

## 19.2: Different Methods

There are numerous procedures currently in use for determining the 'best' wavefunction of the form:

$$\Psi = \sum_I C_I \Phi_I,$$

where  $\Phi_I$  is a spin-and space- symmetry adapted CSF consisting of determinants of the form  $|\phi_{I1}\phi_{I2}\phi_{I3}\dots\phi_{IN}|$ . Excellent overviews of many of these methods are included in **Modern Theoretical Chemistry** Vols. 3 and 4, H. F. Schaefer, III Ed., Plenum Press, New York (1977) and in **Advances in Chemical Physics**, Vols. LXVII and LXIX, K. P. Lawley, Ed., Wiley-Interscience, New York (1987). Within the present Chapter, these two key references will be denoted MTC, Vols. 3 and 4, and ACP, Vols. 67 and 69, respectively.

In all such trial wavefunctions, there are two fundamentally different kinds of parameters that need to be determined- the CI coefficients  $C_I$  and the LCAO-MO coefficients describing the  $\phi_{Ik}$ . The most commonly employed methods used to determine these parameters include:

1. The **multiconfigurational self-consistent field** (MCSCF) method in which the expectation value  $\frac{\langle \Psi | H | \Psi \rangle}{\langle \Psi | \Psi \rangle}$  is treated variationally and simultaneously made stationary with respect to variations in the  $C_I$  and  $C_{n,i}$  coefficients subject to the constraints that the spin-orbitals and the full N-electron wavefunction remain normalized:

$$\langle \phi_i | \phi_j \rangle = \delta_{i,j} = \sum_{\nu,\mu} C_{\nu,i} S_{\nu,\mu} C_{\mu,i}, \text{ and}$$

$$\sum_I C_I^2 = 1.$$

The articles by H.-J. Werner and by R. Shepard in ACP Vol. 69 provide up to date reviews of the status of this approach. The article by A. C. Wahl and G. Das in MTC Vol. 3 covers the 'earlier' history on this topic. F. W. Bobrowicz and W. A. Goddard, III provide, in MTC Vol. 3, an overview of the GVB approach, which, as discussed in Chapter 12, can be viewed as a specific kind of MCSCF calculation.

2. The **configuration interaction** (CI) method in which the LCAO-MO coefficients are determined first (and independently) via either a singleconfiguration SCF calculation or an MCSCF calculation using a small number of CSFs. The CI coefficients are subsequently determined by making the expectation value  $\frac{\langle \Psi | H | \Psi \rangle}{\langle \Psi | \Psi \rangle}$  stationary with respect to variations in the  $C_I$  only. In this process, the optimizations of the orbitals and of the CSF amplitudes are done in separate steps. The articles by I. Shavitt and by B. O. Ross and P. E. M. Siegbahn in MTC, Vol. 3 give excellent early overviews of the CI method.
3. The **Møller-Plesset perturbation method** (MPPT) uses the single-configuration SCF process (usually the UHF implementation) to first determine a set of LCAO-MO coefficients and, hence, a set of orbitals that obey  $F\phi_i = \epsilon_i\phi_i$ . Then, using an unperturbed Hamiltonian equal to the sum of these Fock operators for each of the N electrons  $H^0 = \sum_{i=1,N} F(i)$ , perturbation theory (see Appendix D for an introduction to time-independent perturbation theory) is used to determine the CI amplitudes for the CSFs. The MPPT procedure is also referred to as the many-body perturbation theory (MBPT) method. The two names arose because two different schools of physics and chemistry developed them for somewhat different applications. Later, workers realized that they were identical in their working equations when the UHF  $H^0$  is employed as the unperturbed Hamiltonian. In this text, we will therefore refer to this approach as MPPT/MBPT.

