Chapter 18

The single Slater determinant wavefunction (properly spin and symmetry adapted) is the starting point of the most common mean field potential. It is also the origin of the molecular orbital concept.

I. Optimization of the Energy for a Multiconfiguration Wavefunction

A. The Energy Expression

The most straightforward way to introduce the concept of optimal molecular orbitals is to consider a trial wavefunction of the form which was introduced earlier in Chapter 9.II. The expectation value of the Hamiltonian for a wavefunction of the multiconfigurational form

$$= I C_{I I},$$

where I is a space- and spin-adapted CSF which consists of determinental wavefunctions | I1 I2 I3... IN|, can be written as:

$$E = I_{J} = I_{M} C_{I}C_{J} < I \mid H \mid J > .$$

The spin- and space-symmetry of the I determine the symmetry of the state whose energy is to be optimized.

In this form, it is clear that E is a quadratic function of the CI amplitudes C_J ; it is a quartic functional of the spin-orbitals because the Slater-Condon rules express each < I |H | J > CI matrix element in terms of one- and two-electron integrals < i | f | j > and < i | j | g | k | > over these spin-orbitals.

B. Application of the Variational Method

The <u>variational</u> method can be used to optimize the above expectation value expression for the electronic energy (i.e., to make the functional stationary) as a function of the CI coefficients C_J and the LCAO-MO coefficients {C_i} that characterize the spinorbitals. However, in doing so the set of {C_i} can not be treated as entirely independent variables. The fact that the spin-orbitals {_i} are assumed to be orthonormal imposes a set of constraints on the {C_i}: $<\ _{i}\ |\ _{j}\!>\!=\ _{i,j}=\ _{\mu,}\ C*_{\mu,i}\!<\ _{\mu}\!|\quad >C\ _{,j.}$

These constraints can be enforced within the variational optimization of the energy function mentioned above by introducing a set of Lagrange multipliers $\{\ _{i,j}\}$, one for each constraint condition, and subsequently differentiating

$$\mathrm{E}$$
 - $_{i,j}$ $_{i,j}$ [$_{i,j}$ - $_{\mu}$, $\mathrm{C}^*_{\mu,i}$ < $_{\mu}$ | > C , j]

with respect to each of the C _, i variables.

C. The Fock and Secular Equations

Upon doing so, the following set of equations is obtained (early references to the derivation of such equations include A. C. Wahl, J. Chem. Phys. <u>41</u>,2600 (1964) and F. Grein and T. C. Chang, Chem. Phys. Lett. <u>12</u>, 44 (1971); a more recent overview is presented in R. Shepard, p 63, in Adv. in Chem. Phys. LXIX, K. P. Lawley, Ed., Wiley-Interscience, New York (1987); the subject is also treated in the textbook <u>Second</u> <u>Quantization Based Methods in Quantum Chemistry</u>, P. Jørgensen and J. Simons, Academic Press, New York (1981))) :

 $J_{=1, M} H_{I,J} C_J = E C_{I, I} = 1, 2, ... M$, and F $i_i = j_i i_i j_i$,

where the *i*,*j* are Lagrange multipliers.

The first set of equations govern the {C_J} amplitudes and are called the CI- secular equations. The second set determine the LCAO-MO coefficients of the spin-orbitals { $_j$ } and are called the Fock equations. The Fock operator F is given in terms of the one- and two-electron operators in H itself as well as the so-called one- and two-electron density matrices $_{i,j}$ and $_{i,j,k,l}$ which are defined below. These density matrices reflect the averaged occupancies of the various spin orbitals in the CSFs of $_{-}$. The resultant expression for F is:

$$\mathbf{F}_{i} = \mathbf{j}_{i,j} \mathbf{h}_{j} + \mathbf{j}_{k,l} \mathbf{i}_{i,j,k,l} \mathbf{J}_{j,l} \mathbf{k},$$

where h is the one-electron component of the Hamiltonian (i.e., the kinetic energy operator and the sum of coulombic attractions to the nuclei). The operator $J_{j,l}$ is defined by:

$$J_{j,1} k(r) = {*_j(r') l(r')1/|r-r'| d'} k(r),$$

where the integration denoted d ' is over the spatial and spin coordinates. The so-called spin integration simply means that the or spin function associated with 1 must be the same as the or spin function associated with j or the integral will vanish. This is a consequence of the orthonormality conditions < | > = < | > = 1, < | > = < | > = 0.

D. One- and Two- Electron Density Matrices

The density matrices introduced above can most straightforwardly be expressed in terms of the CI amplitudes and the nature of the orbital occupancies in the CSFs of as follows:

1. $_{i,i}$ is the sum over all CSFs, in which $_i$ is occupied, of the square of the C_I coefficient of that CSF:

$$_{i,i} = I$$
 (with $_i$ occupied) C^2I .

2. $_{i,j}$ is the sum over pairs of CSFs which differ by a single spin-orbital occupancy (i.e., one having $_i$ occupied where the other has $_j$ occupied after the two are placed into maximal coincidence-the sign factor (sign) arising from bringing the two to maximal coincidence is attached to the final density matrix element):

 $i_{i,j} = I_{J}$ (sign)(with i_{i} occupied in I where i_{j} is in J) $C_{I} C_{J}$.

