

# Computational Quantum Chemistry of Chemical Kinetic Modeling

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## Abstract

The earth orbiting the sun, the electron bonded to a proton in the hydrogen atom are both manifestations of particles in motion bound by an inverse-square force and both are governed by the principle of least action (of all the possible paths the particles may take between two points in space and time, they take those paths for which the time integral of the Lagrangian or the difference, kinetic energy-potential energy, is the least) and shaped by the same Hamiltonian (or total energy) structure. For both types of motion, the invariants (or properties that are conserved) are the energy and angular momentum of the relative motion, and the symmetry is that of the rotational motion. Differences arise because the electric force bounding the electron to the proton is forty two orders of magnitude stronger than the gravitational force, and the smallness of the hydrogen atom brings about "quantum effects": the mechanics of the microscopic particles which constitute the atom is wave-like. Yet the central concepts of mechanics are preserved in integrity: least action, invariants or conservation laws, symmetries, and the Hamiltonian structure.

The discussion in the sections that follow on the quantum-mechanical treatment of molecular structures is based for the most part on the books by Pople and Murrell [2,3], and is by no means comprehensive but hopefully will elucidate the most relevant concepts for performing the estimation of thermochemical and kinetic properties of elementary reactions.

The aim of quantum chemistry is to provide a qualitative and quantitative description of molecular structure and the chemical properties of molecules. The principal theories considered in quantum chemistry are valence bond theory and molecular orbital theory. Valence bond theory has been proven to be more difficult to apply and is seldom used, thus this discussion will deal only with the application of molecular orbital theory to molecular structures.

In molecular orbital theory, the electrons belonging to the molecule are placed in orbitals that extend all the different nuclei making-up the molecule (the simplest approximation of a molecular orbital being a simple sum of the atomic orbitals with appropriate linear weighting coefficients, Figure 1 below for carbon Monoxide as example), in contrast to the approach of valence bond theory in which the orbitals are associated with the constituent atoms. The full analytical calculation of the molecular orbitals for most systems of interest may be reduced to a purely mathematical problem, the central feature of which is the calculation and diagonalization of an effective interaction energy matrix for the system. In ab initio molecular orbital calculations, the parameters that appear in such an energy matrix are exactly evaluated from theoretical considerations, while in semi-empirical methods experimental data on atoms and prototype molecular systems are used to approximate the atomic and molecular integrals entering the expression for the elements of the energy interaction matrix.

Ab initio methods can be made as accurate as experiment for many purposes Zeener [4], the principal drawback to "high level" ab initio work is the cost in terms of computer resources which restrict it to systems of ten or fewer atoms even for the most experienced users. This is what draws the chemist to semi-empirical methods that can be easily applied to complex systems consisting of hundreds of atoms. Presently, useful semi-empirical methods are limited in execution by matrix multiplication and diagonalization, both requiring computer time proportional to  $N^3$  where N is the number of atomic orbitals considered in the calculation or basis set.

**Keywords:** Quantum chemistry; Chemistry; Chemical kinetics; Modelling

## Quantum-Chemistry Background

In classical mechanics, one is concerned with the trajectories of particles which theoretically can be calculated from knowledge of the initial conditions and the structure of the Hamiltonian H, or the sum of a kinetic-energy contribution T and potential-energy function V.

$$H=T+V \quad (1)$$

The existence of the atom cannot be explained classically, but rather by the wave properties of the electron bonded to the nucleus. Schrodinger suggested that the proper way to describe the wave character of particles was to replace the classical kinetic and potential energy functions of with linear operator  $\hat{T}$ ,  $\hat{V}$  and a wave equation of the form.

$$\hat{H}\Psi = E\Psi \quad (2)$$

Where the solutions,  $\Psi$  the so called wave functions, would describe the behavior of all the Particles, and the quantum-mechanical Hamiltonian above is or for one electron system such as the hydrogen atom, with the electron centered on the atomic nucleus:

$$\hat{H} = \hat{T} + \hat{V} \quad (3)$$

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$$\hat{T} = -\frac{\hbar^2}{8\pi^2 m} \nabla^2 \quad (4)$$

$$\hat{V} = -\frac{Ze^2}{r} \quad (5)$$

Where  $m$  is the mass of the electron,  $r$  is the distance of the electron from the nucleus,  $Z$  is the atomic number, and  $e$  is the unit of electronic charge, and in equation (5) the Laplacian  $\nabla^2$  is in Cartesian coordinates. For molecules more complex than the simple hydrogen atom (for which exact solutions to the Schrodinger equation can be found), the Born-Oppenheimer approximation states that because the nuclei are so much more massive than the electrons, the electrons adjust essentially instantaneously to any motion of the nuclei, consequently we may consider the nuclei to be fixed at some internuclear separation in order to solve the Schrodinger equation (2) for the electronic wave function [5], or

$$\Psi \approx \Psi_N \Psi_{\text{elec}} \quad (6)$$

Where the first term in the product of equation (6) accounts for the motion of the nuclei and the second term involves the electron motion. Furthermore, introducing center-of-mass and relative coordinates, the nuclear wavefunction reduces to

$$\Psi_N \approx \Psi_{\text{trans}}(\text{C.M.}) \Psi_{\text{rot}} \Psi_{\text{vib}} \quad (7)$$

Where the center-of-mass translation, and rotational and vibrational contributions to the nuclear wave function are now explicitly shown. Thus, the problem of determining the structure of a complex molecule reduces to solving each Schrodinger equation for the electronic motion, the translational motion of the center of mass, and the rotational and vibrational motion of the nuclei separately. Thus, the electronic energy is estimated by the equation (similarly for the other types of motion).