The amplitude for the so-called **reference** CSF used in the SCF process is taken as unity and the other CSFs' amplitudes are determined, relative to this one, by Rayleigh-Schrödinger perturbation theory using the full N-electron Hamiltonian minus the sum of Fock operators  $H-H^0$  as the perturbation. The Slater-Condon rules are used for evaluating matrix elements of  $(H-H^0)$  among these CSFs. The essential features of the MPPT/MBPT approach are described in the following articles: J. A. Pople, R. Krishnan, H. B. Schlegel, and J. S. Binkley, Int. J. Quantum Chem. 14, 545 (1978); R. J. Bartlett and D. M. Silver, J. Chem. Phys. 62, 3258 (1975); R. Krishnan and J. A. Pople, Int. J. Quantum Chem. 14, 91 (1978).

4. The **Coupled-Cluster method** expresses the CI part of the wavefunction in a somewhat different manner (the early work in chemistry on this method is described in J. Cizek, J. Chem. Phys. 45, 4256 (1966); J. Paldus, J. Cizek, and I. Shavitt, Phys.

Rev. A5 , 50 (1972); R. J. Bartlett and G. D. Purvis, Int. J. Quantum Chem. 14 , 561 (1978); G. D. Purvis and R. J. Bartlett, J. Chem. Phys. 76 , 1910 (1982):

$$\Psi = e^T \Phi,$$

where  $\Phi$  is a single CSF (usually the UHF single determinant) which has been used to independently determine a set of spin-orbitals and LCAO-MO coefficients via the SCF process. The operator T generates, when acting on  $\Phi$ , single, double, etc. 'excitations' (i.e., CSFs in which one, two, etc. of the occupied spin-orbitals in  $\Phi$  have been replaced by virtual spin-orbitals). T is commonly expressed in terms of operators that effect such spin-orbital removals and additions as follows:

$$T = \sum_{i,m} t_i^m m^+ i + \sum_{i,j,m,n} t_{i,j}^{m,n} m^+ n^+ j i + \dots,$$

where the operator  $m^+$  is used to denote creation of an electron in virtual spin-orbital  $\phi_m$  and the operator  $j$  is used to denote **removal** of an electron from occupied spin-orbital  $\phi_j$ .

The  $t_i^m$ ,  $t_{i,j}^{m,n}$ , etc. amplitudes, which play the role of the CI coefficients in CC theory, are determined through the set of equations generated by projecting the Schrödinger equation in the form

$$e^{-T} H e^T \Phi = E \Phi$$

against CSFs which are single, double, etc. excitations relative to  $\Phi$ . For example, for double excitations  $\Phi_{i,j}^{m,n}$  the equations read:

$$\langle \Phi_{i,j}^{m,n} | e^{-T} e^T | \Phi \rangle = E \langle \Phi_{i,j}^{m,n} | \Phi \rangle = 0;$$

zero is obtained on the right hand side because the excited CSFs  $|\Phi_{i,j}^{m,n}\rangle$  are orthogonal to the reference function  $|\Phi\rangle$ . The elements on the left hand side of the CC equations can be expressed, as described below, in terms of one- and two-electron integrals over the spin-orbitals used in forming the reference and excited CSFs.

## Integral Transformations

All of the above methods require the evaluation of one- and two-electron integrals over the N atomic orbital basis:  $\langle \chi_a | f | \chi_b \rangle$  and  $\langle \chi_a \chi_b | g | \chi_c \chi_d \rangle$ . Eventually, all of these methods provide their working equations and energy expressions in terms of one- and two electron integrals over the N final **molecular orbitals**:  $\langle \phi_i | f | \phi_j \rangle$  and  $\langle \chi_i \chi_j | g | \chi_k \chi_l \rangle$ . The mo-based integrals can only be evaluated by **transforming** the AO-based integrals as follows:

$$\langle \phi_i \phi_j | g | \phi_k \phi_l \rangle = \sum_{a,b,c,d} C_{a,i} C_{b,j} C_{c,k} C_{d,l} \langle \chi_a \chi_b | g | \chi_c \chi_d \rangle,$$

and

$$\langle \phi_i | f | \phi_j \rangle = \sum_{a,b} C_{a,i} C_{b,j} \langle \chi_a | f | \chi_b \rangle.$$

