APPENDIX

Hartree-Fock Method

The energy and many properties of a stationary state of a molecule can be obtained by solution of the Schrodinger partial differential equation,

$$H\psi = E\psi$$

Here H is Hamiltonian operator, a differential operatoe representing the total energy. E is the numerical value of the energy of the state. ψ is the wave function, the square of the wave function, ψ^2, is interpreted as a measure of the probability distribution of the particles within the molecule.

The Hamiltonian H, like the energy inclassical mechanics, is the sum of kinetic and potential parts,

$$H = T + V$$

The kinetic energy operator T is a sum of differential operators,

$$T = -\frac{h^2}{8\pi^2}\sum_i \frac{1}{m_i}\left(\frac{\partial^2}{\partial x_i^2}+\frac{\partial^2}{\partial y_i^2}+\frac{\partial^2}{\partial z_i^2}\right)$$

The sum is over all particles I (nuclei + electrons) and m_i is the mass of particle i. h is Planck's constant. The potential energy operator is the coulomb interaction,

$$V = \sum_{i<j}\sum\left(\frac{e_i e_j}{r_{ij}}\right)$$

where the sum is over distinct pairs of particles (i,j) with electric charges e_i, e_j separated by a distance r_{ij}. For electrons, $e_i = -e$, while for anucleus with atomic number Z_i, $e_i = +Z_i e$.

Semiempirical Calculations

Due to their greatly increased requirement for central processing unit time and storage space in the computer memory, ab initio quantum chemical methods are limited in their practical applicability. The approximate quantum chemical methods require significantly less computational resources. Semiempirical methods are based on the Roothaan-Hall .

In ab initio calculations all elements of the Fock matrix are calculated, irrespective of whether the basis functions ϕ_μ, ϕ_ν, ϕ_σ and ϕ_λ are on the same atom, on atoms that are bounded or on atoms that are not formally boned. The semiempirical methods consider the Fock matrixelement in three groups: $F_{\mu\mu}$ (the diagonal elements); $F_{\mu\nu}$ (where ϕ_μ and ϕ_ν are on the same atom, and ϕ_σ and ϕ_λ are on different atoms).

The greatest proportion of the time required to perform ab inito Hartree-Fock SCF calculation is invariably calculating and manipulating integrals. The most obvious way to reduce the computational effort is to neglect or approximate some of these integrals. Semiempirical methods achieve this is part by explicit considering into the nuclear core. The overlap matrix, S, is set equal to identity matrix, I. The main implication of this is that the Roothaan-Hall equations are simplified: FC = SCF becomes FC = CE.

The NDDO (neglect of diatomic differential overlap), this theory neglects differential overlap between atomic orbital on different atoms.

The elimination of three- and four-centre integrals greatly reduces the time and storage requirements for an NDDO calculation (which now increase as the square of the number of atoms) relative to that for a full Hartree-Fock treatmemt.

Three levels of NDDO theory are included in SPARTAN'S SEMI EMPIRICAL module: MNDO Modified Neglect of Diatomic Overlap

AM1 Austin Model 1

PM 3 MNDO Parametrization Method 3

In all of these formalisms, only the valence electrons are considered. The one-electron terms are given by,

$$H_{\mu\nu}^{core} = U_{\mu\nu} - Z_A \sum_{B \neq A} Z_B \langle \mu\nu / \delta\delta \rangle$$

Here, μ and ν are located on atom A and the summation is over all other atoms. $U_{\nu\nu}$ is related to the binding energy of an electron in atomic orbital ν, and is determined from spectroscopic data. $U_{\mu\nu}$ is set to zero for $\nu \neq \mu$. The second term in Equation represents the attraction on an electron on atom A from the nuclear framework. The two center integral involves only the s function on atom B.ZA is the charge of atom A without its valence electrons.

All one-centre, two-electronintegrals $(\upsilon\upsilon / \mu\mu)$ and $(\upsilon\mu / \upsilon\mu)$ are fitted to spectroscopic data. The two-centre, two electron repulsion integrals $(\upsilon\mu / \lambda\sigma)$ are approximated by classical multipole-multipole charge interactins between atoms Aand B The multipole chrge separations within an atomare treated as adjustable parameters, i.e. optimized to fit the experimentally derived one-centre integrals.

The $\beta_{\mu\lambda}$ terms appearing in the Fock matrix are the one-electron, two-center core resonance integrals and are approximated as,

$$\beta_{\rho\lambda} = \frac{\beta_\rho + \beta_\lambda}{2} S_{\rho\lambda}$$

Where S is the overlap integral between Slater orbitals and and are adjustable parameters optimized using experimental thermo chemical data for simple molecules. Because all of the adjustable parameters are rooted in experimental data, these methods are known as semiempirical. As in ab initio Hartree-Fock calculations, an SCF procedure is used to converge on a density matrix, and the electronic energy.