$$\hat{H}_{\text{elec}}(1, 2, \dots, n) \Psi_{\text{elec}}(1, 2, \dots, n) = E_{\text{elec}} \Psi_{\text{elec}}(1, 2, \dots, n) \quad (8)$$

for a molecule with  $n$  electrons, and for a given internuclear distance the total energy of the system is

$$E_T \approx E_{\text{elec}} + \sum_{A < B} e^2 Z_A Z_B r_{AB}^{-1} \quad (9)$$

Where the second term is the electrostatic internuclear repulsion energy and  $A, B$  designate the nuclei. Molecular orbital theory is concerned with electronic wave functions only, and henceforth the electronic subscripts will be dropped from the electronic Hamiltonian and wave function. The molecular energy given by (9) is the energy at absolute zero with no contributions from the translational, rotational or vibrational motions. The latter forms of energy must be considered to determine thermochemistry under conditions of practical interest [6].

$$E_T \approx E_{\text{trans}} + E_{\text{vib}} + E_{\text{rot}} + E_{\text{elec}} \quad (10)$$

Once the total energy  $E_T$  of equation (10) is known for a given molecular geometry, a potential energy hyper surface (PES) can be generated as function of geometry, and the minima on the PES corresponds to the most stable configuration, or in mathematical terms for molecules or radicals,

$$\delta E_T^0 / \delta g_i = 0$$

$$\delta^2 E_T^0 / \delta (g_i)^2 > 0$$

Where,  $g_i$  is any geometrical variable.

The heat of formation for the molecule can then be obtained from the total energy of equation (10) via

$$\Delta H_f = E_r - \sum_{k=1}^n E_k^A + \sum_{i=1}^N \Delta H_{fi}^A \quad (11)$$

Where  $E_k^A$  and  $\Delta H_{fi}^A$  are the electron energies and the heats of formation of individual atoms, respectively? Clearly, this approach requires the accurate knowledge of the atomic heats of formation, which may or may not be available [6].

The electronic Hamiltonian (non-relativistic) is the given by the following expression in atomic units ( $\hbar/2\pi = e = m = 1$ )

$$\hat{H} = \sum_p 1/2 \nabla_p^2 - \sum_A \sum_P Z_A r_{AP}^{-1} + \sum_{p < q} r_{pq}^{-1} \quad (12)$$

Where  $A$  -designate the nuclei,  $p, q$  electrons, and  $r$  is the interparticles distance.

The solutions to the electronic Schrodinger equation (8) are infinite but for stationary, bound states only the continuous, single-valued Eigen functions  $i$  that vanish at infinity need to be considered, and the electronic energies are the eigenvalues  $E_i$  or

$$\hat{H} \Psi_i = E_i \Psi_i \quad (13)$$

The Eigen functions are normalizable and mutually orthogonal (i.e., orthonormal) or mathematically they satisfy the condition

$$\int \Psi_i^* \Psi_j d\tau = \langle \Psi_i | \Psi_j \rangle = \delta_{ij} \quad \text{all } i, j \quad (14)$$

In equation (14), the integration is over the volume element for the electron, and we have introduced the matrix or Dirac notation for the integral and  $\delta$  is the Kronecker delta symbol. The electronic energy of the system  $E_i$  is the expectation value of the Hamiltonian

or

$$\int \Psi_i^* \hat{H} \Psi_j d\tau = \langle \Psi_i | \hat{H} | \Psi_j \rangle = E_i \quad (15)$$

The complete treatment of a quantum-mechanical problem involving electronic structure requires the complete solution of the Schrodinger equation (8). This is only possible for one-electron systems, and for many-electron systems, where the electron repulsion term in the Hamiltonian renders an analytical solution impossible, the variation principle is applied (see next section for the application). This method in its full form is completely equivalent to the differential equations, but it has many advantages in the ways it can be adapted to approximate solution wave functions [2]. The variation principle states that if  $\Psi$  is a solution to equation (8) then for any small change  $\delta\Psi$ ,

$$\Delta E = \Delta \langle \Psi | \hat{H} | \Psi \rangle = 0 \quad (16)$$

If this criterion is applied to a completely flexible electronic wavefunction  $\Psi$  (in the appropriate number of dimensions), all the Eigen functions  $\Psi_i$  for the Hamiltonian will be obtained. If only an approximation to the wavefunction  $\Psi$  is used, then the Eigen functions  $\Psi_i$  and eigenvalues  $E_i$  are only approximations to the correct values, with the accuracy of the estimates improving as better approximations for the total wavefunction  $\Psi$  is used.

The orbital approximation suggests that the total electron wavefunction  $\Psi$  can be written as the Hartree product of one-electron wave functions,  $\psi_i(\xi)$ , called spin orbitals [4] consisting of the product

of spatial and spin functions, where  $\psi_\eta(\xi)$  is the spin function that can take values  $\alpha$ , or  $\beta$  or,

$$\Psi(1,2,\dots,n) = O(S)A[\Psi_1(1)\alpha(1)\Psi_2(2)\beta(2)\Psi_3(3)\alpha(3)\dots\Psi_n(n)\beta(n)] \quad (17)$$

In equation (17) A is the antisymmetrizer, ensuring that the wavefunction changes sign on interchange of any two electrons in accordance with the Pauli exclusion principle, and O(S) is a spin projector operator that ensures that the wavefunction remains an Eigen function of the spin-squared operator  $S^2$ .