The two-electron density matrix elements are given in similar fashion:

3.
$$i,j,i,j = I$$
 (with both i and j occupied) $C_I C_I$;

4. $_{i,j,j,i} = -_{I}$ (with both $_{i}$ and $_{j}$ occupied) $C_{I} C_{I} = -_{i,j,i,j}$

(it can be shown, in general that i,j,k,l is odd under exchange of i and j, odd under exchange of k and l and even under (i,j) <=>(k,l) exchange; this implies that i,j,k,l vanishes if i = j or k = l.);

5.
$$_{i,j,k,j} = _{I,J} (sign)(with_{j} in both I and J)$$

and $_{i} in I where_{k} is in J) C_{I}C_{J}$

$$= j_{i,i,j,k} = - i_{i,j,j,k} = - j_{i,i,k,j};$$

6. $_{i,j,k,l} = _{I,J} (sign)($ with $_i$ in I where $_k$ is in J and $_j$ in I where $_l$ is in J) C_I C_J

$$= j_{i,i,l,k} = - j_{i,i,k,l} = - i_{i,j,l,k} = j_{i,i,l,k} \cdot$$

These density matrices are themselves quadratic functions of the CI coefficients and they reflect all of the permutational symmetry of the determinental functions used in constructing ; they are a compact representation of all of the Slater-Condon rules as applied to the particular CSFs which appear in \therefore They contain all information about the spin-orbital occupancy of the CSFs in \therefore The one- and two- electron integrals $< |i| f |_j >$ and $< |i| j | g |_{k = 1} >$ contain all of the information about the magnitudes of the kinetic and Coulombic interaction energies.

II. The Single-Determinant Wavefunction

The simplest trial function of the form given above is the single Slater determinant function:

$$= | 1 2 3 \cdots N|.$$

For such a function, the CI part of the energy minimization is absent (the classic papers in which the SCF equations for closed- and open-shell systems are treated are C. C. J. Roothaan, Rev. Mod. Phys. <u>23</u>, 69 (1951); <u>32</u>, 179 (1960)) and the density matrices simplify greatly because only one spin-orbital occupancy is operative. In this case, the orbital optimization conditions reduce to:

$$F_i = j_{i,j} j_j$$

where the so-called Fock operator F is given by

$$F_i = h_i + j(occupied) [J_j - K_j]_i$$
.

The coulomb (J_i) and exchange (K_i) operators are defined by the relations:

$$\begin{split} J_{j \quad i} &= \ \ ^{*}{}_{j}(r') \ \ _{j}(r')1/|r\text{-}r'| \ d \ \ ^{}_{i}(r) \ \, , \ and \\ K_{j \quad i} &= \ \ ^{*}{}_{j}(r') \ \ _{i}(r')1/|r\text{-}r'| \ d \ \ ^{}_{j}(r) \ \, . \end{split}$$

Again, the integration implies integration over the spin variables associated with the j (and, for the exchange operator, i), as a result of which the exchange integral vanishes unless the spin function of j is the same as that of i; the coulomb integral is non-vanishing no matter what the spin functions of j and i.

The sum over coulomb and exchange interactions in the Fock operator runs only over those spin-orbitals that are occupied in the trial \therefore Because a unitary transformation among the orbitals that appear in = leaves the determinant unchanged (this is a property of determinants- det (UA) = det (U) det (A) = 1 det (A), if U is a unitary matrix), it is possible to choose such a unitary transformation to make the $=_{i,j}$ matrix diagonal. Upon so doing, one is left with the so-called canonical Hartree-Fock equations:

$$F_i = i_j,$$

where $_{i}$ is the diagonal value of the $_{i,j}$ matrix after the unitary transformation has been applied; that is, $_{i}$ is an eigenvalue of the $_{i,j}$ matrix. These equations are of the eigenvalueeigenfunction form with the Fock operator playing the role of an effective one-electron Hamiltonian and the $_{i}$ playing the role of the one-electron eigenfunctions.

It should be noted that the Hartree-Fock equations $F_i = i_j$ possess solutions for the spin-orbitals which appear in (the so-called <u>occupied</u> spin-orbitals) as well as for orbitals which are not occupied in (the so-called <u>virtual</u> spin-orbitals). In fact, the F operator is hermitian, so it possesses a complete set of orthonormal eigenfunctions; only those which appear in appear in the coulomb and exchange potentials of the Fock operator. The physical meaning of the occupied and virtual orbitals will be clarified later in this Chapter (Section VII.A)

III. The Unrestricted Hartree-Fock Spin Impurity Problem

As formulated above in terms of spin-orbitals, the Hartree-Fock (HF) equations yield orbitals that do not guarantee that possesses proper spin symmetry. To illustrate the point, consider the form of the equations for an open-shell system such as the Lithium atom Li. If 1s , 1s , and 2s spin-orbitals are chosen to appear in the trial function , then the Fock operator will contain the following terms:

$$F = h + J_{1s} + J_{1s} + J_{2s} - [K_{1s} + K_{1s} + K_{2s}]$$

Acting on an spin-orbital k with F and carrying out the spin integrations, one obtains

$$F_{k} = h_{k} + (2J_{1s} + J_{2s})_{k} - (K_{1s} + K_{2s})_{k}$$

In contrast, when acting on a spin-orbital, one obtains

$$F_{k} = h_{k} + (2J_{1s} + J_{2s})_{k} - (K_{1s})_{k}$$

Spin-orbitals of and type do <u>not</u> experience the same exchange potential in this model, which is clearly due to the fact that contains two spin-orbitals and only one spin-orbital.

One consequence of the spin-polarized nature of the effective potential in F is that the optimal 1s and 1s spin-orbitals, which are themselves solutions of F $_i = _i _i$, do not have identical orbital energies (i.e., $_{1s}$ $_{1s}$) and are not spatially identical to one another (i.e., $_{1s}$ and $_{1s}$ do not have identical LCAO-MO expansion coefficients). This resultant spin polarization of the orbitals in gives rise to spin impurities in . That is, the determinant | 1s 1s' 2s | is not a pure doublet spin eigenfunction although it is an S_z eigenfunction with $M_s = 1/2$; it contains both S = 1/2 and S = 3/2 components. If the 1s and 1s' spin-orbitals were spatially identical, then | 1s 1s' 2s | would be a pure spin eigenfunction with S = 1/2.