The three methods differ only in the core-replusion terms (they also differ in the detailed parameterization). Core repulsion includes nuclear repulsion and non-valence electron-electron repulsion, which are not explicitly considered in the calculation of the electronic energy. In the MNDO model, the core repulsion energy is given by,

$$E^{CR} = \sum_{A\neq B}\sum_{B\neq A} Z_A Z_B \left\langle \delta(A) / \delta(B) \right\rangle \left(e^{-\sigma_a E_{AB}} + e^{-\sigma_B E_{AB}} \right)$$

where is the intermolecular distance and   and   are adjustable parameters fit to give the correct empirical behavior. Details are provided in the original papers. MNDO tends to overestimate core repulsion between two atoms at van der Waals distances. For this reason, the AM1 model was developed.

The AM1 and PM3 are based on MNDO (the name derives from the fact that PM3 is the third parametrization of MNDO, AM1 being considered the sedond). In AM1 a sum of Gaussians is employed to better represent the cor-core repulsion behavior at Vab der Waals distances just outside bonding distances. PM3 uses a similar core repulsion function, but differs in the parametrization procedure.

Molecular Orbital Theory

Molecular orbital theory is an approach to molecular quantum mechanics which uses one-electron functions or orbitals to approximate the full wave function. A molecular orbital, $\psi(x, y, z)$, is a function of the Cartesian coordinates x, y, z of a single electron. The spin coordinates, ξ, also has to be included. This coordinate takes on one of two possible values $\left(\pm\frac{1}{2}\right)$, and measures the spin angular momentum component along the z axis in units of $h/2\pi$.

The simplest type of wave function appropriate for the description of an n-electron system would be in the form of a product of spin orbitals,

$$\psi_{product} = \chi_1(1)\chi_2(2)\ldots\chi_n(n)$$

where $\chi_i(i)$ is written for $\chi_i(x_i, y_i, z_i, \xi_i)$, the spin orbital of electron i. The spin orbitals may be arranged in a determinantal wave function.

$$\psi_{\det er\min ant} = \begin{vmatrix} \chi_1(1) & \chi_2(2) & \cdots & \chi_n(1) \\ \chi_1(2) & \chi_2(2) & \cdots & \chi_n(2) \\ \vdots & \vdots & \vdots & \vdots \\ \chi_1(n) & \chi_2(n) & \cdots & \chi_n(n) \end{vmatrix}$$

Here the elements of the first row of the determinant contain assignations of electron 1 to all the spin orbitals $\chi_1, \chi_2, \ldots, \chi_n$, the second row all possible assignations of electron 2, and so forth.

Some further properties of molecular orbital wave functions are wort noting. It is possible to force the orbitals to be orthogonal to each other, that is,

$$S_{ij} = \int \psi_i^* \psi_j dxdydz$$

This can be accomplished without changing the value of the whole wave function by mixing columns of the determinant. The spin functions, α and β, are orthogonal by integration over spin space (actually summation over the two possible values of ξ):

$$\sum_{\xi}\alpha(\xi)\beta(\xi)=\alpha\left(+\frac{1}{2}\right)\beta\beta\left(+\frac{1}{2}\right)+\alpha\left(-\frac{1}{2}\right)\beta\beta\left(-\frac{1}{2}\right)=0$$

Molecular orbitals may be normalized, that is

$$S_{ij}=\int\psi_i^*\psi_j dxdydz=1$$

By multiplication of the individual by a constant, normalization corresponds to the requirement that the probability of finding the electron anywhere in space is unity. Given $S_{ij}=1$, the determinantal wave function may be normalized by multiplication by a factor of $(n!)^{-1/2}$, that is,

$$\int\cdots\int\Psi*\Psi d\tau_1\tau_2\cdots d\tau_n=1$$

The determinantal wave function may be normalized by multiplication by a factor of $(n!)^{-1/2}$. We can write down a full many-electron molecular orbital wave function for the closed-shell ground state of a molecule with n(even) electrons, doubly occupying n/2 orbitals:

$$\Psi=(n!)^{-1/2}\begin{vmatrix}\Psi_1(1)\alpha(1) & \Psi_1(1)\beta(1) & \Psi_2(1)\alpha(1) & \cdots & \Psi_{n/2}(1)\beta(1)\\ \Psi_1(2)\alpha(2) & \Psi_1(2)\beta(2) & \Psi_2(2)\alpha(2) & \cdots & \Psi_{n/2}(2)\beta(2)\\ \vdots & \vdots & \vdots & & \vdots\\ \Psi_1(n)\alpha(n) & \Psi_1(n)\beta(n) & \Psi_2(n)\alpha(n) & \cdots & \Psi_{n/2}(n)\beta(n)\end{vmatrix}$$

The determinant is referred to as a Slater determinant.