$$S^2\Psi = S(S+1)\Psi \quad (18)$$

O(S) can become quite complex [4], but for a closed shell molecule, with all electrons paired in the spin Orbits  $O(S)=1$ . Thus, for a closed-shell system with  $2n$  electrons, and two electrons paired in each spatial orbital, the many-electron wavefunction becomes:

$$\Psi(1,2,\dots,n) = A[\Psi_1(1)\alpha(1)\Psi_1(2)\beta(2)\Psi_2(3)\alpha(3)\dots\Psi_n(2n-1)\alpha(2n-1)\Psi_n(n)\beta(n)] \quad (19)$$

### Self-Consistent Molecular Orbital Theory

Having established the proper form for the many-electron wave function for closed shells as a single determinant of spin orbitals (Slater determinant) or equation (19), the discussion now proceeds to the details of the actual determination of the electron spatial orbitals  $\psi_i$  for a closed-shell system (for treatment of systems for which there are unpaired electrons [2]. This involves the application of the variational principle or equation (16) of the previous section. The best molecular orbitals, therefore, are obtained by varying all the contributing one-electron functions  $\psi_1, \psi_2, \psi_3, \dots, \psi_n$  in the Slater determinant equation (19) until the electronic energy achieves its minimum value. This will give the best approximation to the many-electron wavefunction  $\Psi\{1,2, \dots, n\}$ , and the electron orbital or molecular orbitals  $\psi_i$  so obtained are referred to as self-consistent or Hartree-Fock molecular orbitals. Mathematically, the problem involves the minimization of the total electron energy with the orthonormality constraint for the electron orbitals

$$\text{or Minimize } G = E - 2\sum_i \sum_j \epsilon_{ij} S_{ij} \quad (20)$$

$$\text{Orthonormality } S_{ij} = \int \Psi_i^* \Psi_j d\tau = \delta_{ij} \quad (21)$$

$$\text{And } E = \left\langle \Psi(1,2,\dots,n) \left| \hat{H} \right| \Psi(1,2,\dots,n) \right\rangle \quad (22)$$

$\Psi(1,2,\dots,n)$  is given by equation (19)

The minimization consists of setting  $\delta G=0$  and leads to the following differential Equations [2]

$$\left\{ \hat{H}^{\text{core}} + \sum_j 2\hat{F}_j - \hat{K}_j \right\} \Psi_i = \epsilon_i \Psi_i \quad \text{or} \quad (23)$$

$$\hat{F}\Psi_i = \epsilon_i \Psi_i \quad i = 1, 2, \dots, n \quad (24)$$

In equation (24)  $\hat{F}$  is the one-electron Hartree-Fock Hamiltonian operator consisting of the terms defined in equation (23) within the brackets. Equation (24) is known as the Hartree-Fock equation and states that the best molecular orbitals are Eigen functions of the Hartree-Fock Hamiltonian operator. The first operator of the Hartree-Fock Hamiltonian in equation (23) is the one-electron Hamiltonian for an electron moving in the field of the bare nuclei, or

$$\hat{H}(p)^{\text{core}} = -\frac{1}{2}\nabla_p^2 - \sum_A Z_A r_{pA}^{-1} \quad (25)$$

The second operator accounts for the average effective potential of

all other electrons affecting the electron in the molecular orbital  $\psi_i$ , or can be defined by

$$\hat{J}_j(1) = \int \Psi_j^*(2) \frac{1}{r_{12}} \Psi_j(2) d\tau_2 \quad (26)$$

The final operator in the square bracket of equation (23) is the exchange potential and it arises from the effect of the antisymmetric of the total wavefunction on the correlation between electrons of parallel spin, or can be defined by

$$K_j(1)\Psi_i(1) = \left[ \int \Psi_j^*(2) \frac{1}{r_{12}} \Psi_i(2) d\tau_2 \right] \Psi_j(1) \quad (27)$$

To account for the correlation of electrons of different spin, the term missing in equation (23), a method such as CI or Configuration Interaction can be applied. This method incorporates virtual orbitals or nonbonding orbitals into the total wavefunction. This is beyond the scope of this discussion. For more information see Pople et al. [7]. The eigenvalues of equation (24) are the energies of electrons Occupying the orbitals  $\psi_i$  and are thus known as orbital energies, or

$$\epsilon_i = H_{ii}^{\text{core}} + \sum_j (2J_{ij} - K_{ij}) \quad (28)$$

Where the one-electron core energy for an electron moving in the field of bare nuclei is:

$$H_{ii}^{\text{core}} = \int \Psi_i^*(1) \hat{H}^{\text{core}} \Psi_i d\tau_1 \quad (29)$$

The coulomb interaction energy is given by:

$$J_{ij} = \iint \Psi_i^*(2) \frac{1}{r_{12}} \Psi_i(1) \Psi_j(2) d\tau_1 d\tau_2 \quad (30)$$

and the exchange energy is

$$K_{ij} = \iint \Psi_i^*(1) \Psi_j^*(2) \frac{1}{r_{12}} \Psi_j(1) \Psi_i(2) d\tau_1 d\tau_2 \quad (31)$$

The general procedure for solving the Hartree-Fock equations is iterative Figure 2. A first solution for the molecular orbitals  $\psi_i$  is assumed for generating the Hartree-Fock operator  $\hat{F}$ . The set of molecular orbitals generated by this estimate of the Hartree-Fock operator is then used to repeat the calculations and so on until the orbital no longer changes (within a certain tolerance) on further interactions. These orbitals are said to be self-consistent with the potential field they generate. In addition to the  $n$  occupied orbitals, there will be unoccupied orbitals called virtual orbitals of higher energy.