The above single-determinant wavefunction is commonly referred to as being of the **unrestricted Hartree-Fock** (UHF) type because no restrictions are placed on the spatial nature of the orbitals which appear in . In general, UHF wavefunctions are not of pure spin symmetry for any open-shell system. Such a UHF treatment forms the starting point of early versions of the widely used and highly successful Gaussian 70 through Gaussian-

8X series of electronic structure computer codes which derive from J. A. Pople and coworkers (see, for example, M. J. Frisch, J. S. Binkley, H. B. Schlegel, K Raghavachari, C. F. Melius, R. L. Martin, J. J. P. Stewart, F. W. Bobrowicz, C. M. Rohling, L. R. Kahn, D. J. Defrees, R. Seeger, R. A. Whitehead, D. J. Fox, E. M. Fleuder, and J. A. Pople, <u>Gaussian 86</u>, Carnegie-Mellon Quantum Chemistry Publishing Unit, Pittsburgh, PA (1984)).

The inherent spin-impurity problem is sometimes 'fixed' by using the orbitals which are obtained in the UHF calculation to subsequently form a properly spin-adapted wavefunction. For the above Li atom example, this amounts to forming a new wavefunction (after the orbitals are obtained via the UHF process) using the techniques detailed in Section 3 and Appendix G:

 $= 1/2 [|1s \ 1s' \ 2s \ |-|1s \ 1s' \ 2s \ |].$

This wavefunction is a pure S = 1/2 state. This prescription for avoiding spin contamination (i.e., carrying out the UHF calculation and then forming a new spin-pure) is referred to as <u>spin-projection</u>.

It is, of course, possible to first form the above spin-pure as a trial wavefunction and to then determine the orbitals 1s 1s' and 2s which minimize its energy; in so doing, one is dealing with a spin-pure function from the start. The problem with carrying out this process, which is referred to as a <u>spin-adapted</u> Hartree-Fock calculation, is that the resultant 1s and 1s' orbitals still do not have identical spatial attributes. Having a set of orbitals (1s, 1s', 2s, and the virtual orbitals) that form a non-orthogonal set (1s and 1s' are neither identical nor orthogonal) makes it difficult to progress beyond the singleconfiguration wavefunction as one often wishes to do. That is, it is difficult to use a spinadapted wavefunction as a starting point for a correlated-level treatment of electronic motions.

Before addressing head-on the problem of how to best treat orbital optimization for open-shell species, it is useful to examine how the HF equations are solved in practice in terms of the LCAO-MO process.

IV. The LCAO-MO Expansion

The HF equations F $_{i} = _{i}$ comprise a set of integro-differential equations; their differential nature arises from the kinetic energy operator in h, and the coulomb and exchange operators provide their integral nature. The solutions of these equations must be

achieved iteratively because the J_i and K_i operators in F depend on the orbitals $_i$ which are to be solved for. Typical iterative schemes begin with a 'guess' for those $_i$ which appear in $_i$, which then allows F to be formed. Solutions to F $_i = _i _i$ are then found, and those $_i$ which possess the space and spin symmetry of the occupied orbitals of $_i$ and which have the proper energies and nodal character are used to generate a new F operator (i.e., new J_i and K_i operators). The new F operator then gives new $_i$ and $_i$ via solution of the new F $_i = _i _i$ equations. This iterative process is continued until the $_i$ and $_i$ do not vary significantly from one iteration to the next, at which time one says that the process has converged. This iterative procedure is referred to as the Hartree-Fock <u>self-consistent field</u> (SCF) procedure because iteration eventually leads to coulomb and exchange potential fields that are consistent from iteration to iteration.

In practice, solution of F_i = $_{i}$ $_{i}$ as an integro-differential equation can be carried out only for atoms (C. Froese-Fischer, Comp. Phys. Commun. <u>1</u>, 152 (1970)) and linear molecules (P. A. Christiansen and E. A. McCullough, J. Chem. Phys. <u>67</u>, 1877 (1977)) for which the angular parts of the $_{i}$ can be exactly separated from the radial because of the axial- or full- rotation group symmetry (e.g., $_{i} = Y_{l,m} R_{n,l}(r)$ for an atom and $_{i} =$ exp(im) $R_{n,l,m}(r,)$ for a linear molecule). In such special cases, $F_{i} = _{i}$ $_{i}$ gives rise to a set of coupled equations for the $R_{n,l}(r)$ or $R_{n,l,m}(r,)$ which can and have been solved. However, for non-linear molecules, the HF equations have not yet been solved in such a manner because of the three-dimensional nature of the $_{i}$ and of the potential terms in F.

In the most commonly employed procedures used to solve the HF equations for non-linear molecules, the $_{i}$ are expanded in a basis of functions $_{\mu}$ according to the LCAO-MO procedure:

$$_{i} = \mu C_{\mu,i} \mu$$
.

Doing so then reduces F $i = i_i$ to a matrix eigenvalue-type equation of the form:

$$F_{\mu,}$$
 $C_{,i} = _{i}$ $S_{\mu,}$ $C_{,i}$,

where $S_{\mu,} = \langle \mu | \rangle$ is the overlap matrix among the atomic orbitals (aos) and

$$F_{\mu,} \hspace{0.2cm} = \hspace{-0.2cm} < \hspace{0.2cm} \mu |h| \hspace{0.2cm} > \hspace{-0.2cm} + \hspace{0.2cm} , \hspace{0.2cm} [\hspace{0.2cm} , \hspace{0.2cm} < \hspace{0.2cm} \mu \hspace{0.2cm} |g| \hspace{0.2cm} > \hspace{-0.2cm}]$$

is the matrix representation of the Fock operator in the ao basis. The coulomb and exchange- density matrix elements in the ao basis are: $= i(\text{occupied}) C_{i} C_{i}$, and

$$e^{ex} = i(occ., and same spin) C_{i} C_{i}, i$$

where the sum in e^x runs over those occupied spin-orbitals whose m_s value is equal to that for which the Fock matrix is being formed (for a closed-shell species, $e^x = 1/2$,).

