

Fundamentals of Theoretical Organic Chemistry

Lecture 4.

1.2.4. One- and Many-Electronic wave functions (multiplicity)

The wave functions of a given state for an N-particle (i.e. n-electron) system describes the distribution or configuration of these N-particles in the given state, i.e.

$$\Phi(1,2,\dots,N) \quad 1.2.4-1. \text{ eq.}$$

A special case of an N-particle wave function involves the case $N = 1$

$$\Phi(1) = u(1) \quad 1.2.4-2. \text{ eq.}$$

where the one electron function u has a special importance as defined by equation {1.2.4—2. eq.}. It should be recalled that elementary particles have spin characteristic. Depending on the type of particle we have restrictions on the wave functions as given in Table 1.2.4-1.

Table 1.2.4-1 Spin symmetry restrictions

Particles	Spin	Description		
Examples	Type	Eigenvalue	Statistics	Wave function
$\alpha, h\nu$	Bosons	$n\hbar$	Bose-Einstein	Symmetric
e, p, n	Fermions	$(n/2)\hbar$	Fermi-Dirac	Anti-symmetric

For electrons (e), protons (p) and neutrons (n) the one electron wave function u of equation 1.2.4—2. eq. should include both a space function ϕ and spin function (α or β).

$$u(1) = \begin{cases} \phi_1(1)\alpha(1) \\ \phi_1(1)\beta(1) \end{cases} \quad 1.2.4-3. \text{ eq.}$$

The one-electron function u is called spin-orbital while the ϕ is a spatial orbital. The product of ϕ and α or β implies the simultaneous probability of space orbital ϕ and spin α or β .

Many-electron wave functions may be constructed as products of one-electron functions or spin-orbitals.

$$\Phi(1,2,\dots,N) = u_1(1), u_2(2), \dots, u_N(N) \quad 1.2.4-4. \text{ eq.}$$

Since electrons are indistinguishable any permutation of the labels 1.2.4—4. eq. should also be a satisfactory wave functions thus yielding $N!$ terms. For this reason, all fully permuted many-electron wave functions must be renormalized through dividing by $\sqrt{N!}$

$$\Phi(1,2,\dots,N) = \hat{A}\{u_1(1), u_2(2), \dots, u_N(N)\} = \frac{1}{\sqrt{N!}} \sum_{\nu=1}^{N!} (-1)^\nu \hat{P}_\nu u_1(1) u_2(2) \dots u_N(N)$$

1.2.4—5. eq.

which equivalent to the formula for a determinant.

$$\Phi(1,2,\dots,N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} u_1(1) & \cdots & u_N(1) \\ \vdots & & \vdots \\ u_1(N) & \cdots & u_N(N) \end{vmatrix}$$

1.2.4—6. eq.

The spin-orbitals may be replaced by the product of a space and spin function from which it follows that an orbital may appear only twice in a determinantal wave function once with α -spin and once with β -spin. Otherwise the determinant would vanish as it will be identically zero.

$$\Phi(1,2,\dots,2M) = \frac{1}{\sqrt{(2M)!}} \begin{vmatrix} \phi_1(1)\alpha(1) & \phi_1(1)\beta(1) & \cdots & \phi_M(1)\alpha(1) & \phi_M(1)\beta(1) \\ \vdots & \vdots & & \vdots & \vdots \\ \phi_1(2M)\alpha(2M) & \phi_1(2M)\beta(2M) & \cdots & \phi_M(2M)\alpha(2M) & \phi_M(2M)\beta(2M) \end{vmatrix}$$

1.2.4—7. eq.

This determinantal form of wave function is referred to as a ‘‘Slater determinant’’.

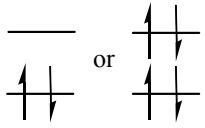
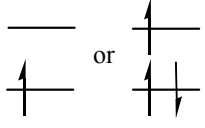
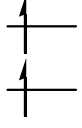

The concepts of multiplicity of the electronic system need to be introduced in connection with the construction of many electron wave functions. Multiplication (m) is related to the total spin: $|S|$ of the electronic system.

$$m = 2|S| + 1$$

1.2.4—8. eq.

In this fashion the multiplicity is increasing with the number of unpaired electrons the electronic system contains as shown in Table 1.2.4-2

Table 1.2.4-2 Relationship between spin, multiplicity and quantum description

Number of odd electrons	S	m	Name	Occupancy	Number of possible wave functions
0	0	1	Singlet		1
1	1/2	2	Doublet		2
2	1	3	Triplet		3
3	1 1/2	4	Quadruplet		4

The multiplicity shows the numbers of possible wave functions the electronic system may have. These wave functions give identical energy values in the absence of the magnetic field but the degenerate energy values do split up in the presence of an external magnetic field (B) as shown in Figure 1.2.4—1

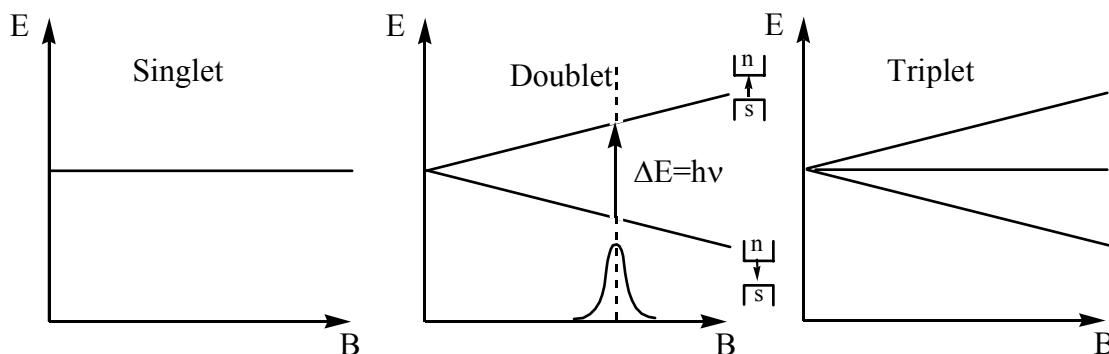
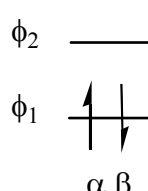


Figure 1.2.4—1 Variation of energy levels with increasing magnetic field strength (B) for system of different multiplicities

We perhaps should note, at this stage that electron spin resonance (ESR) or paramagnetic of resonance (EPR) spectroscopy is related to the splitting up these energy levels. The singlet and triplet wave functions may be illustrated for a two electron system such as He or H₂.

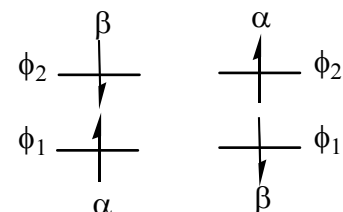
The ground electronic configuration is represented by the single Slater determinant Φ_0 (1,2)

$$\Phi_0(1,2) = \frac{1}{\sqrt{2}} \begin{vmatrix} \phi_1(1)\alpha(1) & \phi_1(1)\beta(1) \\ \phi_1(2)\alpha(2) & \phi_1(2)\beta(2) \end{vmatrix}$$


1.2.4—9. eq.

which incorporates only the lowest MO (ϕ_1).

Single substitution involves the replacement of ϕ_1 in one of the 2 columns by ϕ_2 but, for a closed electronic shell each MO occurs twice so that there are two possibilities for replacement. These involve substitution in the column containing a spin and in the column having the β spin associated with the same spatial function

$$\begin{vmatrix} \phi_1(1)\alpha(1) & \phi_2(1)\beta(1) \\ \phi_1(2)\alpha(2) & \phi_2(2)\beta(2) \end{vmatrix} \text{ and } \begin{vmatrix} \phi_2(1)\alpha(1) & \phi_1(1)\beta(1) \\ \phi_2(2)\alpha(2) & \phi_1(2)\beta(2) \end{vmatrix}$$


1.2.4—10. eq.

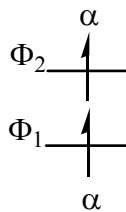
Neither of these determinants has physical significance but with a linear combination of the two, for the description of both types of spin arrangement may be equally important. The linear combinations, having negative and positive signs, yield wave functions of singlet and triplet multiplicity respectively.

$${}^1\Phi_1(1,2) = \frac{1}{\sqrt{2}} \left\{ \frac{1}{\sqrt{2}} \begin{vmatrix} \phi_1(1)\alpha(1) & \phi_2(1)\beta(1) \\ \phi_1(2)\alpha(2) & \phi_2(2)\beta(2) \end{vmatrix} - \frac{1}{\sqrt{2}} \begin{vmatrix} \phi_2(1)\alpha(1) & \phi_1(1)\beta(1) \\ \phi_2(2)\alpha(2) & \phi_1(2)\beta(2) \end{vmatrix} \right\}$$

1.2.4—11. eq.