The method outlined above for solving the Hartree-Fock equations is impractical for molecular systems of any size and other approaches must be found [2]. The most rewarding approach consists of approximating the molecular orbitals by a linear combination of atomic orbitals or LCAO in the form

$$\Psi_i = \sum_{\mu} C_{\mu i} \phi_{\mu} \quad (32)$$

Where the  $\phi_{\mu}$  are the atomic orbitals constituting the molecular orbital or basis set.

In carrying out numerical calculations of molecular orbitals, it is necessary to have convenient analytical forms for the atomic orbitals of equation (32) for each type of atom in the molecule. These are the solutions of the Schrodinger equation for one-electron systems (H-atom) can be written in the form

$$Y_{lm}(\theta, \varphi) = \Theta(\theta)\Phi(\varphi)$$

Where  $r$ ,  $\theta$ , and  $\phi$ , are the spherical coordinates centered on the atom. The angular part of the above equation or  $Y_l, m(\theta, \phi)$  are the well-known spherical harmonics defined as:

$$Y_{lm}(\theta, \phi) = \Theta(\theta)\Phi(\phi)$$

Where  $l$  is the azimuthal quantum number and  $m$  is the magnetic quantum number. For the radical part of the atomic function, the so called Slater Type Orbitals (STO) are used with the form

$$R_{n,l}(r) = (2\zeta)^{n+1/2} [(2n)]^{-1/2} r^{n-1} \exp(-\zeta r)$$

Where  $n$  is the principal quantum number, and  $\zeta$ ; is the orbital exponent, a function of the atomic number.

The variational principle is then applied as previously outlined except the total electron wavefunction consists of the product of molecular orbitals such as given in equation (32) above and the orthonormality of the electron wavefunction leads to

$$\sum_{\mu\nu} C_{\mu i}^* C_{\nu j} S_{\mu\nu} = \delta_{ij} \quad (33)$$

Where  $S_{\mu\nu}$  is the overlap integral for the atomic orbitals, or

$$S_{\mu\nu} = \int \phi_{\mu}(1)\phi_{\nu}(1) d\tau_1 \quad (34)$$

This leads to the so called Roothan equations given by:

$$\sum_{\nu} (F_{\mu\nu} - \epsilon_i S_{\mu\nu}) C_{\nu i} = 0 \quad i = 1, 2, \dots, n \quad (35)$$

Where the elements of the matrix representation of the Hartree-Fock Hamiltonian are

$$F_{\mu\nu} = H_{\mu\nu} + \sum_{\lambda\sigma} P_{\lambda\sigma} [( \mu\nu | \lambda\sigma ) - 1/2( \mu\nu | \lambda\sigma )] \quad (36)$$

and

$$P_{\mu\nu} = 2 \sum_{\text{occ}} C_{\mu i}^* C_{\nu i} \quad (37)$$

$$H_{\mu\nu} = \int \phi_{\mu}(1) \bar{H}^{\text{core}} \phi_{\nu}(1) d\tau_1 \quad (38)$$

$$( \mu\nu | \lambda\sigma ) = \iint \phi_{\mu}^*(1)\phi_{\nu}^*(1) \frac{1}{r_{12}} \phi_{\lambda}(2)\phi_{\sigma}(2) d\tau_1 d\tau_2 \quad (39)$$

The matrix of elements  $P_{\mu\nu}$  is the electron density matrix,  $H_{\mu\nu}$  are the elements of the core Hamiltonian with respect to atomic orbitals, and equation (39) is the general two- electron interaction integral over atomic orbitals. Equation (35) is an algebraic equation in contrast with the differential equation (24) previously derived.

The Roothan equation (35) can be written in matrix form as

$$FC = SCE \quad (40)$$

Where  $E$  is the diagonal matrix of the  $\epsilon_i$ . The matrix elements of the Hartree-Fock Hamiltonian operator  $F$  are dependent on the orbitals through the elements  $P_{\mu\nu}$ , and the Roothan equations are solved by first assuming an initial set of linear expansion coefficients  $c_{\mu i}$  generating the corresponding density matrix  $P_{\mu\nu}$  and computing a first guess to  $F_{\mu\nu}$ .

With the transformations  $F^* = S^{-1/2} F S^{-1/2}$  and  $C^* = S^{1/2} C$ , equation (40) can be made into an eigenvalue form or

$$F^* C^* = C^* E \quad (40b)$$

The diagonalization procedure is affected by standard matrix eigenvalue techniques, and new expansion coefficients are calculated.

The whole process is repeated until the coefficients no longer change within a given tolerance on repeated iteration [2]. It is useful at this point to summarize the hierarchy of approximations involved in the SCF-MO model since we have now discussed all the necessary approximations [8]:

(1) The first level of approximations corresponds to the non-relativistic, fixed nucleus Schrodinger equation,

$$H\Psi = E\Psi$$

(2) The variational solution of the Schrodinger Equation corresponds to the best possible solution in the mean or integrated value, the differential Schrodinger equation has point by point solutions.

(3) The orbital model where the wave function  $\Psi$  is expressed as the product of the electron wave functions, equation (17) is an exact solution of the Schrodinger equation when the interaction between particles is neglected. Thus its use in the full Hamiltonian is an approximation that does not fully take into account the correlated motion of the electrons (physically this means interpreting the distribution of  $n$  electrons in terms of the separate distributions of the model one-electron orbitals. As the above analysis showed, a correlation term for electrons of different spin is missing).