It should be noted that by moving to a matrix problem, one does not remove the need for an iterative solution; the F_{μ} , matrix elements depend on the C _{,i} LCAO-MO coefficients which are, in turn, solutions of the so-called Roothaan matrix Hartree-Fock equations- F_{μ} , C _{,i} = _i S_µ, C _{,i}. One should also note that, just as $F_{i} = _{i} _{j}$ possesses a complete set of eigenfunctions, the matrix F_{μ} , whose dimension M is equal to the number of atomic basis orbitals used in the LCAO-MO expansion, has M eigenvalues _i and M eigenvectors whose elements are the C _{,i}. Thus, there are occupied and virtual molecular orbitals (mos) each of which is described in the LCAO-MO form with C _{,i} coefficients obtained via solution of

$$F_{\mu,}$$
 C $_{,i}$ = $_{i}$ S $_{\mu,}$ C $_{,i}$.

V. Atomic Orbital Basis Sets

A. STOs and GTOs

The basis orbitals commonly used in the LCAO-MO-SCF process fall into two classes:

1. Slater-type orbitals

$$n,l,m(r, ,) = N_{n,l,m}, Y_{l,m}(,) r^{n-1} e^{-r},$$

which are characterized by quantum numbers n, l, and m and exponents (which characterize the 'size' of the basis function) . The symbol $N_{n,l,m}$, denotes the normalization constant.

2. Cartesian Gaussian-type orbitals

$$a,b,c$$
 (r, ,) = N' $_{a,b,c}$, $x^{a} y^{b} z^{c} exp(-r^{2})$,

characterized by quantum numbers a, b, and c which detail the angular shape and direction of the orbital and exponents which govern the radial 'size' of the basis function. For example, orbitals with a, b, and c values of 1,0,0 or 0,1,0 or 0,0,1 are p_x , p_y , and p_z orbitals; those with a,b,c values of 2,0,0 or 0,2,0 or 0,0,2 and 1,1,0 or 0,1,1 or 1,0,1 span the space of five d orbitals and one s orbital (the sum of the 2,0,0 and 0,2,0 and 0,0,2 orbitals is an s orbital because $x^2 + y^2 + z^2 = r^2$ is independent of and).

For both types of orbitals, the coordinates r, , and refer to the position of the electron relative to a set of axes attached to the center on which the basis orbital is located. Although Slater-type orbitals (STOs) are preferred on fundamental grounds (e.g., as demonstrated in Appendices A and B, the hydrogen atom orbitals are of this form and the exact solution of the many-electron Schrödinger equation can be shown to be of this form (in each of its coordinates) near the nuclear centers), STOs are used primarily for atomic and linear-molecule calculations because the multi-center integrals < $a \ b| g | c d >$ (each basis orbital can be on a separate atomic center) which arise in polyatomic-molecule calculations can not efficiently be performed when STOs are employed. In contrast, such integrals can routinely be done when Gaussian-type orbitals (GTOs) are used. This fundamental advantage of GTOs has lead to the dominance of these functions in molecular quantum chemistry.

To understand why integrals over GTOs can be carried out when analogous STObased integrals are much more difficult, one must only consider the orbital products ($_a c$ (r_1) and $_b d(r_2)$) which arise in such integrals. For orbitals of the GTO form, such products involve exp(- $_a (\mathbf{r}-\mathbf{R}_a)^2$) exp(- $_c (\mathbf{r}-\mathbf{R}_c)^2$). By completing the square in the exponent, this product can be rewritten as follows:

$$\exp(-_{a} (\mathbf{r} - \mathbf{R}_{a})^{2}) \exp(-_{c} (\mathbf{r} - \mathbf{R}_{c})^{2})$$
$$= \exp(-(_{a} + _{c})(\mathbf{r} - \mathbf{R}')^{2}) \exp(-_{(\mathbf{R}_{a} - \mathbf{R}_{c})^{2}),$$

where

$$\mathbf{R}' = \begin{bmatrix} a \mathbf{R}_a + c \mathbf{R}_c \end{bmatrix} / \begin{pmatrix} a + c \end{pmatrix}$$
 and

$$' = a c/(a + c).$$

Thus, the product of two GTOs on different centers is equal to a single other GTO at a center \mathbf{R} ' between the two original centers. As a result, even a four-center two-electron integral over GTOs can be written as, at most, a two-center two-electron integral; it turns out that this reduction in centers is enough to allow all such integrals to be carried out. A similar reduction does not arise for STOs because the product of two STOs can not be rewritten as a new STO at a new center.

To overcome the primary weakness of GTO functions, that they have incorrect behavior near the nuclear centers (i.e., their radial derivatives vanish at the nucleus whereas the derivatives of STOs are non-zero), it is common to combine two, three, or more GTOs, with combination coefficients which are fixed and <u>not</u> treated as LCAO-MO parameters, into new functions called contracted GTOs or CGTOs. Typically, a series of tight, medium, and loose GTOs (i.e., GTOs with large, medium, and small values, respectively) are multiplied by so-called contraction coefficients and summed to produce a CGTO which appears to possess the proper 'cusp' (i.e., non-zero slope) at the nuclear center (although even such a combination can not because each GTO has zero slope at the nucleus).

B. Basis Set Libraries

Much effort has been devoted to developing sets of STO or GTO basis orbitals for main-group elements and the lighter transition metals. This ongoing effort is aimed at providing standard basis set libraries which:

1. Yield reasonable chemical accuracy in the resultant wavefunctions and energies.

2. Are cost effective in that their use in practical calculations is feasible.

3. Are relatively transferrable in the sense that the basis for a given atom is flexible enough to be used for that atom in a variety of bonding environments (where the atom's hybridization and local polarity may vary).

C. The Fundamental Core and Valence Basis

In constructing an atomic orbital basis to use in a particular calculation, one must choose from among several classes of functions. First, the size and nature of the primary core and valence basis must be specified. Within this category, the following choices are common:

1. A <u>minimal basis</u> in which the number of STO or CGTO orbitals is equal to the number of core and valence atomic orbitals in the atom.