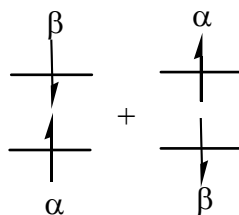
This is a wave function of a singlet excited electron configuration. For the triplet excited states we have these for 3 distinctly different wave functions, which nevertheless are energetically degenerate in the absence of an external magnetic field.

$${}^3\Phi_1(1,2) = \frac{1}{\sqrt{2}} \begin{vmatrix} \phi_1(1)\alpha(1) & \phi_2(1)\beta(1) \\ \phi_1(2)\alpha(2) & \phi_2(2)\beta(2) \end{vmatrix} \text{ i.e.}$$



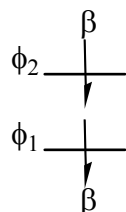
1.2.4—12. eq.

$${}^3\Phi_1(1,2) = \frac{1}{\sqrt{2}} \left\{ \frac{1}{\sqrt{2}} \begin{vmatrix} \phi_1(1)\alpha(1) & \phi_2(1)\beta(1) \\ \phi_1(2)\alpha(2) & \phi_2(2)\beta(2) \end{vmatrix} + \frac{1}{\sqrt{2}} \begin{vmatrix} \phi_2(1)\alpha(1) & \phi_1(1)\beta(1) \\ \phi_2(2)\alpha(2) & \phi_1(2)\beta(2) \end{vmatrix} \right\} \text{ i.e.}$$



1.2.4—13. eq.

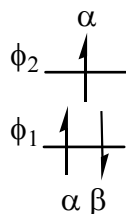
$${}^3\Phi_1(1,2) = \frac{1}{\sqrt{2}} \begin{vmatrix} \phi_2(1)\alpha(1) & \phi_1(1)\beta(1) \\ \phi_2(2)\alpha(2) & \phi_1(2)\beta(2) \end{vmatrix} \text{ i.e.}$$



1.2.4—14. eq.

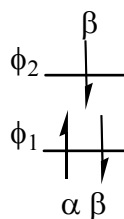
The doublet state can be demonstrated on a 3 electron system such as Li.

$${}^2\Phi_1(1,2,3) = \frac{1}{\sqrt{6}} \begin{vmatrix} \phi_1(1)\alpha(1) & \phi_1(1)\beta(1) & \phi_2(1)\alpha(1) \\ \phi_1(2)\alpha(2) & \phi_1(2)\beta(2) & \phi_2(2)\alpha(2) \\ \phi_1(3)\alpha(3) & \phi_1(3)\beta(3) & \phi_2(3)\alpha(3) \end{vmatrix} \text{ i.e.}$$



1.2.4—15. eq.

$${}^2\Phi_1(1,2,3) = \frac{1}{\sqrt{6}} \begin{vmatrix} \phi_1(1)\alpha(1) & \phi_1(1)\beta(1) & \phi_2(1)\beta(1) \\ \phi_1(2)\alpha(2) & \phi_1(2)\beta(2) & \phi_2(2)\beta(2) \\ \phi_1(3)\alpha(3) & \phi_1(3)\beta(3) & \phi_2(3)\beta(3) \end{vmatrix} \text{ i.e.}$$

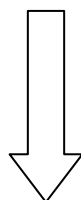


1.2.4—16. eq.

1.2.5. The Hartree-Fock method and its limitations (Correlation Energy)

The Schrödinger equation for a many electron system includes the many-electron Hamiltonian operator which describes all the electronic interactions in the field of all the positively charged atomic nuclei. Thus, the Hamiltonian operator is the mathematical equivalent of the chemical molecular structure. The electronic Schrödinger equation also includes the many-electron wave function from which the total electron distribution may be calculated. The Hartree Fock method converts this single many-electron wave equation to many one-electron wave equations called the Hartree-Fock wave equations.

$$\text{One many - electron wave - equation : } \hat{H}(1,2,\dots)\Psi(1,2,\dots) = E(1,2,\dots)\Psi(1,2,\dots) \quad 1.2.5—1. \text{ eq.}$$



Variational Theorem
(using a Slater determinant w.f)

$$\text{Many one - electron wave - equations} \left\{ \begin{array}{l} \hat{F}(1)\Phi_1(1) = \varepsilon_{11}(1)\Phi_1(1) \\ \hat{F}(1)\Phi_2(1) = \varepsilon_{22}(1)\Phi_2(1) \\ \vdots \\ \hat{F}(1)\Phi_N(1) = \varepsilon_{NN}(1)\Phi_N(1) \end{array} \right. \quad 1.2.5—2. \text{ eq.}$$

In this conversion the many electron wave function is constructed as a single Slater-determinant and the variational theorem is applied. The Fock operator, \hat{F} describes all the interactions of a single electron in the field of all the other electrons as well as the atomic nuclei.

Converting a Hartree-Fock equation to its integrated form

$$F^{\Phi}_{ij} = \int \phi_j \hat{F} \phi_i d\tau = \varepsilon_{ij} \int \phi_j \phi_i d\tau = \varepsilon_{ij} S^{\Phi}_{ij} \quad 1.2.5-3. \text{ eq.}$$

we can deal with actual numbers since now we have definite integrals. This expression can be generalized in the form of a matrix equation

$$\underline{\underline{F}}^{\phi} = \underline{\underline{S}}^{\phi} \underline{\underline{\varepsilon}} \quad 1.2.5-4. \text{ eq.}$$

Where the $i^{\text{th}}, j^{\text{th}}$ elements of $\underline{\underline{S}}^{\phi}$ defined as $\langle \phi_i | \phi_j \rangle$. For an orthonormal set of functions $\{\phi_i\}$ $\underline{\underline{S}}^{\phi} = 1$ (i.e the unit matrix). Consequently $\underline{\underline{F}}^{\phi} = \underline{\underline{\varepsilon}}$ will be a diagonal matrix. Transformation of AO(η) to MO(ϕ) for a system with 2M electrons and N different AO we obtain:

$$\langle \phi | \equiv \underbrace{(\phi_1 \phi_2 \cdots \phi_M)}_{\text{occupied}} \overbrace{(\phi_{M+1} \cdots \phi_N)}^{\text{HOMO LUMO virtual}} = (\eta_1, \eta_2, \cdots, \eta_N) \begin{pmatrix} c_{11} & c_{12} & \cdots & c_{1M} & c_{1M+1} & \cdots & c_{1N} \\ c_{21} & c_{22} & \cdots & c_{2M} & c_{2M+1} & \cdots & c_{2N} \\ \vdots & \vdots & & \vdots & \vdots & & \vdots \\ c_{N1} & c_{N2} & \cdots & c_{NM} & c_{NM+1} & \cdots & c_{NN} \end{pmatrix} \quad 1.2.5-5. \text{ eq.}$$

Coefficients for the M doubly occupied MO

Necessary to generate M doubly occupied MO or in vector notation:

$$\langle \phi | = \langle \eta | \underline{\underline{C}} \quad 1.2.5-6. \text{ eq.}$$

where $\underline{\underline{C}}$ is transforming matrix converting AOs to MOs. After substituting this expansion of the MOs in terms of AOs our integrated Hartree-Fock equation assumes the following form:

$$\underline{\underline{\varepsilon}} = \underline{\underline{C}}^+ \underline{\underline{F}}^{\eta} \underline{\underline{C}} \quad 1.2.5-7. \text{ eq.}$$

$$\begin{pmatrix} \varepsilon_{11} & 0 & 0 & 0 \\ 0 & \varepsilon_{22} & 0 & 0 \\ 0 & 0 & \ddots & 0 \\ 0 & 0 & 0 & \varepsilon_{NN} \end{pmatrix} = \begin{pmatrix} c_{11} & c_{21} & \cdots & c_{N1} \\ c_{12} & c_{22} & \cdots & c_{N2} \\ \vdots & \vdots & & \vdots \\ c_{1N} & c_{2N} & \cdots & c_{NN} \end{pmatrix} \begin{pmatrix} F_{11}^{\eta} & F_{12}^{\eta} & \cdots & F_{1N}^{\eta} \\ F_{21}^{\eta} & F_{22}^{\eta} & \cdots & F_{2N}^{\eta} \\ \vdots & \vdots & & \vdots \\ F_{N1}^{\eta} & F_{N2}^{\eta} & \cdots & F_{NN}^{\eta} \end{pmatrix} \begin{pmatrix} c_{11} & c_{12} & \cdots & c_{1N} \\ c_{21} & c_{22} & \cdots & c_{2N} \\ \vdots & \vdots & & \vdots \\ c_{N1} & c_{N2} & \cdots & c_{NN} \end{pmatrix}$$

Diagonal Real symmetric

From the coefficients of the M doubly occupied MO we may generate the density matrix(ρ) which is a symmetric matrix

$$\underline{\underline{C}} \underline{\underline{C}}^\dagger = \underline{\underline{\rho}}$$

$$\begin{pmatrix} c_{11} & c_{12} & \cdots & c_{1M} \\ c_{21} & c_{22} & \cdots & c_{2M} \\ \vdots & \vdots & & \vdots \\ c_{N1} & c_{N2} & \cdots & c_{NM} \end{pmatrix} \begin{pmatrix} c_{11} & c_{21} & \cdots & c_{N1} \\ c_{12} & c_{22} & \cdots & c_{N2} \\ \vdots & \vdots & & \vdots \\ c_{1M} & c_{2M} & \cdots & c_{NM} \end{pmatrix} = \begin{pmatrix} \rho_{11} & \rho_{12} & \cdots & \rho_{1N} \\ \rho_{21} & \rho_{22} & \cdots & \rho_{2N} \\ \vdots & \vdots & & \vdots \\ \rho_{N1} & \rho_{N2} & \cdots & \rho_{NN} \end{pmatrix}$$

$\underbrace{\hspace{10em}}_{N \times M}$
 $\underbrace{\hspace{10em}}_{M \times N}$
 $\underbrace{\hspace{10em}}_{\substack{N \times N \\ \text{Real_symmetric}}}$

1.2.5—8. eq.