(4) By using a single configuration for the form of the wave function  $\Psi$ , equation (17), the exact form of the optimum total electron wave function is lost here. A more exact solution is of the form where the wave function is a linear superposition of all possible configurations that are solutions to the Schrodinger equation with the same ground energy  $E$ . Due to the approximate nature of the one-electron wave functions that make-up  $\Psi$ , the configurations differ in in the form of the component electron wavefunction but the electron energies sum to the same ground energy  $E$ .

$$\Psi = \sum C_i \Psi_{i\text{-config}}$$

(5) With the LCAO approximation the exact form of optimum AO is lost. The molecular orbitals are limited by the capabilities of the AO.

## Semi-Empirical Methods

This method is part of the software package MOPAC or general-purpose semi-empirical molecular orbital package developed through the Quantum Chemistry Program Exchange at Indiana University. As stated at the very outset, semi-empirical methods are considerable less costly than ab-initio calculations in terms of computer resources and can be applied to systems consisting of hundreds of atoms. In semi-empirical methods the matrix elements of the Hartree-Fock Hamiltonian or equation (24) are based on experimental data on atoms and prototype molecular systems. It is important to note here that by deriving the elements of the energy matrix semi-empirically, semi-empirical quantum chemistry methods make some allowance for electron correlation effects that are normally neglected in the M.O. approach [9].

Tables 1a-1c on the pages that follow outlines the most important semi-empirical Molecular Orbital (M.O.) methods. Historically, the first M.O. semi-empirical method was Ruckel's M.O. theory of  $\pi$ -electrons where the molecular orbitals are a LCAO and solutions were sought for the Hamiltonian operator. The electrons were considered as moving in the effective potential of the inner core-electrons. The overlap integral on two different atoms  $M, N$  or  $S_{\mu\nu}$  is the Kronecker delta. This method was very important in that it showed rather quickly those M.O.

methods that diagonalized energy matrices gave qualitatively important results [4]. The next important development is the self-consistent field (SCF)-M.O. theory of Pariser-Parr-Pople (PPP) as applied to a  $\pi$ -electron system or Zero-Differential Overlap (ZDO) where solutions are sought for the Hartree-Fock equation (24). In the ZDO-SCF-M.O. method, the only two electron two center repulsion integral retained is an integral of the type  $(\mu\mu|\lambda\lambda)$ , all others are neglected. Other elements needed to complete the energy matrix diagonalization are given by semi-empirical values. The next level of complexity is ZDO-All Valence Electrons methods (Table 1b) where all valence electrons are considered (and not just  $\pi$  electrons in a conjugated system such as benzene) in the effective potential of the core composed of the nuclei and inner electrons (the so called core approximation). As Tables 1b,1c shows, semi-empirical methods CNDO, PNDO, INDO, MINDO, and NDDO fall within the ZDO approximation.

The CNDO method makes the s-orbital approximation to retain two-electron two center integrals of the type  $(\mu\mu|\lambda\lambda)$ . Murrell states [3]: "If the full SCF equations are solved without any approximations then the calculated energies and electron distribution will be the same whatever the choice of coordinate axes. In other words, it does not matter how we choose to direct our angle-dependent orbitals (p,d etc). The results must also be the same whether we choose to take a linear combination of atomic orbitals or a linear combination of hybridized orbitals which are themselves linear combinations of atomic orbitals". What this means is that the SCF calculations need to be invariant to an orthogonal transformation of the atomic orbital basis and approximations to the SCF equations may not satisfy the conditions of rotational and hybridizational invariance. This problem does not arise in  $\pi$ -electron theory as the molecular symmetry leads to

## 2.2 ZDO- All Valence Electrons Methods

**The core approximation is used: The valence electrons are assumed to move in the field of a fixed core composed of the nuclei and inner shell electrons.**

$$S_{\mu\nu} = \int \phi_{\mu}(1)\phi_{\nu}(1)d\tau_1 = \delta_{\mu\nu} \text{ orbitals are on two different atoms M, N}$$

$$S_{\mu\nu} = 0 \text{ for orbitals on the same atom due to orthonormality}$$

**The two-electron interaction integrals (one or two centre) are evaluated as described below. All other integrals in Roothan equations are evaluated semi-empirically.**

### 2.2.1 CNDO (Complete Neglect of Differential Overlap)

Due to invariance to rotations and hybridization use **s-orbital approximation** to evaluate two-electron integrals or

$$(\mu\mu|\lambda\lambda) = (s_M^2|s_N^2) = \gamma_{M,N} \text{ two atoms M, N}$$

$$\text{and } (\mu\mu|\lambda\lambda) = (s_M^2|s_M^2) = \gamma_{M,M} \text{ same atom M}$$

All other two-electron repulsion integrals are neglected. **One-centre integrals are evaluated semi-empirically**

### 2.2.2 PNDO (Partial Neglect of Differential Overlap)

s-orbital approximation of CNDO **no longer used.**

$(\mu\mu|\lambda\lambda)$  on two atoms M, N given empirical values

same atom M integrals of the form  $(\mu\mu|\lambda\lambda)$  or  $(\mu\lambda|\mu\lambda)$  given an empirical value depending on electron spin

### 2.2.3 INDO (Intermediate Neglect of Differential Overlap)

**uses s-orbital approximation** as CNDO except that one-centre

**Table 1b:** The Development of Semi-empirical Methods.

## 1. Huckel M.O. Theory of $\pi$ -electrons (1930)

$\pi$ -electrons (on different atoms as in benzene) move in the effective potential of the  $\sigma$ -framework.

