*These are lectures from the previous part, part one of the course unit (computational chemistry I)*

## The MCSCF Method

It is possible to work with a truncated $CI$ expansion of the wavefunction and try to compensate for the truncation by obtaining not only the variationally optimal $CI$ coefficients ( $C_I$s of equation $12-19$ ) but also the variationally best set of spin orbitals $\{\phi_i s\}$ appearing in the different $CSF$ consistent with the truncated $CI$ wave function. This approach has been known as the multiconfigurational self consistent field method (MCSCF).

The simultaneous optimization of $\{C_I s\}$ and $\{\phi_{is}\}$ leads to two sets of equations

$$HC = \varepsilon 1.C$$

$$V = S\alpha\lambda$$

where the MOs are expressed as linear combinations of the atomic orbitals (AOs)

$$(\phi_1 \ldots\ldots\ldots \phi_m) = (\chi_1 \ldots\ldots \chi_n)\alpha$$

$\lambda$ is the matrix of Lagrange multiplier, $S$ the AO overlap matrix. The matrix of the MCSCF operator in AO × MO basis is represented by $V$ where

$$V = h(1)\alpha P^1 + Z(1,2) = S\alpha\lambda$$

$Z(1,2)$ contains two-electron interactions

$$Z_{pi} = \sum_{jkl}\sum_{qrs} \alpha^{\dagger}_{jp} \langle \chi_p \chi_q | \chi_r \chi_s \rangle \alpha_{rk} \alpha_{sl} P^2_{kl,ij}$$

$P^2$ stands for the two-electron density matrix in the MO basis. The two equations are to be solved in tandem for the CI coefficients $(C_I s)$ and orbital coefficients $(\alpha_k s)$ till self-consistency is achieved. The convergence of the iterative procedure can pose problem. The methods of steepest descent, conjugate gradient, etc. have been used to handle the problem of convergence. The difficulties arise whenever the coupling between the CI coefficients $(C_I s)$ and the orbital expansion coefficients $\left(\alpha_k s\right)$ is strong.

The simultaneous variational optimization of the $C_I$ s and $\{\phi_i\}$ s required in the MCSCF description is now-a-days carried out by expanding energy to the second order in the Molecular orbital and $CI$ coefficients and invoking Newton-Raphson or NR-like methods to force the iterations to converge (For other option, see, Self consistent field method: Theory and Applications, Ed. R. Carbo & M. Klobukowski).

The basic problem with the *MCSCF* methods lies in selecting the appropriate configurations for the particular problem of interest. The most popular method has been to partition the MOs into active and inactive spaces. The MOs in the active space come from the topmost (the $n$ th) doubly occupied MO (HOMO) down to say, $m'$ lower doubly occupied MOs (HOMO-1, HOMO-2 - - - HOMO-$m$) and the lowest unoccupied ($n+1$)th MO and up to the $m'$ unoccupied MOs (LUMO, LUMO+1, - - - LUMO+$m'$). The corresponding MCSCF is generally called the CASSCF method. Even with a small active space ($m$, $m'$ are small) the CASSCF becomes unmanageably large. That forces one to repartition the active space further into restrictive spaces (RAS1, RAS2 and RAS3). The RSA3 space is spanned by MOs that are unoccupied in the HF determinant, RAS2 space is spanned by the highest occupied MO and $m$ lower ones along with the lowest unoccupied MO and the $m'$ higher ones. All possible excitations in this space are allowed. The RSA1 space is spanned by some of the doubly occupied orbitals in the HF determinant not accomodated in the RSA2 space. These orbitals are allowed to be either singly or doubly excited into the RAS3 space orbital or are left to remain unexcited.

The selection of the active space for an MCSCF calculation requires exercise of caution and analysis. It is necessary to select the important orbitals. The HOMO and LUMO are the obvious choices. The choice of the other orbitals in the active space based on the orbital energy orders may run into problems when extended basis sets are used where there could be many virtual orbitals with low energies. The RHF energies of the orbitals in the virtual space are more akin to the occupied orbital energies of the anion and such orbitals may not be suitable for inducing correlation correction. In situations where the actual ground state wave function has significant contributions from more than one CSF, RHF ground state wave function may not be the correct wave function to start with. It is advisable in such situation to perform a small scale

CISD calculation, ascertain the occupation numbers of the natural orbitals. Only the orbitals with significantly large occupation numbers may be incorporated in the active space.

We may note here that in the $CI$ methods described so far, we have considered CSFs that are generated by exciting electrons from a single determinant. That means, we have so far used the HF - wave function as the reference. However, an MCSCF wave function can also be chosen as the reference wave function, leading to what has become known as MRCI method. In that case, a CISD would, for example, involve excitations of one or two electrons out of all the determinants used in the MCSCF reference wave function. The number of CSFs increases by a factor of `$n'$ where `$n'$ is the number of determinants in the multiconfiguatation reference wave-function, which quickly leads to a computational bottleneck for all but small molecules. One can resort to having a control on the configuration to be selected in the MR-CI expansion by choosing a cut-off level of interaction among the reference $(n)$ configuration and the configurations created by excitations from the reference determinants. However, such a prescription may create difficulties in case one is interested in computing the PES. A single cut-off value may not work for different regions of the PES, as the same configurations may come closer in one region and move away from other in another region of PE surface.