The elements of the Fock matrix F_{ij}^η are evaluated from the one-electron integrals (h_{ij}^η) and the two-electron integrals, the Coulombs (J_{ij}^η) and the exchange (K_{ij}^η) integrals, as well as the elements of the density matrix (ρ)

$$F_{ij}^\eta = h_{ij}^\eta + 2J_{ij}^\eta - K_{ij}^\eta = h_{ij}^\eta + \sum_{k=1}^N \sum_{l=1}^N [2\{\eta_i \eta_j | \eta_k \eta_l\} - \{\eta_i \eta_k | \eta_j \eta_l\}] \rho_{kl} \quad (2)$$

1.2.5—9. eq.

The total electronic energy (E) can also be calculated from the same components

$$E = 2 \sum_{i=1}^N \sum_{j=1}^N \rho_{ij}^{(1)} h_{ij}^\eta + \sum_{i=1}^N \sum_{j=1}^N \rho_{ij}^{(1)} [2J_{ij}^\eta - K_{ij}^\eta]$$

1.2.5—10. eq.

Let us illustrate the overall process for the case of the H₂ molecule. We begin with a non-orthogonal (but normalized) set of AO $\{\eta\}$ which are transformed directly to an orthonormal set of MO $\{\phi\}$. This is performed in two steps. The first involves orthogonalization; this transformation introduces “kinks” in the orbitals at the position of the other nuclei so that the product of any two functions (e.g. $\chi_1 \chi_2$) of the orthogonalized orbitals (OO) contains equal; “negative and positive contributions” which cancel upon integration.

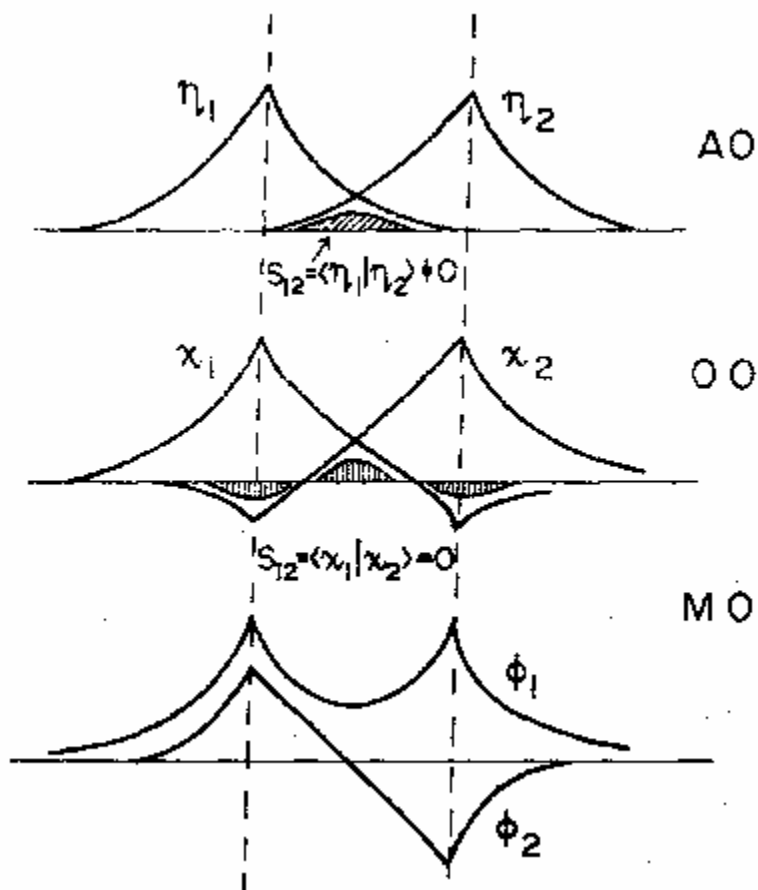


Figure 1.2.5—1 A schematic illustration for the sequence transformation of AO to MO.

Transformation from the OO basis set (χ) to the MO basis set (ϕ) involves an orthogonal transformation which is mathematically equivalent to the rotation of one N-dimensional vector space into another without changing the orthonormality:

$$\begin{array}{ccccc}
 & \overline{\quad} & \underline{\underline{C}} & \overline{\quad} & \\
 \eta & \xrightarrow{\underline{\underline{V}}} & \chi & \xrightarrow{\underline{\underline{U}}} & \phi \\
 \text{AO} & & \text{OO} & & \text{MO}
 \end{array}$$

eq. 1.2.5—11

This two process requires a separation of the $\underline{\underline{C}}$ matrix into two separate matrices: $\underline{\underline{V}}$ and $\underline{\underline{U}}$. Matrix $\underline{\underline{V}}$ performs the orthogonalization of η and $\underline{\underline{U}}$ rotates χ into ϕ . (For real orbitals $\underline{\underline{U}}$ is an orthogonal matrix, otherwise it is unitary.)

In matrix notation the process is written as

$$\phi = \underline{\eta C} = \underline{\eta V U} = \underline{\chi U}$$

eq. 1.2.5—12

and in details

$$\begin{aligned}
 (\phi_1 \quad \phi_2 \quad \cdots \quad \phi_n) &= (\eta_1 \quad \eta_2 \quad \cdots \quad \eta_n) \underbrace{\begin{pmatrix} c_{11} & c_{12} & \cdots & c_{1n} \\ c_{21} & c_{22} & \cdots & c_{2n} \\ \vdots & \vdots & & \vdots \\ c_{n1} & c_{n2} & \cdots & c_{nn} \end{pmatrix}}_{N \times M} = \\
 (\eta_1 \quad \eta_2 \quad \cdots \quad \eta_n) &\underbrace{\begin{pmatrix} v_{11} & v_{12} & \cdots & v_{1n} \\ v_{21} & v_{22} & \cdots & v_{2n} \\ \vdots & \vdots & & \vdots \\ v_{n1} & v_{n2} & \cdots & v_{nn} \end{pmatrix}}_{N \times M} \underbrace{\begin{pmatrix} u_{11} & u_{12} & \cdots & u_{1n} \\ u_{21} & u_{22} & \cdots & u_{2n} \\ \vdots & \vdots & & \vdots \\ u_{n1} & u_{n2} & \cdots & u_{nn} \end{pmatrix}}_{N \times M} = \\
 (\chi_1 \quad \chi_2 \quad \cdots \quad \chi_n) &\underbrace{\begin{pmatrix} u_{11} & u_{12} & \cdots & u_{1n} \\ u_{21} & u_{22} & \cdots & u_{2n} \\ \vdots & \vdots & & \vdots \\ u_{n1} & u_{n2} & \cdots & u_{nn} \end{pmatrix}}_{N \times M}
 \end{aligned}$$

eq. 1.2.5—13

It is easy to illustrate the vector analogy of orbital transformations for the case of H₂ because of the two dimensional nature of the problem. The vector analogy is valid for larger molecules even though a pictorial description of the process is impossible.

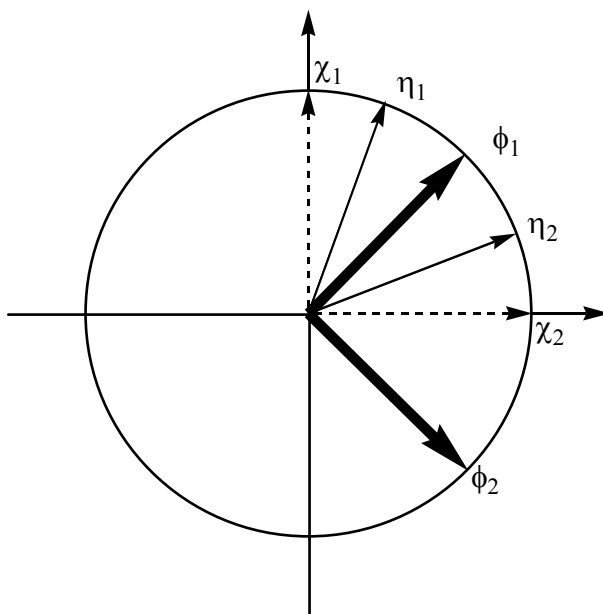


Figure 1.2.5—2 A vector model of AO and MO orbitals associated with H₂

The atomic orbitals $\{\eta\}$ of the expansion are called the basis set and its size is noted by the letter N . Of course, N can be large and, in general, with increasing N , i.e. with increasing basis set size, we improve the result of the calculations. In the limiting sense we generate MOs at the Hartree-Fock limit (HFL) which produces the energy of the Hartree-Fock limit (E_{HFL})

$$\phi_i^{\text{HFL}} = \lim_{N \rightarrow \infty} \sum_{j=1}^N C_{ij} \eta_j$$

1.2.5—14. eq.