M.O.  $\psi_i = \sum_{\mu} c_{\mu} \phi_{\mu}$  or LCAO

$\psi_i$  are solutions to  $H\psi_i = E_i\psi_i$  where H is the Hamiltonian operator

Coulomb  $(\mu|\hat{H}|\mu)$  integrals and resonance integrals  $(\mu|\hat{H}|\lambda)$  empirically determined.

$$S_{\mu\nu} = \int \phi_{\mu}(1)\phi_{\nu}(1)d\tau_1 = \delta_{\mu\nu} \text{ orbitals are on two different atoms M, N}$$

$$S_{\mu\nu} = 0 \text{ for orbitals on the same atom due to orthonormality}$$

## 2. SCF-M.O. Theory

M.O.  $\psi_i = \sum_{\mu} c_{\mu} \phi_{\mu}$  or LCAO

$\psi_i$  are solutions to  $F\psi_i = E_i\psi_i$  where F is the Hartree-Fock operator

**Two-electron integrals of Roothan equations evaluated per methods outlined in this Table**

$$(\mu\nu|\lambda\sigma) = \iint \phi_{\mu}^*(1)\phi_{\nu}^*(1)\frac{1}{r_{12}}\phi_{\lambda}(2)\phi_{\sigma}(2)d\tau_1d\tau_2 \text{ (general two-electron integral, only one or two centre integrals are considered)}$$

### 2.1 ZDO (Zero Differential Overlap) of $\pi$ -electrons

$\pi$ -electrons on different atoms as in benzene

$$S_{\mu\nu} = \int \phi_{\mu}(1)\phi_{\nu}(1)d\tau_1 = \delta_{\mu\nu} \text{ orbitals are on two different atoms M, N}$$

$$S_{\mu\nu} = 0 \text{ for orbitals on the same atom due to orthonormality}$$

**Two-electron, two centre integrals retained are of the type  $(\mu\mu|\lambda\lambda)$  where the orbitals are on atoms M, N, and given semi-empirical values all other two-electron repulsion integrals are taken to be zero. Other integrals in Roothan equations also given semi-empirical values.**

**Table 1a:** The Development of Semi-Empirical Quantum Chemistry Methods.

a natural choice of axis for the  $\pi$  orbitals, or an axis perpendicular to the molecular plane. Thus, in the CNDO method the invariance conditions require that all two-center and one-center integrals be calculated using the s-orbital approximation or

$$(\mu\mu|\lambda\lambda) = (s_M^2|s_N^2) = \gamma_{MN} \text{ Two atoms M, N}$$

Two atoms M, N (41) and s same atom M (42)

$$(\mu\mu|\lambda\lambda) = (s_M^2|s_M^2) = \gamma_{M,M} \text{ Same atom M}$$

All other integrals necessary to diagonalize the energy matrix are given semi-empirical values [3]. In the PNDO approximation, the s-orbital approximation is abandoned with the two-centre two-electron integrals given semi-empirical values. The most important feature of the PNDO method is that the two-electron two-centre integrals are evaluated only after transforming to a set of symmetry axis for the two atoms involved in the integral. The INDO method retains the s-orbital approximation for two-centre integrals except that one-centre two electron integrals are given empirical values. The MINDO method of Baird and Dewar is based on INDO with some modifications and the semi-empirical parameters were given values such as to get a best fit to the experimental heats of formation of some chosen molecules. This philosophy differs from that of the Pople School in which is tried to reproduce the results of non-empirical SCF calculations using the same set of atomic orbitals [3].

The NDDO method comes the closest to the full SCF equations of Roothan and is therefore more difficult to apply than the previous methods discussed in the NDDO method, in addition to retaining two-

centre integrals of the type  $(\mu\mu | \lambda\lambda)$ , the two-centre integral is retained. The MNDO method of the MOPAC software (the method chosen for this dissertation) falls within this level of approximation. AMI is the second parametrization of the original MNDO, with PM3 being the third.

$$(\mu_M \lambda_M | \mu_N \lambda_N)$$

To illustrate the MNDO Fock matrix elements, we will use the notation of Dewar and Thiel [9]. The atomic orbitals (A.O)  $\phi_\mu$  and  $\phi_\nu$  are centered on atom A and AO.  $\phi_\lambda$  and  $\phi_\sigma$  at atom B. If necessary, superscripts A or B will assign a particular symbol to atom A or B, respectively. Thus, the MNDO Fock matrix elements are [9]:

$$F_{\mu\mu} = U_{\mu\mu} + \sum_B V_{\mu\mu,B} + \sum_v P_{vv}[(\mu\mu, vv) - 1/2(\mu v, \mu v)] + \sum_B \sum_{\lambda,\sigma} P_{\lambda,\sigma}(\mu\mu, \lambda\sigma) \quad (43)$$

$$F_{\mu\nu} = \sum_B V_{\mu\nu,B} + \sum_v 1/2 P_{vv}[3(\mu\nu, \mu\nu) - (\mu\mu, \nu\nu)] + \sum_B \sum_{\lambda,\sigma} P_{\lambda,\sigma}(\mu\nu, \lambda\sigma) \quad (44)$$

$$F_{\mu\lambda} = \beta_{\mu\lambda} - 1/2 \sum_v \sum_{\alpha} P_{v,\sigma}(\mu\nu, \lambda\sigma) \quad (45)$$

The Fock matrix terms of equations (43), (45) are as follows:

(a) One-center one-electron energies  $U_\mu$  which represent the sum of the kinetic energy of an electron in A.O.  $\phi_\mu$  at atom A and its potential energy due to the attraction by the core of atom A.