2. A <u>double-zeta</u> (DZ) basis in which twice as many STOs or CGTOs are used as there are core and valence atomic orbitals. The use of more basis functions is motivated by a desire to provide additional variational flexibility to the LCAO-MO process. This flexibility allows the LCAO-MO process to generate molecular orbitals of variable diffuseness as the local electronegativity of the atom varies. Typically, double-zeta bases include pairs of functions with one member of each pair having a smaller exponent (or value) than in the minimal basis and the other member having a larger exponent.

3. A <u>triple-zeta</u> (TZ) basis in which three times as many STOs or CGTOs are used as the number of core and valence atomic orbitals.

4. Dunning has developed CGTO bases which range from approximately DZ to substantially beyond TZ quality (T. H. Dunning, J. Chem. Phys. <u>53</u>, 2823 (1970); T. H. Dunning and P. J. Hay in <u>Methods of Electronic Structure Theory</u>, H. F. Schaefer, III Ed., Plenum Press, New York (1977))). These bases involve contractions of primitive GTO bases which Huzinaga had earlier optimized (S. Huzinaga, J. Chem. Phys. <u>42</u>, 1293 (1965)) for use as uncontracted functions (i.e., for which Huzinaga varied the values to minimize the energies of several electronic states of the corresponding atom). These Dunning bases are commonly denoted, for example, as follows for first-row atoms: (10s,6p/5s,4p), which means that 10 s-type primitive GTOs have been contracted to produce 5 separate s-type CGTOs and that 6 primitive p-type GTOs were contracted to generate 4 separate p-type CGTOs. More recent basis sets from the Dunning group are given in T. Dunning, J. Chem. Phys. <u>90</u>, 1007 (1990).

5. Even-tempered basis sets (M. W. Schmidt and K. Ruedenberg, J. Chem. Phys. <u>71</u>, 3961 (1979)) consist of GTOs in which the orbital exponents $_k$ belonging to series of orbitals consist of geometrical progressions: $_k = a^{-k}$, where a and characterize the particular set of GTOs.

6. STO-3G bases were employed some years ago (W. J. Hehre, R. F. Stewart, and J. A. Pople, J. Chem. Phys. <u>51</u>, 2657 (1969)) but are less popular recently. These bases are constructed by least squares fitting GTOs to STOs which have been optimized for various electronic states of the atom. When three GTOs are employed to fit each STO, a STO-3G basis is formed.

7. 4-31G, 5-31G, and 6-31G bases (R. Ditchfield, W. J. Hehre, and J. A. Pople, J. Chem. Phys. <u>54</u>, 724 (1971); W. J. Hehre, R. Ditchfield, and J. A. Pople, J. Chem.

Phys. <u>56</u>, 2257 (1972); P. C. Hariharan and J. A. Pople, Theoret. Chim. Acta. (Berl.) <u>28</u>, 213 (1973); R. Krishnan, J. S. Binkley, R. Seeger, and J. A. Pople, J. Chem. Phys. <u>72</u>, 650 (1980)) employ a single CGTO of contraction length 4, 5, or 6 to describe the core orbital. The valence space is described at the DZ level with the first CGTO constructed from 3 primitive GTOs and the second CGTO built from a single primitive GTO.

The values of the orbital exponents (s or s) and the GTO-to-CGTO contraction coefficients needed to implement a particular basis of the kind described above have been tabulated in several journal articles and in computer data bases (in particular, in the data base contained in the book <u>Handbook of Gaussian Basis Sets: A. Compendium for Ab</u> <u>initio Molecular Orbital Calculations</u>, R. Poirer, R. Kari, and I. G. Csizmadia, Elsevier Science Publishing Co., Inc., New York, New York (1985)).

Several other sources of basis sets for particular atoms are listed in the Table shown below (here JCP and JACS are abbreviations for the Journal of Chemical Physics and the Journal of The American Chemical Society, respectively).

Literature Reference	Basis Type Atoms	
Hehre, W.J.; Stewart, R.F.; Pople, J.A. JCP <u>51</u> , 2657 (1969). Hehre, W.J.; Ditchfield, R.; Stewart, R. Pople, J.A. JCP <u>52</u> , 2769 (1970).	STO-3G .F.;	H-Ar
Binkley, J.S.; Pople, J.A.; Hehre, W.J. JACS <u>102</u> , 939 (1980).	3-21G	H-Ne
Gordon, M.S.; Binkley, J.S.; Pople, J.A. Pietro, W.J.; Hehre, W.J. JACS <u>104</u> , 27		Na-Ar
Dobbs, K.D.; Hehre, W.J. J. Comput. Chem. <u>7</u> , 359 (1986).	3-21G	K,Ca,Ga
Dobbs, K.D.; Hehre, W.J. J. Comput. Chem. <u>8,</u> 880 (1987).	3-21G	Sc-Zn
Ditchfield, R.; Hehre, W.J.; Pople, J.A. JCP <u>54</u> , 724 (1971).	6-31G	Н

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(4s/3s) H (9s5p/3s2p) B-F (9s5p/4s2p) B-F
(9s5p/3s2p) B-F (9s5p/4s2p) B-F
(9s5p/4s2p) B-F
(9s5p/5s3p) B-F
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(10s/4s) Li
(10s/5s) Be
(10s6p/5s3p) B-Ne
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(9s5p/3s2) Li,Be,C-Ne
(12s8p/4s3p) Na-Ar
Dunning, unpublished VTZ. (5s/3s) H
(6s/3s) H

(12s6p/4s3p) Li,Be,C-Ne (17s10p/5s4p) Mg-Ar

Dunning, unpublished VQZ.	(7s/4s)	Н	
	(8s/4s)	Н	
	(16s7p/5s4p)	B-Ne	
Dunning, T. JCP <u>90</u> , 1007 (1989).	(4s1p/2s1p) H	
(pVDZ,pVTZ,pVQZ correlation-consis		·	
	(6s3p1d1f/4s3p2d	-	
		,	
	(9s4p1d/3s2p1d)		
(10s5p2d1f/4s3p2d1f) B-Ne			
(12s6	p3d2f1g/5s4p3d2	flg) B-Ne	
Huzinaga, S.; Klobukowski, M.; Tatew	/aki, H. (14s/2	2s) Li,B	e
Can. J. Chem. <u>63</u> , 1812 (1985).	(14s9p/2	s1p) B-Ne	
	(16s9p	/3s1p) Na-M	⁄lg
	(16s11p/3s2p) Al-Ar		
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THEOCHEM. <u>44</u> , 1 (1988).	(17s10p/3s	1p) Na-Mg	g
	(17s13p/3	3s2p) Al-Ai	r
	(20s13p/4s		
	(20s13p10d/4s2p1d) Sc-Zn		
	(20s14p9d/4	1 /	
	(-
McLean, A.D.: Chandler, G.S.	(12s8p/4s2p)	Na-Ar. P ⁻ .S ⁻ .C	C1-