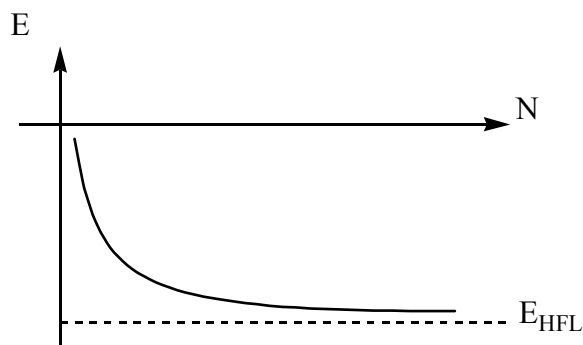


Figure 1.2.5—3 Convergence to the Hartree-fock limit (HFL) with increasing basis set size(N).

The energy obtained in this way does not correspond to the experimental energy because we did use only a single Slater determinant for our many-electron wave function and because our Hamilton Operator was non-relativistic. The gap between the HFL and the non-relativistic limit (NRL) is called the electron correlation or correlation energy (E_{corr})

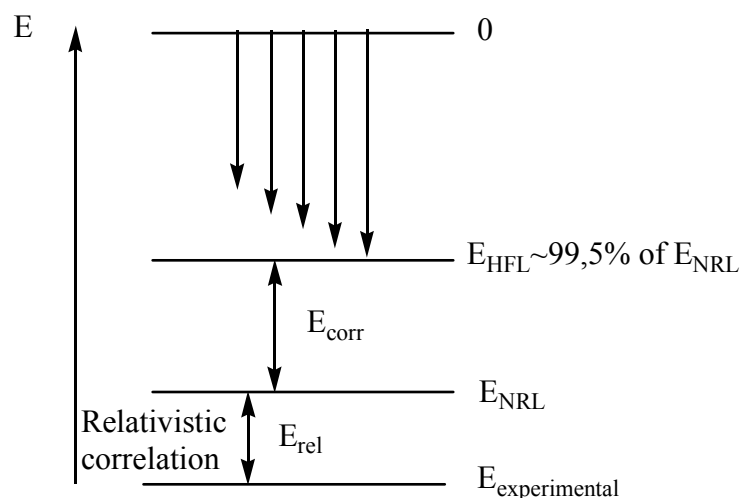


Figure 1.2.5—4 The concept of correlation energy and other components.

The correlation energy is a systematic error due to double occupancy. As a result of occupancy we allow two electrons (both negatively charged) to occupied the same region of space (the same MO) thus, their motion is not correlated.

For example for NH_3 :

$$\begin{array}{r} E_{\text{HFL}} = -56.225 \text{ hartree} \\ E_{\text{NRL}} = -56.554 \text{ hartree} \\ \hline E_{\text{corr}} = 0.229 \text{ hartree} \end{array}$$

the E_{corr} is 0.4% of E_{NRL} thus E_{HFL} recovers 99.6% of the E_{NRL} . Yet this 0.4% corresponds to

$$E_{\text{corr}} = 0.229 \times 627.51 = 143.7 \text{ kcal/mol} = 601.2 \text{ kJ/mol} \quad \text{eq. 1.2.5—15}$$

which is larger than the bond dissociation energy (BDE) of an N-H bond not mentioning the pyramidal inversion of NH_3 which is about

$$\text{BDE}(\text{N-H}) = 5 \text{ kcal/mol} = 20.9 \text{ kJ/mol} \quad \text{eq. 1.2.5—16}$$

As it was clear from the equations presented at the early part of the chapter the Fock matrix (F) was a function of electron density

$$F = f(\rho) \quad \text{1.2.5—17. eq.}$$

Yet the electron density, ρ , was to be computed from the coefficient matrix \underline{C} . Since \underline{C} is expected as one of the solutions of the Hartree-Fock problem we need to know the solution in order to set up the problem to be solved. Thus the solution is to be obtained iteratively. In the traditional approach (c.f. Figure 1.2.5—5) molecular integrals were to be computed initially and they were to be stored and used over and over in each cycle of the iterative process

Nowadays the integral evaluation in terms of Gaussian (GTF) is faster than reading from a disk therefore they are evaluated directly at each cycle of the iteration. In this way the calculation is more accurate since for storage the last several digits after the decimal point had to be eliminated.

Calculating the Fock matrix elements from several millions of integrals lead to some accumulated numerical errors. Consequently, this “direct SCF” computation, illustrated in the next flowchart below.
(Figure 1.2.5—6)

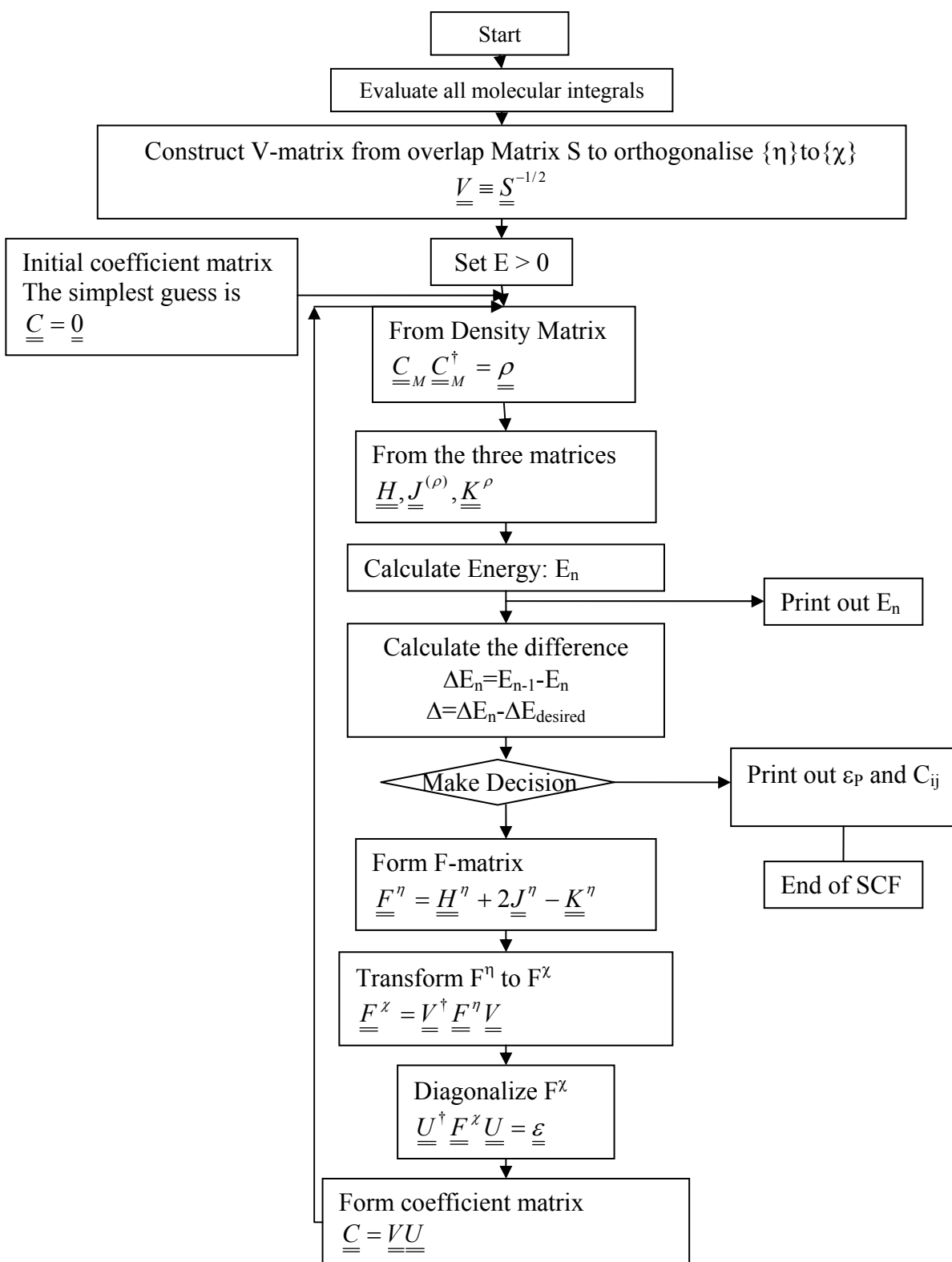


Figure 1.2.5—5 Flowchart for the iterative traditional Self-Consistent-Field (SCF) method. †

