. A diagram illustrating how a calculation of the wave function of a many-electron system converges with respect to the number of basis functions and the number Slater determinants in a CI calculation, i.e. the level of correlation included in the theoretical method.

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 in general 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 per molecule that is obtained. 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 the 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 approximation 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.