(b) One-center two-electron repulsion integrals

$$(\mu\mu, \lambda\sigma) \text{ and } (\mu\nu, \lambda\sigma)$$

(c) Two-center one-electron core resonance integral

$$\beta_{\mu\lambda} = \int \phi_\mu (-1/2 \nabla^2 + V_A + V_B) \phi_\lambda d\tau \quad (46)$$

where  $V_A$  and  $V_B$  are the effective potentials of the atom cores.

(d) Two-center one-electron attractions  $V_{\mu\nu,B}$ , between an electron in the distribution  $\phi_\mu \phi_\nu$  at atom A and the core of atom B.

(e) Two-center two-electron repulsion integrals

$$(\mu\mu, \lambda\sigma) \text{ and } (\mu\nu, \lambda\sigma)$$

In the MNDO method, the various Fock matrix elements are determined either from experimental data or from semi-empirical expressions which contain numerical atomic parameters that can be adjusted to fit experimental data. The experimental data to be fitted include heats of formation, geometrical variables (e.g., bond angle), dipole moments, and first vertical ionization potentials for chosen standard molecules. Atomic parameters were optimized for H, B, C, N, O, and F [9].

Table 2 depicts a comparison of MNDO with AMI and PM3 methods. As table shows, MNDO estimates of the heats of formation of PAH (Polycyclic Aromatic Hydrocarbons) are superior to others. Zemer [4] states that reaction barriers using MNDO are generally too high, whereas those obtained from AMI are in some instances considerably better, although also often too high. To quote Dewar [10] "A major problem in studying reactions by any current theoretical model is the lack of experimental data for the intermediate sections of potential surfaces and for the geometries of transition states. Calculations for these consequently involve the extrapolation of an empirical procedure into areas where it has not been, and indeed cannot be, tested. Such an extrapolation is safer, the better the performance of the method in question in all areas where it can be tested".

## Group Equivalent Corrections to MNDO

Group equivalent corrections were applied to semi-empirically calculated heats of formation as demonstrated by Schulman et al., Peck et al. [11,12] and more recently by Wang. The underlying principle of the group equivalent correction is similar to that of Benson's group additivity method [13]. In Benson's method, a molecule's structural group contributes a portion of the total property of the molecule, while in the group equivalent corrections; it is assumed that this same structural group contributes a given amount of error to the deviation of the semi-empirically calculated heat of formation, for example, from experimentally determined values. Thus according to the group equivalent method, the heat of formation of a given molecule is calculated from the following expression

$$\Delta H_{f,298} = \Delta H_{f,298}(S/E) - \sum_{i=1}^n GE_i$$

Where  $\Delta H_{f,298}(S/E)$  is the semi-empirical heat of formation and  $GE_i$  is the group equivalent correction assumed to be independent of the overall structure of the molecule.

The group equivalent method will be illustrated for two molecules, benzene and naphthalene. Benzene, according to Benson's group additivity method, consists of six Cs- (H) groups. The experimentally

### 2.2 ZDO-All Valence-Electrons Methods (Cont'd.)

#### 2.2.4 MNDO (Modified Intermediate Neglect of Differential Overlap)

Baird and Dewar modified INDO and choosed parameters to best fit heats of formation of molecules in their ground state. The one-centre two electron repulsion integrals are given the values of the PNDO method (spin dependent).

#### 2.2.5 NDDO (Neglect of diatomic differential Overlap)

In contrast to all the methods described above, in addition to retaining two-centre two electron integrals of the type  $(\mu\mu|\lambda\lambda)$  the two-centre integral  $(\mu_M \lambda_M | \mu_N \lambda_N)$  is retained, and as with other integrals given semi-empirical values. The orbitals are on atoms M, N in both integrals.

Two electron one-centre integrals are also given semi-empirical values.

**MNDO method of Dewar used in the MOPAC software belongs to the NDDO level of approximation. AMI is the second parametrization of the original MNDO, with PM3 being the third.**

Table 1c: The Development of Semi-Empirical Methods.

Species	$\square H_f$ (Kcal/ Mol)			
	Experiment	PM3	MNDO	AMI
Cyclopentadiene	32.10	-0.40	-0.08	4.90
Benzene	19.81	3.58	1.44	2.14
Naphthalene	36.05	4.51	2.15	4.42
Biphenyl	43.53	4.39	2.39	3.93
Anthracene	55.20	6.30	3.47	7.56

Table 2: Heats of Formation (MOPAC 93 Manual).

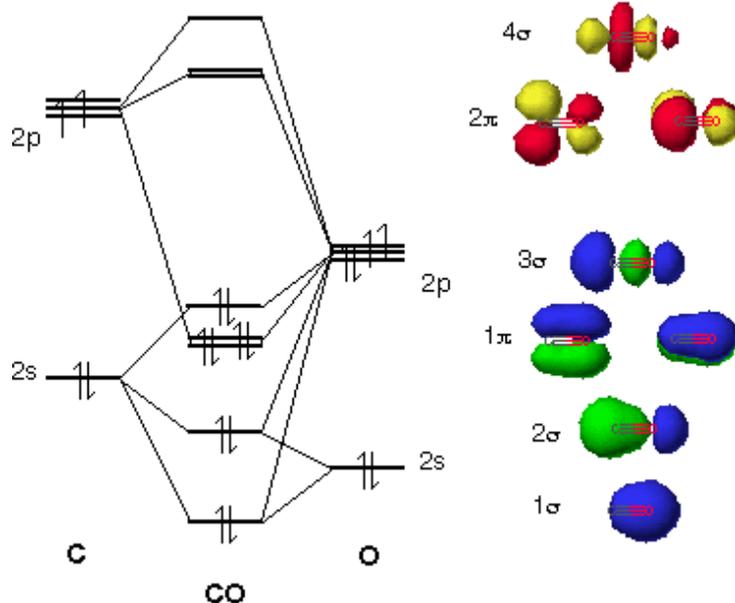


Figure 1: Carbon Monoxide Molecular Orbital Diagram.