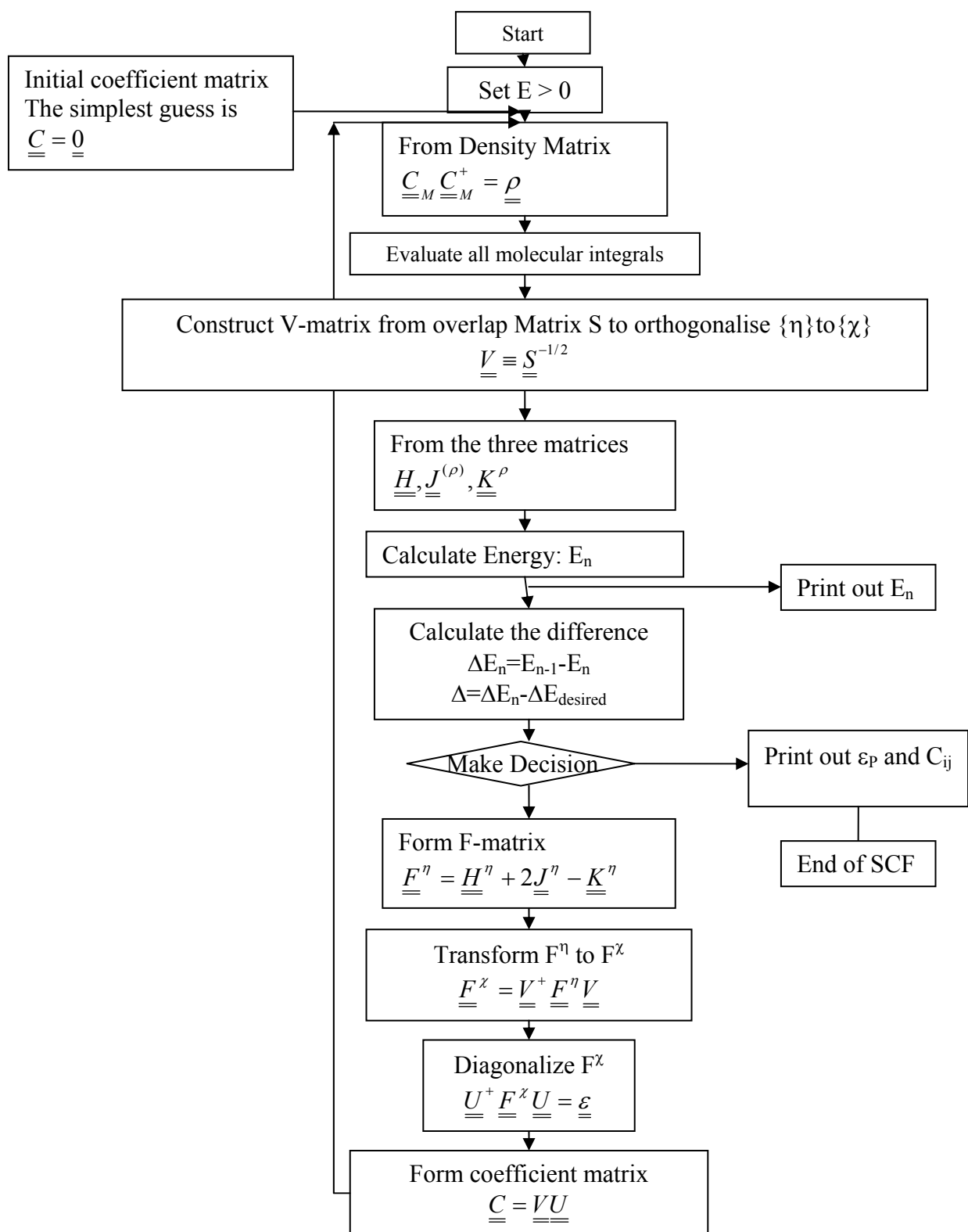


Figure 1.2.5—6 Flowchart for the iterative Direct Self-Consistent-Field (SCF) method.

1.2.6. Post-Hartree-Fock methods

Post Hartree-Fock methods

Although the correlation energy (E_{corr}) usually amounts to less than 1% of the total experimental energy of a molecule, for many systems this amount nevertheless is larger than or comparable to the energies associated with physical or chemical phenomena. Thus for ammonia the correlation energy is estimated to be 206.5 kcal/mole (0.329 hartree) but the barrier to pyramidal inversion is only 5.8 kcal/mole and the proton affinity is 206.4 kcal/mole. It is generally believed that these quantities are reproduced fairly accurately at the HFL, i.e. that there exists a cancellation of errors. [For the two quantities mentioned this means that the $E_{\text{Corr}}(\text{planar}) \approx E_{\text{Corr}}(\text{pyramidal})$ and $E_{\text{Corr}}(\text{NH}_4^+) \approx E_{\text{Corr}}(\text{NH}_3)$.] For phenomena in which electrons are unpaired (e.g. excitation, dissociation) the correlation energy cannot be ignored and it is necessary to go beyond the HFL. A wave function that does that is referred to as a correlated wave function and such a process referred to as Post Hartree-Fock methods. Its aim is to recover at least a portion of this systematic error.

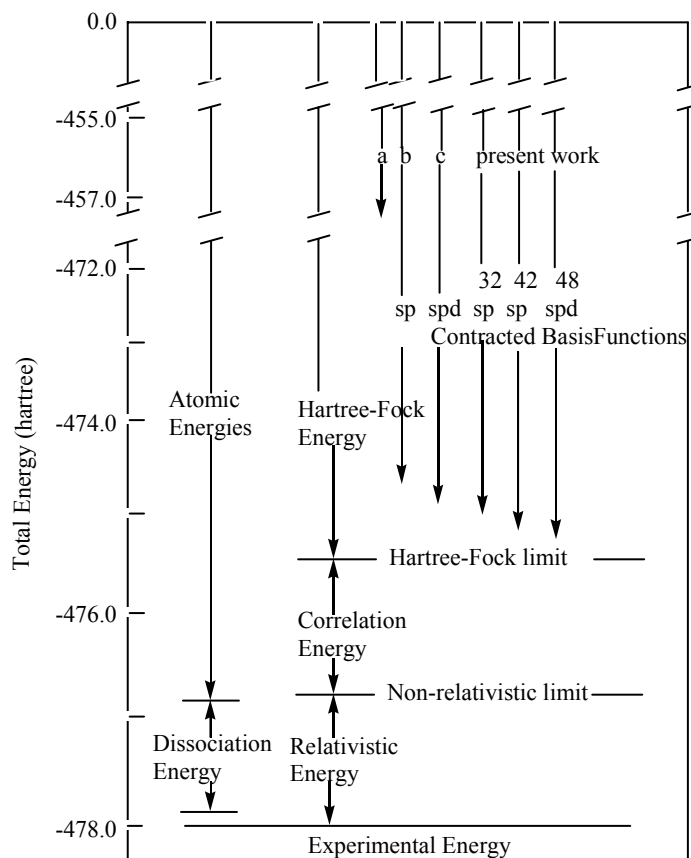


Figure 1.2.6—1 A breakdown of total energy for episulfide ($\text{C}_2\text{H}_4\text{S}$) to experimentally observable and quantum chemically calculable fraction. The results obtained by the different atomic basis sets are shown on the upper right-hand side of the figure.

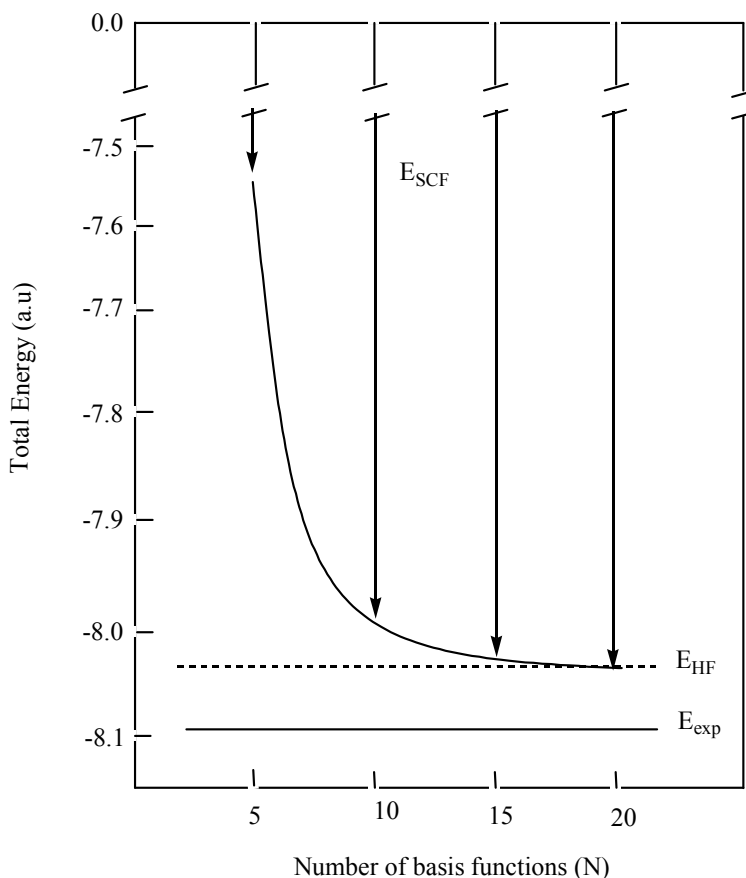


Figure 1.2.6—2 The convergence of E_{SCF} to E_{HF} with increasing basis set size for the ground state of LiH. [cf. *J. Chem. Phys.* 44, 1849 (1966)]

From a mathematical standpoint the correlation energy is the result of a systematic error of in the wave function computed by the HF method.

