#### **Configuration Interaction**

One of the most direct approaches to determine  $\psi$  is to use the configuration interaction method in which one writes the exact wavefunction as a linear combination of determinants formed from the HF determinant by systematically replacing the occupied orbitals in  $\psi_{HF}$  by the virtual orbitals. For example if the occupied orbitals are

$$\varphi_1, \varphi_2, \varphi_3, \dots \varphi_n$$

with the associated Hartree-Fock wavefunction

$$\psi_{HF} = \mathcal{A}\varphi_1\varphi_2\varphi_3...\varphi_n$$

and if one has *m* virtual orbitals

$$\varphi_{n+1}, \varphi_{n+2}, \varphi_{n+3}, \dots \varphi_{n+m}$$

one may form singly excited determinants by replacing one of the occupied orbitals, say the ith by one of the virtuals, say the  $\mu$ th

$$\phi_i^{\mu} = \mathcal{A}\varphi_1\varphi_2 \dots \varphi_{i-1}\varphi_{\mu}\varphi_{i+1}\dots \varphi_n$$

Continuing in this spirit one may replace two occupied by two virtual

$$\phi_{ij}^{\mu\nu} = \mathcal{A}\varphi_1\varphi_2 \dots \varphi_{i-1}\varphi_{\mu}\varphi_{i+1}\dots\varphi_{j-1}\varphi_{\nu}\varphi_{j+1}\dots \varphi_n$$

and so on. One then writes the exact wavefunction as the sum of the Hartree-Fock function, all single excitations, all doubles, all triples, etc. Clearly since there are only n occupied orbitals we can have no more than n fold excitations. Note that even though one has a finite number of classes of excitation one can have a very large number of determinants in each class, especially if the number of virtual orbitals is large). A very good approximation to the exact wavefunction is then

$$\psi = c_0 \psi_{HF} + \Phi^{(1)} + \Phi^{(2)} + \dots + \Phi^{(m)}$$

where

$$\Phi^{(1)} = \sum_{i=1}^{n} \sum_{\mu=1}^{m} C_i^{\mu} \phi_i^{\mu} \quad \text{(single excitations)}$$

J. F. Harrison

$$\Phi^{(2)} = \sum_{i=1}^{n} \sum_{j=i+1}^{n} \sum_{\mu=1}^{m} \sum_{\nu=\mu+1}^{m} C_{ij}^{\mu\nu} \phi_{ij}^{\mu\nu} \text{ (double excitations)}$$

$$\Phi^{(m)} = \sum_{i=1}^{n} \sum_{j=i+1}^{n} \dots \sum_{\mu=1}^{m} \sum_{\nu=\mu+1}^{m} \dots C_{ij\dots k}^{\mu\nu\dots\lambda} \phi_{ij\dots k}^{\mu\nu\dots\lambda} \quad (m \text{ fold excitations})$$

The coefficients  $C_{ij...k}^{\mu\nu...\lambda}$  are determined by the Variation Method. For example if we write  $\psi = \sum_{i=1}^{N} a_i \chi_i$  where  $a_i \equiv C_{ij...k}^{\mu\nu...\lambda}$  and  $\chi_i \equiv \phi_{ij...k}^{\mu\nu...\lambda}$  where *N* equals the total number of determinants in the expansion we may determine the coefficients  $a_i$  as follows.

The total energy of the system is given by  $E = \frac{\langle \psi | \hat{H} | \psi \rangle}{\langle \psi | \psi \rangle}$  where

$$\langle \psi | \hat{H} | \psi \rangle = \sum_{i=1}^{N} \sum_{j=1}^{N} a_i a_j H_{ij}$$
 and  $\langle \psi | \psi \rangle = \sum_{i=1}^{N} a_i^2$  where  $H_{ij} = \langle \chi_i | \hat{H} | \chi_j \rangle$  and we have noted

that since the determinants  $\chi_i$  are built with orthonormal molecular orbitals the overlap integral  $\langle \chi_i | \chi_j \rangle = \delta_{ij}$ . Since the Hamiltonian matrix  $H_{ij}$  is known once one has the molecular orbitals, the energy is a function of the expansion coefficients,  $E = E(a_1, a_2, \dots, a_N)$ . Differentiating with respect to  $a_k$  results in the *N* equations  $\sum_{i=1}^{N} H_{ki}a_i = Ea_k$ ;  $k = 1, 2, \dots, N$  which in matrix form are  $H\vec{a} = E\vec{a}$ . Solving for the coefficients  $a_k$  is then equivalent to diagonalizing the Hamiltonian matrix. The lowest eigenvalue is the energy and the corresponding eigenvector contains the coefficients. There are many other approaches to the problem of "going beyond Hartree-Fock" and we

will discuss them latter. All of these methods use the language of Configuration Interaction in that they speak of single excitations, double excitations, etc.