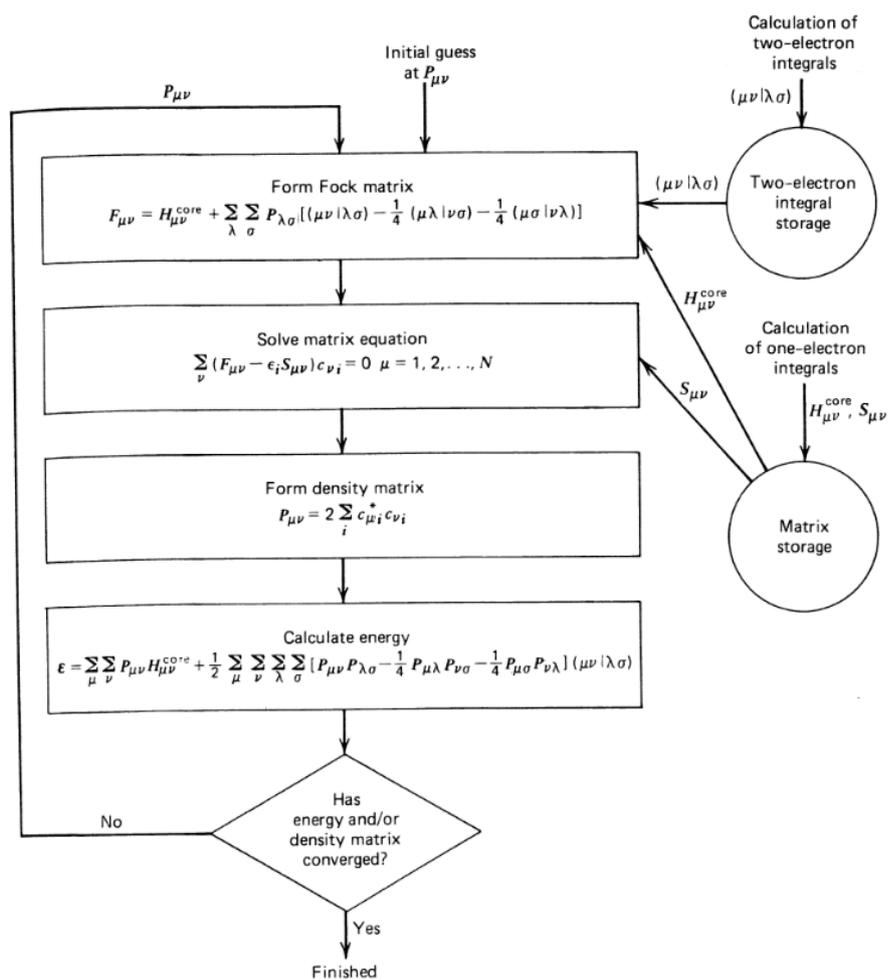


Figure 2: HF SCF Computation Procedure Flow Chart (Closed Shell) [14].

determined heat of formation is 19.81 kcal/mol and from the MOPAC 93 MANUAL, the MNDO calculated heat of formation is 1.44 kcal/mol higher than experimental. Thus, the GE correction for each group is

$$GE_{CB-H} = 144/6 = 0.24 \text{ kcal/mol}$$

or a 0.24 kcal/mol correction for each CB-H group. With the first GE correction determined, the next GE correction for a more complex aromatic such as naphthalene can be evaluated. Naphthalene consists of 8 CB-H groups and 2 CBF- (CB)<sub>2</sub>(CBF) groups, with the experimental value for the heat of formation as 36.05 kcal/mol and the MNDO calculated value being 2.15 kcal/mol higher (MOPAC 93 MANUAL). The GE correction for the CBF- (CB)<sub>2</sub>(CBF) group is the calculated as follows or a 0.115 kcal/mol correction for each group. This same procedure would be followed to determine the GE correction for new groups in the next more complex PAH such as phenanthrene and so on.

$$GE_{C_{B,F}-(C_B)_2(CBF)} = \frac{2.15 - 8GE_{CB-H}}{2} = \frac{2.15 - 8(0.24)}{2} = 0.115 \text{ kcal/mol}$$

### Computational Chemistry Software & Guides

A very extensive compilation of Quantum Chemistry software can be found in Wikipedia at:

[https://en.wikipedia.org/wiki/List\\_of\\_quantum\\_chemistry\\_and\\_solid-state\\_physics\\_software](https://en.wikipedia.org/wiki/List_of_quantum_chemistry_and_solid-state_physics_software)

Software is available to conduct semi-empirical, ab-initio (HF SCF, post HF), density functional theory, molecular mechanics calculations. The author is most familiar with MOPAC for semi-empirical calculations and Spartan for ab-initio computations.

There are a good number of books or guides to Computational Quantum Chemistry that are most popular. These are the following:

- a. Introduction to Computational Chemistry, Jensen, Frank, 2007
- b. Molecular Modeling Principles and Applications, Bleach, Andrew R, 2001

- c. Understanding Molecular Simulations, Frenkel D, Smit B 2002
- d. Essentials of Computational Chemistry, Cramer, Christopher J 2004
- e. Computational Chemistry: A Practical Guide for Applying Techniques to Real World problems, Young, David C 2001.

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