This error is the result of our construction of a $2M \times 2M$ determinantal wave function.

$$\Phi_0(1,2,\dots,2M) = \det | \phi_1(1)\alpha(1)\phi_1(2)\beta(2)\dots\phi_M(2M-1)\alpha(2M-1)\phi_M(2M)\beta(2M) |$$

1.2.6—1. eq.

Using only M m.o. from the very extensive set of N m.o. ($N > M$) obtained from the HF-SCF. This is illustrated in 1.2.6—2. eq. where $\{\eta\}$ is the set of AO and $\{\phi\}$ represents the set of MO in column vector notation

$$\left(\underbrace{\phi_1, \phi_2, \dots, \phi_M, \dots, \phi_N}_{\text{M doubly occupied}} \right) = (\eta_1, \eta_2, \dots, \eta_N) = \begin{pmatrix} a_{11} & a_{12} & \dots & a_{1N} \\ a_{21} & a_{22} & \dots & a_{2N} \\ \vdots & \vdots & & \vdots \\ a_{M1} & a_{M2} & \dots & a_{MN} \\ \vdots & \vdots & & \vdots \\ a_{N1} & a_{N2} & \dots & a_{NN} \end{pmatrix}$$

1.2.6—2. eq.

Even if $\{\eta\}$ had represented a complete set [i.e. $\{\phi\}$ would also represent a complete set] the Slater determinant is computed from much less than the complete set of $\{\phi\}$. For example we might have employed 50 basis functions ($N=50$) for a calculation on NH_3 even though there are only 5 occupied MO ($N=5$). The remaining 45 empty MO would be discarded (cf. the partitioning in equation 1.2.6—2. eq. in constructing the Slater determinant).

From a physical standpoint the correlation problem is related to the position of one electron with respect to any other.

The non-relativistic Hamiltonian includes the reciprocal values of all r_{ij}

$$H(1,2,\dots) = \sum_{i=1} h(i) + \sum_{i,j} \frac{1}{r_{ij}}$$

1.2.6—3. eq.

The terms in r_{ij}^{-1} constituting the mutual repulsion between electrons i and j .

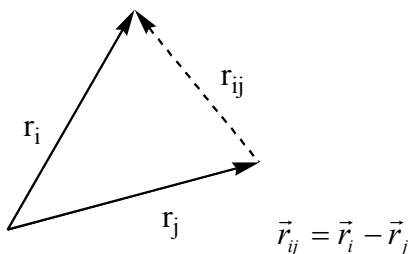


Figure 1.2.6—3 Vector model of electron-electron repulsion

Since $r_{ij}^{-1} \rightarrow \infty$ as $r_{ij} \rightarrow 0$ the approach of two electrons, to each other, is not favourable and each is surrounded by a „Coulomb hole”. As r_i approaches r_j (i.e. $r_{ij} \rightarrow 0$) as shown in Figure 1.2.5—5) the motion of the two electron becomes „correlated”.

Since the Pauli principle has been incorporated in the wave function in the form of an antisymmetrised orbital product (Slater determinant):

$$\Phi_0(1,2,\dots) = \det \left| \overbrace{\phi_1(1)\alpha(1)}^{u_1(1)} \overbrace{\phi_1(2)\beta(2)}^{u_2(2)} \dots \right| = \hat{A}[u_1(1)u_2(2)\dots]$$

1.2.6—4. eq.

In this expression (where $u_i(i)$ represents for the i^{th} spin-orbital), the probability of finding two electrons at the same position is zero or in other words the 2-electrons probability density vanishes

for $r_i = r_j$ in the case of two electrons having the same spin (“Fermi hole”). For this reason the correlation problem can be thought of as the search for proper treatment of the “Coulomb” correlation between electrons having antiparallel spin. The correlation between electrons of antiparallel spin may involve numerous interactions.

One way to deal with the correlation problem is to include a function of r_{12} explicitly in the total wave function which will not permit r_{12} to become zero. Thus instead of equation 1.2.6—4. eq. we may write, for a two electron system, the following expression

$$\Psi(1,2) = \hat{A}[u_1(1)u_2(2)]f(1,2) \quad 1.2.6—5. \text{ eq.}$$

For systems that contain more than 2 electrons this explicit correlated wave function is not practical and the correlation problem is usually tackled by some implicit method. The most general “implicit” method (where r_{ij} is not included explicitly in the wave function) is known as the method of configuration interaction (CI).

The previously unused (virtual) molecular orbital are substituted into the expression for Φ_0 (this is possible because of the nodal properties of these virtual MO are appropriate which is a consequence of their orthogonality to the occupied MO)

$$\Phi_0 = [u_1(1) \dots u_i(i) \dots u_j(j) \dots u_N(N)] \quad 1.2.6—6. \text{ eq.}$$

Substitution may take place at 1, 2 or more sites. Thus, for a triple substitution, the wave function associated with the new configuration would be

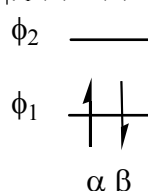
$$\Phi_u(1,2,\dots,N) = \Phi_{\dots i \dots j \dots k}^{\dots a \dots b \dots c} = \hat{A}[u_1(1) \dots u_a(i) \dots u_b(j) \dots u_c(k) \dots u_N(N)] \quad 1.2.6—7. \text{ eq.}$$

Where spin orbital a, b, c have replaced spin-orbitals i, j, k. The exact wave function is then written as the linear combination of these different substituted configurations.

$$\Psi^{CI} = C_0 \Phi_0^{SCF} + \sum_{i,a} C_i^a \Phi_i^a + \sum_{ij,ab} C_{ij}^{ab} \Phi_{ij}^{ab} + \sum_{ijk,abc} C_{ijk}^{abc} \Phi_{ijk}^{abc} + \dots \quad 1.2.6—8. \text{ eq.}$$

where the set of many electron functions $\{\Phi\}$ represents configurations. The general approach will be illustrated for the case of H_2 (a 2 orbital -2 electron problem).

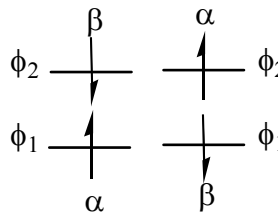
The ground electronic configuration is represented by the single Slater determinant $\Phi(1, 2)$.

$$\Phi_0(1,2) = \frac{1}{\sqrt{2}} \begin{vmatrix} \phi_1(1)\alpha(1) & \phi_1(1)\beta(1) \\ \phi_1(2)\alpha(2) & \phi_1(2)\beta(2) \end{vmatrix} \text{ i.e.}$$


1.2.6—9. eq.

Which incorporates only the lowest MO(ϕ_1).

Single substitution involves the replacement of ϕ_1 in one of the 2 columns by ϕ_2 but, for a closed electronic shell each MO occurs twice so that there are two possibilities for replacement. These involve substitution in the column containing α spin and in the column the β spin associated with the same spatial function

$$\begin{vmatrix} \phi_1(1)\alpha(1) & \phi_2(1)\beta(1) \\ \phi_1(2)\alpha(2) & \phi_2(2)\beta(2) \end{vmatrix} \text{ and } \begin{vmatrix} \phi_2(1)\alpha(1) & \phi_1(1)\beta(1) \\ \phi_2(2)\alpha(2) & \phi_1(2)\beta(2) \end{vmatrix} \text{ i.e.}$$


1.2.6—10. eq.

Neither of these determinants has physical significance but with linear combination of the two both types of spin arrangement may be equally important. The linear combinations having positive and negative signs yield wave function of triplet and singlet multiplicity respectively.

$${}^3\Phi_1(1,2) = \frac{1}{\sqrt{2}} \left\{ \frac{1}{\sqrt{2}} \begin{vmatrix} \phi_1(1)\alpha(1) & \phi_2(1)\beta(1) \\ \phi_1(2)\alpha(2) & \phi_2(2)\beta(2) \end{vmatrix} + \frac{1}{\sqrt{2}} \begin{vmatrix} \phi_2(1)\alpha(1) & \phi_1(1)\beta(1) \\ \phi_2(2)\alpha(2) & \phi_1(2)\beta(2) \end{vmatrix} \right\}$$

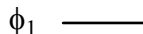
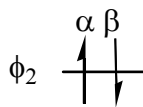
1.2.6—11. eq.