Hatree-Fock Theory

An exact solution to the Schrodinger equation is not possible for any but the most trivial molecular systems. However, a number of simplifying assumptions and procedures do make an approximate solution possible for a large range of molecules. To simplify the treatment further, the next step is to assume thet the electrons are non-interacting. This implies that (apart from the constant nuclear-nuclear repulsion term) which can rewrite the total n-electron Hamiltonian as a sum of n one-electron Hamiltonians,

$$H_{el} = \sum_{i=1}^{N} h(i)$$

$$h(i) = \left(-\frac{1}{2}\nabla_i^2 - \sum_{A=1}^{M} \frac{Z_A}{r_{iA}} \right)$$

This is clearly an oversimplication, since have neglected the electron-electron repulsion term $\frac{1}{r_{ij}}$. $H_{el} = \sum_{i=1}^{N} h(i)$ defines the independent particle model. The one-electron Hamiltonians are termed core-Hamiltonians, since the only interactions included are those between the electrons and the bare nuclei. Including an average interaction term in the {h(i)}, these become effective one-electron Hamiltonians. As a consequence of Equation, the total wave function can be rewritten as a product of n single-particle wave functions,

$$\psi(\vec{r}) = \phi_1(\vec{r}_1)\phi_2(\vec{r}_2)\ldots\phi_n(\vec{r}_n)$$

or, take the electron spin into account,

$$\psi = \chi_1(\vec{x}_1)\chi_2(\vec{x}_2)\ldots\chi_n(\vec{x}_n)$$

The spin orbitals $\{\chi_i(\vec{x}_i)\}$ are the products of the spatial orbitals $\phi_i(\vec{r}_i)$ and the spin functions $(\alpha(\omega))$ and $(\beta(\omega))$; $\vec{x}_i$ denotes both the space and spin coordinates of electron i. The total independent particle spin-orbital wave function is called a Hartree-product. The corresponding eigenvalue is a sum of the single-particle spin-orbital energies,

$$E_{el} = \sum_{i=1}^{N} \varepsilon_i$$

A further requirement on the state wave function is that it must be anti-symmetric with respect to the interchange of coordinate r (both space and spin) of any two electrons,

$$\begin{gathered} |\psi(\vec{x}_1, \vec{x}_2, \ldots, \vec{x}_n)|^2 = |\psi(\vec{x}_2, \vec{x}_1, \ldots, \vec{x}_n)|^2 \\ \psi(\vec{x}_1, \vec{x}_2, \ldots, \vec{x}_n) = \pm\psi(\vec{x}_2, \vec{x}_1, \ldots, \vec{x}_n) \end{gathered}$$

It is also possible to write Equation in terms of a n x n determinant, a slater determinant, which has the same antisymmetric properties:

$$\psi = (n!)^{-1/2} \begin{vmatrix} \chi_1(\vec{x}_1) & \chi_2(\vec{x}_1) & \cdots & \chi_n(\vec{x}_1) \\ \chi_1(\vec{x}_2) & \chi_2(\vec{x}_2) & & \\ \cdots & & \cdots & \\ \chi_1(\vec{x}_n) & \chi_2(\vec{x}_n) & \cdots & \chi_n(\vec{x}_n) \end{vmatrix}$$

This commonly is written like:

$$|\psi\rangle = (n!)^{-1/2} | \chi_1(\vec{x}_1), \chi_2(\vec{x}_2), \ldots, \chi_n(\vec{x}_n)\rangle$$

It can easily be varied that the slater determinant obeys the Pauli principle, as the determinant then becomes zero. The pre-factor $(n!)^{-1/2}$ is a normalization constant, and the $\{\chi_i\}$ are assumed orthonormal. By antisym-metrizing the Hartree-product in the term of a Slater determinant, that the probability of finding any two electrons at the same point in space (i.e. $\vec{x}_1 = \vec{x}_2$) is zero.