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Hood, D.M.; Pitzer, R.M.; Schaefer, H.F.III (14s11p6d/10s8p3d) Sc-Zn JCP <u>71</u>, 705 (1979).

Schmidt, M.W.; Ruedenberg, K.	([N]s), N=3-10	Н
JCP <u>71</u> , 3951 (1979).	([2N]s), N=3-10	He
(regular even-tempered)	([2N]s), N=3-14	Li,Be
	([2N]s[N]p),N=3-11	B,N-Ne
	([2N]s[N]p),N=3-13	С
	([2N]s[N]p),N=4-12	Na,Mg
	([2N-6]s[N]p),N=7-15	Al-Ar

D. Polarization Functions

In addition to the fundamental core and valence basis described above, one usually adds a set of so-called <u>polarization functions</u> to the basis. Polarization functions are functions of one higher angular momentum than appears in the atom's valence orbital space (e.g, d-functions for C, N, and O and p-functions for H). These polarization functions have exponents (or) which cause their radial sizes to be similar to the sizes of the primary valence orbitals

(i.e., the polarization p orbitals of the H atom are similar in size to the 1s orbital). Thus, they are <u>not</u> orbitals which provide a description of the atom's valence orbital with one higher l-value; such higher-l valence orbitals would be radially more diffuse and would therefore require the use of STOs or GTOs with smaller exponents.

The primary purpose of polarization functions is to give additional angular flexibility to the LCAO-MO process in forming the valence molecular orbitals. This is illustrated below where polarization d orbitals are seen to contribute to formation of the bonding orbital of a carbonyl group by allowing polarization of the Carbon atom's p orbital toward the right and of the Oxygen atom's p orbital toward the left.



Polarization functions are essential in strained ring compounds because they provide the angular flexibility needed to direct the electron density into regions between bonded atoms.

Functions with higher l-values and with 'sizes' more in line with those of the lower-l orbitals are also used to introduce additional angular correlation into the calculation by permitting polarized orbital pairs (see Chapter 10) involving higher angular correlations to be formed. Optimal polarization functions for first and second row atoms have been tabulated (B. Roos and P. Siegbahn, Theoret. Chim. Acta (Berl.) <u>17</u>, 199 (1970); M. J. Frisch, J. A. Pople, and J. S. Binkley, J. Chem. Phys. <u>80</u>, 3265 (1984)).

E. Diffuse Functions

When dealing with anions or Rydberg states, one must augment the above basis sets by adding so-called diffuse basis orbitals. The conventional valence and polarization functions described above do not provide enough radial flexibility to adequately describe either of these cases. Energy-optimized diffuse functions appropriate to anions of most lighter main group elements have been tabulated in the literature (an excellent source of Gaussian basis set information is provided in <u>Handbook of Gaussian Basis Sets</u>, R. Poirier, R. Kari, and I. G. Csizmadia, Elsevier, Amsterdam (1985)) and in data bases. Rydberg diffuse basis sets are usually created by adding to conventional valence-pluspolarization bases sequences of primitive GTOs whose exponents are smaller than that (call it diff) of the most diffuse GTO which contributes strongly to the valence CGTOs. As a 'rule of thumb', one can generate a series of such diffuse orbitals which are liniarly independent yet span considerably different regions of radial space by introducing primitive GTOs whose exponents are $\frac{diff}{3}$, $\frac{diff}{9}$, $\frac{diff}{27}$, etc.

Once one has specified an atomic orbital basis for each atom in the molecule, the LCAO-MO procedure can be used to determine the C $_{,i}$ coefficients that describe the

occupied and virtual orbitals in terms of the chosen basis set. It is important to keep in mind that the basis orbitals are <u>not</u> themselves the true orbitals of the isolated atoms; even the proper atomic orbitals are combinations (with atomic values for the C_i coefficients) of the basis functions. For example, in a minimal-basis-level treatment of the Carbon atom, the 2s atomic orbital is formed by combining, with opposite sign to achieve the radial node, the two CGTOs (or STOs); the more diffuse s-type basis function will have a larger C_i, coefficient in the 2s atomic orbital. The 1s atomic orbital is formed by combining the same two CGTOs but with the same sign and with the less diffuse basis function having a larger C_i i coefficient. The LCAO-MO-SCF process itself determines the magnitudes and signs of the C_i.

VI. The Roothaan Matrix SCF Process

The matrix SCF equations introduced earlier

$$F_{\mu}$$
, $C_{i} = i$ S_{μ} , C_{i}

must be solved both for the occupied and virtual orbitals' energies $_{i}$ and C $_{,i}$ values. Only the occupied orbitals' C $_{,i}$ coefficients enter into the Fock operator

but both the occupied and virtual orbitals are solutions of the SCF equations. Once atomic basis sets have been chosen for each atom, the <u>one- and two-electron integrals</u> appearing in F_{μ} , must be evaluated. Doing so is a time consuming process, but there are presently several highly efficient computer codes which allow such integrals to be computed for s, p, d, f, and even g, h, and i basis functions. After executing one of these '<u>integral packages</u>' for a basis with a total of N functions, one has available (usually on the computer's hard disk) of the order of N²/2 one-electron and N⁴/8 two-electron integrals over these atomic basis orbitals (the factors of 1/2 and 1/8 arise from permutational symmetries of the integrals). When treating extremely large atomic orbital basis sets (e.g., 200 or more basis functions), modern computer programs calculate the requisite integrals but never store them on the disk. Instead, their contributions to F_{μ} , are accumulated 'on the fly' after which the integrals are discarded.