The double substituted wavefunction has the following form:

$$\Phi_1(1,2) = \frac{1}{\sqrt{2}} \left\{ \frac{1}{\sqrt{2}} \begin{vmatrix} \phi_1(1)\alpha(1) & \phi_2(1)\beta(1) \\ \phi_1(2)\alpha(2) & \phi_2(2)\beta(2) \end{vmatrix} - \frac{1}{\sqrt{2}} \begin{vmatrix} \phi_2(1)\alpha(1) & \phi_1(1)\beta(1) \\ \phi_2(2)\alpha(2) & \phi_1(2)\beta(2) \end{vmatrix} \right\}$$

1.2.6—12. eq.

$$\Phi_2(1,2) = \frac{1}{\sqrt{2}} \begin{vmatrix} \phi_2(1)\alpha(1) & \phi_2(1)\beta(1) \\ \phi_2(2)\alpha(2) & \phi_2(2)\beta(2) \end{vmatrix}$$



eq. 1.2.6—13

The three configurations Φ_0 , Φ_1 , Φ_2 are now treated as the many electron basis for the calculation of a state wave function (just as atomic orbital constituted the one electron basis functions for the calculation of MO). For example, for the ground electronic state Ψ_0 we may write

$$\Psi_0(1,2) = C_{00}\Phi_0(1,2) + C_{10}\Phi_1(1,2) + C_{20}\Phi_2(1,2)$$

1.2.6—14. eq.

However, since one may obtain as many as 3 state functions from three basis functions, we write

$$[\Psi_0(1,2)\Psi_1(1,2)\Psi_2(1,2)] = [\Phi_0(1,2)\Phi_1(1,2)\Phi_2(1,2)] \begin{pmatrix} c_{00} & c_{01} & c_{02} \\ c_{10} & c_{11} & c_{12} \\ c_{20} & c_{21} & c_{22} \end{pmatrix}$$

1.2.6—15. eq.

This linear transformation can be viewed as the rotation of a 3 dimensional vector space into another 3-dimensional vector space, as illustrated graphically in the next figure.

Computation of the coefficient matrix, $\underline{\underline{C}}$, constitutes an eigen-value problem.

$$\underline{\underline{C}}^\dagger \underline{\underline{H}} \underline{\underline{C}} = \underline{\underline{C}}^\dagger \underline{\underline{S}} \underline{\underline{C}} \underline{\underline{E}}$$

1.2.6—16. eq.

In which $\underline{\underline{H}}$ is the matrix representative of the many-electron Hamiltonian $H(1,2 \dots)$ over the configurational basis chosen (including single, double, ... etc. substitution). The matrix is shown in
1.2.6—17. eq.

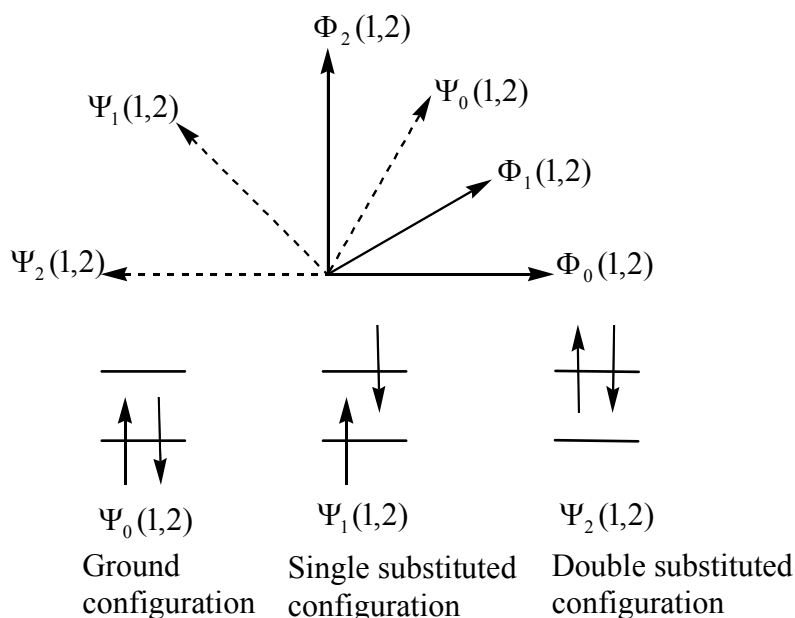


Figure 1.2.6—4A vector model depicting the linear transformation of a 3D configurational vector space (configurations → states) for the case of H_2

$$\underline{\underline{H}} = \begin{vmatrix} \overbrace{\langle \Phi_0 | \hat{H} | \Phi_0 \rangle}^{H.F.} & \overbrace{\langle \Phi_0 | \hat{H} | \Phi_0 \rangle \dots}^{Singlesubstitution} & \overbrace{\langle \Phi_0 | \hat{H} | \Phi_{ij}^{ab} \rangle \dots}^{Doublesubstitution} \\ \langle \Phi_i^a | \hat{H} | \Phi_i^a \rangle \dots & \langle \Phi_i^a | \hat{H} | \Phi_{ij}^{ab} \rangle \dots & \langle \Phi_{ij}^{ab} | \hat{H} | \Phi_{ij}^{ab} \rangle \dots \end{vmatrix}$$

1.2.6—17. eq.

It is readily appreciated that the size of the many electron basis, i.e. the number of configurations that can be constructed, increases greatly as the number of available orbitals increases. For examples a full CI (including all possible substitutions for 10 electrons and 10 MO involves the order of 10^5 configurations.) This means that the $\underline{\underline{H}}$ matrix has a dimension 100,000 x 100,000 and it is not possible to diagonalise such a matrix. It is evident that CI calculations cannot be performed in general, but only in some limited way.

An example of the use of CI in a conformational problem is the calculation of barrier heights discussed below. The orbitals used for CH_3^- and NH_3 are shown schematically in Figure 1.2.6—5. These MO yielded a total of 5260 configurations. From this set 911 were selected by perturbation theory. A CI calculation performed over these 911 configurations, lowered the total (i.e. those that contribute most) at every geometry (solid curve) because if the same 911 configuration were used at each geometry the barrier became anomalously high (broken curve) as indicated in Figure 1.2.6—6. The overall energy change is shown in Figure 1.2.6—7 together with some computed results which are also summarized in Table 1.2.6-1

In closing it might be appropriate to take this opportunity to emphasize that most of the chemist's language is based on a HF scheme (i.e. double occupancy, distribution of electrons in

molecular orbitals, excitation of electrons by jumping from one orbital to different one, atomic configurations like $1s^2, 2s^2, 2s^6, 3s^2, 3p^5$ for chlorine, etc.).

The language “works” because the HF wave function is a very good approximation (99.5%) but it is not everything. All that chemical language vanishes and means nothing when a more sophisticated wave function is used. It is like a “Law of Complementarities”: The simpler the wave function, the easier to interpret and explain qualitatively the conclusions; on the other hand the better the wave function, the more it becomes pure mathematical entity and it is more difficult to talk about in a lecture room.

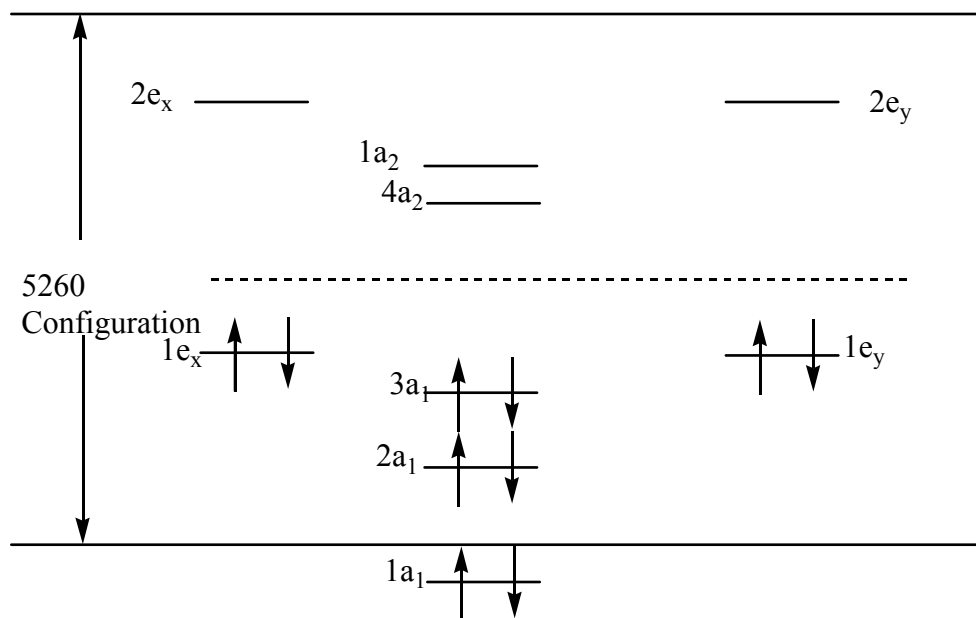


Figure 1.2.6—5 Molecular orbitals involved in the CI calculations of CH_3^- and NH_3