#### Size of the Hamiltonian Matrix

The number of determinants in a CI calculation and thus the dimensions of the Hamiltonian matrix can be computed as follows. If there are *n* electrons and *m* virtual orbitals we have *nm* single excitations,  $\binom{n}{2}\binom{m}{2}$  double excitations,  $\binom{n}{3}\binom{m}{3}$  triple excitations, etc. The total number is then  $\sum_{k=0}^{n}\binom{n}{k}\binom{m}{k}$ . Another way of looking at this is to ask how many ways can one distribute *n* electrons among *n*+*m* orbitals. The answer is

$$\binom{n+m}{n}$$
 so  $\sum_{k=0}^{n} \binom{n}{k} \binom{m}{k} = \binom{n+m}{n}$ 

Consider for example a calculation on  $CH_2$  in a 6-311g\*\* basis. In this calculation the number of basis functions is 48, and since n=8, we have m=40 so the number of

determinants is  $\binom{48}{8} = \frac{48!}{8!40!} \approx 2.4 \times 10^9$ , a very large number for a very modest basis set.

Hamiltonian matrices of this size are very difficult to diagonalize. Of course the determinants that are generated have all possible spin multiplicities consistent with 8 electrons and the number with a specific spin is much smaller.

In order to reduce the size of the Hamiltonian matrix for a given problem one may expand the wavefunction in Configuration State Functions (CSF's) instead of individual determinants. A CSF is a linear combination of determinants that has a particular spin multiplicity and a particular spatial symmetry. For example the determinants  $\psi_1 = \hat{A}a\alpha b\beta$ and  $\psi_2 = \hat{A}a\beta b\alpha$  might appear is the list of all possible determinants for a two electron problem. Neither one is an eigenfuction of  $\hat{S}^2$  but the sum  $\psi_1 + \psi_2$  is a singlet and the difference  $\psi_1 - \psi_2$  is a triplet. Taking linear combinations of the individual determinants to form spin eigenfunctions and then using these as the expansion basis can significantly reduce the size of the Hamiltonian matrix. For example, in CH2 we have 8 electrons and therefore possible multiplicities of 2S + 1 = 9,7,5,3,1 so we can take linear combinations of the various determinants to form these multiplicities and then expand the singlet's in the singlet space, etc.



Additionally we may further partition the CSF's according to spatial symmetry. Since CH<sub>2</sub> has C<sub>2V</sub> symmetry we can divide the CSF space into  $A_1$ ,  $B_1$ ,  $B_2$ , &  $A_2$  symmetries.

# Structure of Hamiltonian H

### **Excitation Level**

	0	1	2	3	4	 Ν
0	E <sub>HF</sub>	0	H <sup>(0,2)</sup>	0	0	 0
1	0	H <sup>(1,1)</sup>	H <sup>(1,2)</sup>	H <sup>(1,3)</sup>	0	 0
2	H <sup>(2,0)</sup>	H <sup>(2,1)</sup>	H <sup>(2,2)</sup>	H <sup>(2,3)</sup>	H <sup>(2,4)</sup>	 0
3	0	H <sup>(3,1)</sup>	H <sup>(3,2)</sup>	H <sup>(3,3)</sup>	H <sup>(3,4)</sup>	 0
4	0	0	H <sup>(4,2)</sup>	H <sup>(4,3)</sup>	H <sup>(4,4)</sup>	 0
Ν	0	0	0	0	0	 H <sup>(N,N)</sup>

## Special Types of CI Wavefunctions

CIS CI singles

$$\psi_{CIS} = c_o \psi_{HF} + \Phi^{(1)}$$

CISD CI singles and doubles

 $\psi_{CISD} = c_o \psi_{HF} + \Phi^{(1)} + \Phi^{(2)}$ 

CID CI doubles

 $\psi_{CID} = c_o \psi_{HF} + \Phi^{(2)}$