Through the wave functions, the effective potential is generated. This potential allows to refine wave functions, from which a new potential is obtained. The procedure is repeated until a stable, self-consistent solution is reached. Due to the iterative procedure, the initial guess of the wave function, can of course be chosen. However, the better the initial guess is, the easier it is to reach a stable solution to the eigenvalue problems in a relatively short computational time, is provided by the variation principle. This can be stated in the following way. Given any approximate wave function, satisfying the correct boundary conditions, the expectation value of the energy obtained by this wave function never lies below the exact energy of the ground state. Expressed in mathematical terms:

$$E_e = \frac{\langle \psi | H_e | \psi \rangle}{\langle \psi / \psi \rangle} \geq E_{exact}$$

A conceptually appealing model for the (trial) wave function of our molecular system, is to regard it as being constructed from molecular orbitals (MO). This description in analogous to the method used for the atomic orbitals (AO). The MO's, the elements of the wave function determinant, are in turn thought of as being constructed by a Linear Combination of Atomic Orbitals (LCAO),

$$\psi_i^{MO} = \sum_{\mu} c_{\mu i} \phi_{\mu}^{AO}$$

The variationsl principle leads to following equations describing the molecular orbital expansion coefficients, $c_{\upsilon i}$, derived by Roothaan and by Hall:

$$\sum_{\upsilon=1}^{N} \left(F_{\mu\upsilon} - \varepsilon_i S_{\mu\upsilon} \right) c_{\upsilon i} = 0 \qquad \mu = 1,2,\ldots,N$$

Equation can be rewritten in matrix form:

$$FC = SC\varepsilon$$

With

$$F_{\mu\upsilon} = H_{\mu\upsilon}^{core} + \sum_{\lambda\sigma} P_{\lambda\upsilon}\left[(\mu\upsilon/\lambda\sigma) - \frac{1}{2}(\mu\upsilon/\lambda\sigma)\right]$$

$$F_{\mu\upsilon} = H_{\mu\upsilon}^{core} + G_{\mu\upsilon}$$

Where $H_{\mu\upsilon}^{core}$, core-Hamiltonian matrix defined as

$$H_{\mu\upsilon}^{core} = \int dr_1 \varphi_1^*(1) h(1) \varphi_\upsilon(1)$$

The matrix P is the density matrix or change- and bond-order matrix,

$$P_{\mu\upsilon} = 2\sum_{a}^{N/2} C_{\mu\upsilon} C_{\upsilon a}^*$$

The matrix S is the overlap matrix, indicating the overlap between orbitals.

$$S_{\mu\upsilon} = \int dr_1 \phi_\mu^*(1) \phi_\upsilon(1)$$

The term $(\mu\upsilon/\lambda\sigma)$ in Equation signified the two-electron repulsion integrals, defined as

$$(\mu\upsilon/\lambda\sigma) = \int dr_1 dr_2 \phi_\mu^*(1) \phi_\upsilon(2) r_{12}^{-1} \phi_\lambda^*(2) \phi_\sigma(2)$$

The (initial) wave function is used to generated an effective otential, which apply this potential in order to refine the coefficient matrix. The modified MO’s form the new input in the Roothaan or Pople-Nesbet equations, and a new potential is generated. The iterative procedure is repeated until convergence is reached, i.e. when the changes in energy and/or charge density in two subsequent iterations are below a pre-set threshold value.

Before a more technical description of the SCF-procedure is presented, first need to define a new transformation matrix X, used for ortogonalisation of the basis set. This orthogonolization can be either symmetric or canonical. A symmetric orthonalization implies that X is formed through the relation

$$X = S^{-1/2} = Us^{-1/2}U^{\tau}$$

Where S is the overlap matrix, U is an unitary matrix diagonalizes S, and the diagonal matrix of the eigenvalues of S is given by the relations. In the canonical orthogonalization procedure, X is instead given by

$$X = Us^{-1/2}$$

Consider a new coefficient matrix C' related to the old coefficient matrix C by

$$C' = X^{-1}C, \quad C = XC^{-1}$$

where assumed that X possesses an inverse. Substituting $C = XC^{-1}$ into the Roothaan equations gives

$$FXC' = SXC'\varepsilon$$

Multiplying on the left by X^{τ} gives

$$\left(X^{\tau}FX\right)C' = \left(X^{\tau}SX\right)C'\varepsilon$$

If define a new matrix F^{τ} by

$$F^{\tau} = X^{\tau}FX$$

And use $\sum_{\upsilon=1}^{N}\left(F_{\mu\upsilon}-\varepsilon_i S_{\mu\upsilon}\right)c_{\upsilon i}=0$, then

$$F'C' = C'\varepsilon$$

Matrix Equation can be solved using standard methods. The matrix element of the Hartree-Fock Hamiltonian operator are dependent of other orbitals through the element , and the Roothaan equations are solved by first assuming an initial set of linear expansion coefficients. The whole process is then reported until the coefficients no longer change within a given tolerance on repeated iteration. The solution is then said to be self-consistent and the method is then referred to as the SCF method.