Table 1.2.6-1 A comparison of SCF and CI energies of NH₃

Author	Code for Figure 1	Reference in J. Chem. Phys.	Basis ^a	Method ^b	E(Hartree)
Kaldor <i>et al.</i>	a	45, 888 (1966)	13 STO	SCF	-56.0992
Clementi	b	46, 3851 (1967)	53 GTF	SCF	-56.0108
Ritchie <i>et al.</i>	c	47, 564 (1967)	60 GTF	SCF	-56.2015
Clementi <i>et al.</i>	d	49, 4916 (1968)	67 GTF	SCF	-56.2109
Rauk <i>et al.</i>	e	52, 4133 (1970)	91 GTF	SCF	-56.2219
Stevens	f	55, 1729 (1971)	37 STO	SCF	-56.2211
Kari <i>et al.</i>	g	56, 4337 (1972)	73 GTF	SCF	-56.2117
				CI	-56.3747

^aSTO Slater type orbitals; GTF Gaussian type functions

^bSCF Self-Consistent Field; CI Configuration interaction (911 configurations)

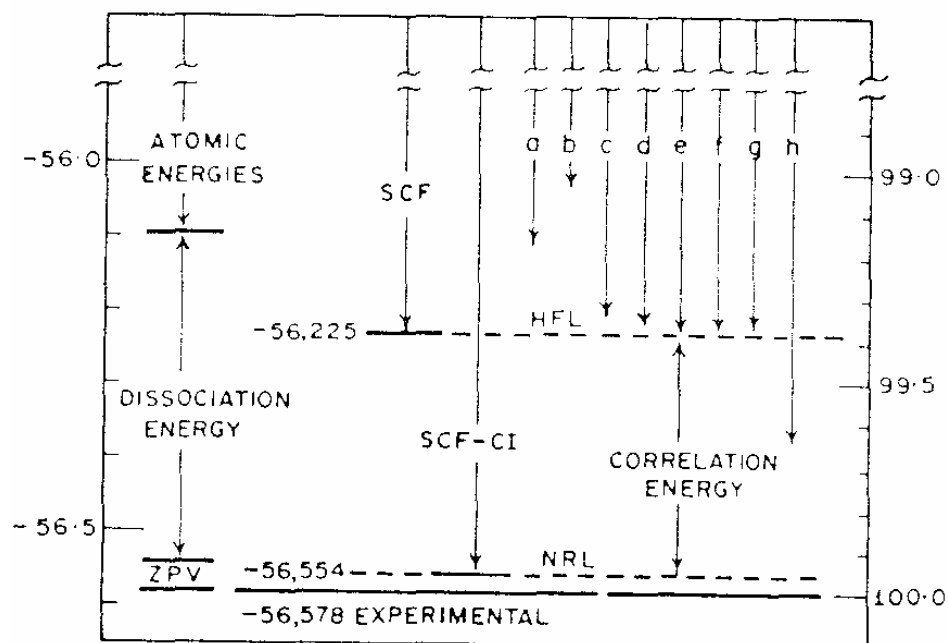


Figure 1.2.6—7A breakdown of the total energy for NH₃ to experimentally observable and quantum chemically calculable fractions. The computed energy values (a-h) are summarized in Table VIII-4

As it was outlined in the case of CI calculations carried out for: CH_3^- and $:\text{NH}_3$ the selection of configurations are crucial since the number of configurations that may be generated are astronomical. The 2nd, 3rd or higher order Moller-Plesset (MP2, MP3,...) methods and the coupled cluster (CC) methods achieve that goal rather successfully.

Density functional theory

Energy is a function of the electron density (ρ) which is in turn a function of the geometry

$$E = F[\rho(\text{Geometry})] \quad 1.2.6\text{---}18. \text{ eq.}$$

In the Hartree-Fock formalism

$$E = \underbrace{T[\rho]}_{\text{Kinetic Energy}} + \underbrace{V_{ne}[\rho] + V_{ee}[\rho]}_{\text{Potential Energy}} \quad 1.2.6\text{---}19. \text{ eq.}$$

$$E = \underbrace{T[\rho] + V_{ne}[\rho]}_{h[\rho]} + \underbrace{V_{ee}[\rho]}_{2J[\rho] - K[\rho]}$$

Figure 1.2.6—8

The first two terms are written as a one electron contribution $h[\rho]$ while the third term is split into Coulomb ($J[\rho]$) and Exchange ($K[\rho]$) contributions

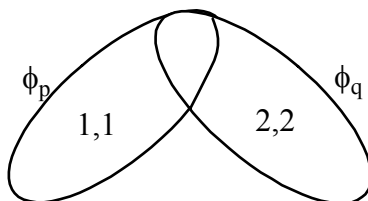
$$E = h[\rho] + 2J[\rho] - K[\rho] \quad 1.2.6\text{---}20. \text{ eq.}$$

$$J_{pq}[\rho] = \left\langle \phi_p(1)\phi_q(2) \left| \frac{1}{r_{1,2}} \right| \phi_q(2)\phi_p(1) \right\rangle = \sum_k^N \sum_l^N \left\langle \phi_p(1)\eta_k(2) \left| \frac{1}{r_{1,2}} \right| \eta_l(2)\phi_p(1) \right\rangle \rho_{kl}(2)$$

eq. 1.2.6—21

$$J_{pq}[\rho] = \sum_i^N \sum_j^N \sum_k^N \sum_l^N \rho_{ij}(1) \left\langle \eta_i(1)\eta_k(2) \left| \frac{1}{r_{1,2}} \right| \eta_l(2)\eta_j(1) \right\rangle \rho_{kl}(2)$$

eq. 1.2.6—22

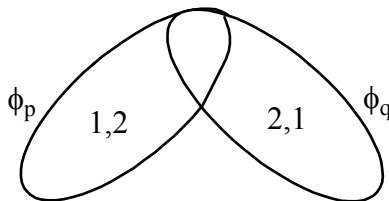


$$K_{pq}[\rho] = \left\langle \phi_p(1)\phi_p(2) \left| \frac{1}{r_{1,2}} \right| \phi_q(2)\phi_q(1) \right\rangle = \sum_j^N \sum_k^N \left\langle \phi_p(1)\eta_j(2) \left| \frac{1}{r_{1,2}} \right| \eta_k(2)\phi_q(1) \right\rangle \rho_{kl}(2)$$

eq. 1.2.6—23

$$J_{pq}[\rho] = \sum_i^N \sum_j^N \sum_k^N \sum_l^N \rho_{ij}(1) \left\langle \eta_i(1)\eta_j(2) \left| \frac{1}{r_{1,2}} \right| \eta_k(2)\eta_l(1) \right\rangle \rho_{kl}(2)$$

eq. 1.2.6—24



The exchange terms are more problematic than the Columbic term because both electrons are in both orbitals. In 1930 Dirac suggested on the basis of homogeneous electron gas model the following relationship which is frequently referred to as the “local density approximation” (LDA)

$$E_{exchange}^{LDA} = E_x^{LDA} = -\frac{3}{2} \left(\frac{3}{4\pi} \right)^{\frac{1}{3}} \int \rho^{\frac{4}{3}} dr$$

1.2.6—25. eq.

Becke modified this expression in 1988 to the following

$$E_x^{B88} = E_x^{LDA} - b \int \frac{\rho^{\frac{4}{3}} x^2}{(1 + 6b \sinh^{-1} x)} dr$$

1.2.6—26. eq.

In which b is an empirically fitted parameter and x contains the gradient of the electron density ($\nabla \rho$). However, exchange, E_x , is only one of the problems; correlation energy (E_{Corr}) is another

$$E = h[\rho] + 2J[\rho] - \underbrace{K[\rho] + E_c[\rho]}_{E_{xc}}$$

1.2.6—27. eq.

The last two terms are usually combined as exchange (x) correlation(c) contribution denoted by E_{xc} .

Various methods as well as their mixed or “hybrid” versions are in used nowadays. All of these include a variety of fitted parameters which were optimized to give the best fit of the calculated energy to molecular atomization energies. In all these methods instead of the LDA approximation Local Spin Density Approximation (LSDA) is used in which electrons of α and β spins are assigned to different orbital thus correcting the uniform electron gas model.

$$E_{xc}^{B3PW} = E_x^{LSDA} + C_0(E_x^{HF} - E_{xc}^{LSDA}) + C_x E_x^{B88} + E_c^{VWN} + C_c \Delta E_c^{PW}$$

1.2.6—28. eq.

or

$$E_{xc}^{B3LYP} = (1 - a_0 - a_x) E_x^{LSDA} + a_0 E_x^{HF} + a_x E_x^{B88} + (1 - a_c) E_c^{VWN} + a_c E_c^{LYP}$$

1.2.6—29. eq.

Where E_x^{HF} is the HF exchange energy functional, E_x^{B88} is the Becke 88 exchange functional mentioned above, E_c^{VWN} is the Vosko, Wilk, Nusair function (VWN, or Slater VWN, SVWN function), which forms part of the accurate functional for the homogeneous electron gas of the LDA and the LSDA and E_c^{LYP} is the LYP correlation functional. Note that E_x and E_c of the last three terms are gradient corrected.