To begin the SCF process, one must input to the computer routine which computes F_{μ} , <u>initial 'guesses'</u> for the C_i values corresponding to the occupied orbitals. These initial guesses are typically made in one of the following ways:

1. If one has available C $_{,i}$ values for the system from an SCF calculation performed earlier at a nearby molecular geometry, one can use these C $_{,i}$ values to begin the SCF process.

2. If one has C _{,i} values appropriate to fragments of the system (e.g., for C and O atoms if the CO molecule is under study or for CH_2 and O if H_2CO is being studied), one can use these.

3. If one has no other information available, one can carry out one iteration of the SCF process in which the two-electron contributions to F_{μ} , are ignored (i.e., take F_{μ} , $= < \mu |h| >$) and use the resultant solutions to F_{μ} , $C_{,i} = i \quad S_{\mu}$, $C_{,i}$ as initial guesses for the C_i. Using only the one-electron part of the Hamiltonian to determine initial values for the LCAO-MO coefficients may seem like a rather severe step; it is, and the resultant C_i values are usually far from the converged values which the SCF process eventually produces. However, the initial C_i obtained in this manner have proper symmetries and nodal patterns because the one-electron part of the Hamiltonian has the same symmetry as the full Hamiltonian.

Once initial guesses are made for the C $_{,i}$ of the occupied orbitals, the full $F_{\mu,}$ matrix is formed and new $_i$ and C $_{,i}$ values are obtained by solving F_{μ} , C $_{,i} = _i$ S_{μ} , C $_{,i}$. These new orbitals are then used to form a new F_{μ} , matrix from which new $_i$ and C $_{,i}$ are obtained. This iterative process is carried on until the $_i$ and C $_{,i}$ do not vary (within specified tolerances) from iteration to iteration, at which time one says that the SCF process has converged and reached self-consistency.

As presented, the Roothaan SCF process is carried out in a fully <u>ab initio</u> manner in that all one- and two-electron integrals are computed in terms of the specified basis set; no experimental data or other input is employed. As described in Appendix F, it is possible to introduce approximations to the coulomb and exchange integrals entering into the Fock matrix elements that permit many of the requisite F_{μ} , elements to be evaluated in terms of experimental data or in terms of a small set of 'fundamental' orbital-level coulomb interaction integrals that can be computed in an <u>ab initio</u> manner. This approach forms the basis of so-called 'semi-empirical' methods. Appendix F provides the reader with a brief introduction to such approaches to the electronic structure problem and deals in some detail with the well known Hückel and CNDO- level approximations.

VII. Observations on Orbitals and Orbital Energies

A. The Meaning of Orbital Energies

The physical content of the Hartree-Fock orbital energies can be seen by observing that $F_i = i_i$ implies that i_i can be written as:

$$i = \langle i | F | i \rangle = \langle i | h | i \rangle + j(\text{occupied}) \langle i | J_j - K_j | i \rangle$$

$$= \langle i | h | i \rangle + j(\text{occupied}) [J_{i,j} - K_{i,j}].$$

In this form, it is clear that $_{i}$ is equal to the average value of the kinetic energy plus coulombic attraction to the nuclei for an electron in $_{i}$ plus the sum over all of the spinorbitals occupied in $_{i}$ of coulomb minus exchange interactions between $_{i}$ and these occupied spin-orbitals. If $_{i}$ itself is an occupied spin-orbital, the term [$J_{i,i} - K_{i,i}$] disappears and the latter sum represents the coulomb minus exchange interaction of $_{i}$ with all of the N-1 other occupied spin-orbitals. If $_{i}$ is a virtual spin-orbital, this cancellation does not occur, and one obtains the coulomb minus exchange interaction of $_{i}$ with all N of the occupied spin-orbitals.

In this sense, the orbital energies for occupied orbitals pertain to interactions which are appropriate to a total of N electrons, while the orbital energies of virtual orbitals pertain to a system with N+1 electrons. It is this fact that makes SCF virtual orbitals not optimal (in fact, not usually very good) for use in subsequent correlation calculations where, for instance, they are used, in combination with the occupied orbitals, to form polarized orbital pairs as discussed in Chapter 12. To correlate a pair of electrons that occupy a valence orbital requires double excitations into a virtual orbital that is not too dislike in size. Although the virtual SCF orbitals themselves suffer these drawbacks, the space they span can indeed be used for treating electron correlation. To do so, it is useful to recombine (in a unitary manner to preserve orthonormality) the virtual orbitals to 'focus' the correlating power into as few orbitals as possible so that the multiconfigurational wavefunction can be formed with as few CSFs as possible. Techniques for effecting such reoptimization or improvement of the virtual orbitals are treated later in this text.

B.. Koopmans' Theorem

Further insight into the meaning of the energies of occupied and virtual orbitals can be gained by considering the following model of the vertical (i.e., at fixed molecular geometry) detachment or attachment of an electron to the original N-electron molecule: 1. In this model, <u>both</u> the parent molecule and the species generated by adding or removing an electron are treated at the single-determinant level.

2. In this model, the Hartree-Fock orbitals of the parent molecule are used to describe both the parent and the species generated by electron addition or removal. It is said that such a model neglects '<u>orbital relaxation</u>' which would accompany the electron addition or removal (i.e., the reoptimization of the spin-orbitals to allow them to become appropriate to the daughter species).