It would seem that the process of evaluating all  $N^4$  of the  $\langle \phi_i \phi_j | g | \phi_k \phi_l \rangle$ , each of which requires  $N^4$  additions and multiplications, would require computer time proportional to  $N^8$ . However, it is possible to perform the full transformation of the two-electron integral list in a time that scales as  $N^5$ . This is done by first performing a transformation of the  $\langle \chi_a \chi_b | g | \chi_c \chi_d \rangle$  to an intermediate array  $\langle \chi_a \chi_b | g | \chi_c \phi_1 \rangle$  labeled as follows:

$$\langle \chi_a \chi_b | g | \chi_c \phi_1 \rangle = \sum_d C_{d,i} \langle \chi_a \chi_b | g | \chi_c \chi_d \rangle.$$

This partial transformation requires  $N^5$  multiplications and additions. The list  $\langle \chi_a \chi_b | g | \chi_c \phi_1 \rangle$  is then transformed to a second-level transformed array  $\langle \chi_a \chi_b | g | \phi_k \phi_1 \rangle$ :

$$\langle \chi_a \chi_b | g | \phi_k \phi_1 \rangle = \sum_c C_{c,k} \langle \chi_a \chi_b | g | \chi_c \phi_1 \rangle,$$

which requires another  $N^5$  operations. This sequential, one-index-at-a-time transformation is repeated four times until the final  $\langle \phi_i \phi_j | g | \phi_k \phi_l \rangle$  array is in hand. The entire transformation done this way requires  $4N^5$  multiplications and additions.

Once the requisite one- and two-electron integrals are available in the molecular orbital basis, the multiconfigurational wavefunction and energy calculation can begin. These transformations consume a large fraction of the computer time used in most such calculations, and represent a severe bottleneck to progress in applying **ab initio** electronic structure methods to larger systems.

### Configuration List Choices

Once the requisite one- and two-electron integrals are available in the molecular orbital basis, the multiconfigurational wavefunction and energy calculation can begin. Each of these methods has its own approach to describing the configurations  $\{\Phi_J\}$  included in the calculation and how the  $\{C_J\}$  amplitudes and the total energy  $E$  is to be determined.

The **number of configurations** ( $N_C$ ) varies greatly among the methods and is an important factor to keep in mind when planning to carry out an *ab initio* calculation. Under certain circumstances (e.g., when studying Woodward-Hoffmann forbidden reactions where an avoided crossing of two configurations produces an activation barrier), it may be essential to use more than one electronic configuration. Sometimes, one configuration (e.g., the SCF model) is adequate to capture the qualitative essence of the electronic structure. In all cases, many configurations will be needed if highly accurate treatment of electron-electron correlations are desired.

The value of  $N_C$  determines how much computer time and memory is needed to solve the  $N_C$ -dimensional  $\sum_J H_{I,J} C_J = E C_I$  secular problem in the CI and MCSCF methods. Solution of these matrix eigenvalue equations requires computer time that scales as  $N_C^2$  (if few eigenvalues are computed) to  $N_C^3$  (if most eigenvalues are obtained).

So-called **complete-active-space** (CAS) methods form **all** CSFs that can be created by distributing  $N$  valence electrons among  $P$  valence orbitals. For example, the eight noncore electrons of  $H_2O$  might be distributed, in a manner that gives  $M_S = 0$ , among six valence orbitals (e.g., two lone-pair orbitals, two OH  $\sigma$  bonding orbitals, and two OH  $\sigma^*$  antibonding orbitals). The number of configurations thereby created is 225. If the same eight electrons were distributed among ten valence orbitals 44,100 configurations results; for twenty and thirty valence orbitals, 23,474,025 and 751,034,025 configurations arise, respectively. Clearly, practical considerations dictate that CAS-based approaches be limited to situations in which a few electrons are to be correlated using a few valence orbitals. The primary advantage of CAS configurations is discussed below in Sec. II. C.

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