Within this simplified model, the energy difference between the daughter and the parent species can be written as follows ($_k$ represents the particular spin-orbital that is added or removed):

1. For electron detachment:

$$\begin{split} E^{N-1} - E^{N} &= < | \ 1 \ 2 \ \cdots \ k-1 \cdots \ N | \ H \ | \ 1 \ 2 \ \cdots \ k-1 \cdots \ N | > - \\ &< | \ 1 \ 2 \ \cdots \ k-1 \ k \cdots \ N | \ H \ | \ | \ 1 \ 2 \ \cdots \ k-1 \ k \cdots \ N | > \\ &= \ - \ <_k \ | \ h \ | \ _k > - \ \ _{j=(1,k-1,k+1,N)} \ [\ J_{k,j} - K_{k,j} \] = - \ _k \ ; \end{split}$$

2. For electron attachment:

$$\begin{split} E^{N} - E^{N+1} &= < \mid \ _{1 \ 2 \ \cdots \ N} \mid H \mid \ _{1 \ 2 \ \cdots \ N} \mid > - \\ &< \mid \ _{1 \ 2 \ \cdots \ N} \mid k \mid H \mid \mid \ _{1 \ 2 \ \cdots \ N} \mid k \mid > \\ &= \ _{-} <_{k} \mid h \mid \ _{k} > - \ \ _{j=(1,N)} \left[\ J_{k,j} - K_{k,j} \ \right] = - \ _{k} \, . \end{split}$$

So, within the limitations of the single-determinant, frozen-orbital model set forth, the ionization potentials (IPs) and electron affinities (EAs) are given as the negative of the occupied and virtual spin-orbital energies, respectively. This statement is referred to as Koopmans' theorem (T. Koopmans, Physica <u>1</u>, 104 (1933)); it is used extensively in quantum chemical calculations as a means for estimating IPs and EAs and often yields results that are at least qualitatively correct (i.e., ± 0.5 eV).

C. Orbital Energies and the Total Energy

For the N-electron species whose Hartree-Fock orbitals and orbital energies have been determined, the total SCF electronic energy can be written, by using the Slater-Condon rules, as:

 $E = \ _{i(occupied)} < \ _{i} \mid h \mid \ _{i} > + \ _{i > j(occupied)} \left[\ J_{i,j} - K_{i,j} \ \right].$

For this same system, the sum of the orbital energies of the occupied spin-orbitals is given by:

$$i(\text{occupied}) \quad i = i(\text{occupied}) < i \mid h \mid i > i$$

+ i,j(occupied) [$J_{i,j} - K_{i,j}$].

These two seemingly very similar expressions differ in a very important way; the sum of occupied orbital energies, when compared to the total energy, double counts the coulomb minus exchange interaction energies. Thus, within the Hartree-Fock approximation, the sum of the occupied orbital energies is <u>not</u> equal to the total energy. The total SCF energy can be computed in terms of the sum of occupied orbital energies by taking one-half of $_{i(occupied)}$ i and then adding to this one-half of $_{i(occupied)} < i |h| i >$:

 $E = 1/2 [i_{(occupied)} < i | h | i > + i_{(occupied)} i].$

The fact that the sum of orbital energies is not the total SCF energy also means that as one attempts to develop a qualitative picture of the energies of CSFs along a reaction path, as when orbital and configuration correlation diagrams are constructed, one must be careful not to equate the sum of orbital energies with the total configurational energy; the former is higher than the latter by an amount equal to the sum of the coulomb minus exchange interactions.

D. The Brillouin Theorem

The condition that the SCF energy $< | _{1} \dots _{N} | H | _{1} \dots _{N} | >$ be stationary with respect to variations $_{i}$ in the occupied spin-orbitals (that preserve orthonormality) can be written

$$<|_{1}\dots _{i}\dots _{N}|H|_{1}\dots _{i}\dots _{N}|P=0.$$

The infinitesimal variation of $_{i}$ can be expressed in terms of its (small) components along the other occupied $_{i}$ and along the virtual $_{m}$ as follows:

$$_{i} = _{j=occ} U_{ij j} + _{m} U_{im m}.$$

When substituted into $|_{1}$... $|_{i}$, the terms $|_{j'=occ}|_{1}$... $|_{N}|U_{ij}$ vanish because $|_{j}$ already appears in the original Slater determinant $|_{1}$... $|_{N}|$, so $|_{1}$... $|_{j}$... | contains $|_{j}$ twice. Only the sum over virtual orbitals remains, and the stationary property written above becomes

$$_{\rm m} U_{\rm im} < |_{1} \dots |_{\rm m} |_{\rm N} |_{\rm N} |_{\rm I} |_{1} \dots |_{\rm N} |_{\rm N} > = 0.$$

The Slater-Condon rules allow one to express the Hamiltonian matrix elements appearing here as

$$<\mid_{1}\ldots \mid_{m}\ldots \mid_{N}\mid H\mid_{1}\ldots \mid_{i}\ldots \mid_{N}\mid > = <\mid_{m}\mid h\mid_{i} > + \mid_{j=occ, i} <\mid_{m}\mid [J_{j}-K_{j}]\mid_{i} >,$$

which (because the term with j=i can be included since it vanishes) is equal to the following element of the Fock operator: $\langle m|F| \rangle = |i| m = 0$. This result proves that Hamiltonian matrix elements between the SCF determinant and those that are singly excited relative to the SCF determinant vanish because they reduce to Fock-operator integrals connecting the pair of orbitals involved in the 'excitation'. This stability property of the SCF energy is known as the Brillouin theorem (i.e., that $|1|_{i=N}|$ and $|1| \dots |m| \dots |N|$ have zero Hamiltonian matrix elements if the s are SCF orbitals). It is exploited in quantum chemical calculations in two manners:

(i) When multiconfiguration wavefunctions are formed from SCF spin-orbitals, it allows one to neglect Hamiltonian matrix elements between the SCF configuration and those that are 'singly excited' in constructing the secular matrix.

(ii) A so-called generalized Brillouin theorem (GBT) arises when one deals with energy optimization for a multiconfigurational variational trial wavefunction for which the orbitals and C_I mixing coefficients are simultaneously optimized. This GBT causes certain Hamiltonian matrix elements to vanish, which, in turn, simplifies the treatment of electron correlation for such wavefunctions. This matter is treated in more detail later in this text.