

APPENDIX 2¹

Semiempirical PM3 (Parametrization Method #3)

A. Background information.

When analytical solutions cannot be obtained, Schrödinger equation may be solved:

- (i) Numerically.
- (ii) By approximation procedures (perturbation theory, variation theory).
- (iii) The method of self-consistent field (SCF).

PM3 is a *semiempirical* (see below) method that uses parameters from experimental data to simplify calculation.

Ab initio computational methods are based solely on the laws of quantum mechanics and physical constants such as Planck constant, masses and charges of electrons and nuclei and on the speed of light.

The SCF method was created by Douglass Hartree and further developed by Vladimir Fock. Molecular orbitals are expressed as a **linear combination of atomic orbitals (LCAO)**²:

$$\Phi_i = \sum_{\mu=1}^N C_{\mu i} \chi_{\mu}$$

Φ_i are molecular orbitals (1)

$C_{\mu i}$ molecular expansion coefficients

χ_{μ} are atomic orbitals

The Hartree-Fock and LCAO approximations applied to the electronic Schrödinger equation, lead to Roothan-Hall equations:

$$\sum_{\nu} (F_{\mu\nu} - \epsilon_i S_{\mu\nu}) C_{\nu i} = 0 \quad (1)$$

In matrix form (1) can be re-written as:

¹ This appendix is still under construction. Please address any suggestion to Dr. Mircea D. Gheorghiu (mircea@mit.edu)

² The usual notation convention: **Roman** subscripts on **molecular orbital functions** and **Greek** subscripts on **basis functions (pre-defined set such as for, example, atomic orbitals)**.

$$\mathbf{FC} = \mathbf{SC}\boldsymbol{\varepsilon} \quad (2)$$

\mathbf{F} is the **Fock matrix** (analogous to Hamiltonian in the Schrödinger equation) For closed systems³, **Fock matrix** elements are:

$$\mathbf{F}_{\mu\nu} = \mathbf{H}_{\mu\nu}^{\text{core}} + \sum_{\lambda=1}^N \sum_{\sigma=1}^N \mathbf{P}_{\lambda\sigma} [(\mu\nu|\lambda\sigma) - \frac{1}{2}(\mu\lambda|\nu\sigma)] \quad (3)$$

where:

- $\mathbf{H}_{\mu\nu}^{\text{core}}$ is a matrix representing the energy of a single electron in the field of the core. **In semiempirical methods the core is defined as the nuclei and nonvalence electrons. The valence electrons are assumed to move in the potential field of the core.** $\mathbf{H}_{\mu\nu}^{\text{core}} = \langle \chi_{\mu}(\mathbf{1}) | \mathbf{H}^{\text{core}} | \chi_{\nu}(\mathbf{1}) \rangle$; $\mathbf{H}^{\text{core}}(\mathbf{1}) = -\frac{1}{2}\nabla^2 - \sum_{A=1}^M \frac{Z_A}{r_{1A}}$; Z_A is the atomic number of atom A.
- $\mathbf{P}_{\lambda\sigma}$ is the **density matrix**. The molecular expansion coefficients are summed only over the double occupied molecular orbitals (number 2 in front of summation):

$$\mathbf{P}_{\lambda\sigma} = 2 \sum_{i=1}^{\text{occupied MOs}} \mathbf{C}_{\lambda i}^* \mathbf{C}_{\sigma i} \quad (4)$$

- The quantities $(\mu\sigma|\lambda\nu)$ are **two-electron repulsion integrals** (representing the coulombic interaction between the cloud of electron 1 and cloud of electron 2)

$$\iint \chi_{\mu}(\mathbf{1}) \chi_{\sigma}(\mathbf{1}) \frac{1}{r_{12}} \chi_{\lambda}(\mathbf{2}) \chi_{\nu}(\mathbf{2}) d\mathbf{v}$$

- The quantities $(\mu\lambda|\sigma\nu)$ are **two-electron exchange integrals**. It represents the correction required for the Coulomb integral to take into effect the spin correlation. For two electrons with the same spin, the true average repulsion energy will be less than the value of Coulomb integral, because such electrons

$$\text{avoid each other: } \iint \chi_{\mu}(\mathbf{1}) \chi_{\sigma}(\mathbf{2}) \frac{1}{r_{12}} \chi_{\lambda}(\mathbf{1}) \chi_{\nu}(\mathbf{2}) d\mathbf{v}$$

\mathbf{S} is the overlap matrix; its elements are given by $\mathbf{S}_{\mu\nu} = \langle \chi_{\mu}(\mathbf{1}) | \chi_{\nu}(\mathbf{1}) \rangle$

$\boldsymbol{\varepsilon}$ is a diagonal matrix of orbital energies with elements $\boldsymbol{\varepsilon}_i$, the one-electron orbital energy.

The Roothan-Hall equations are not linear. The Fock matrix depends on the molecular orbital coefficients, through the density matrix. Its solution requires an iterative process. To begin the calculation, we must pick a preliminary set of wave functions to calculate the Fock operator, for example, wave functions from extended

³ All electrons are paired.

Hückel type methods. In the first cycle a new set of orbitals are generated which become the the starting orbitals for the second cycle. The cycle is repeated until the set of orbitals going through the cycle are returned unchanged. The orbitals are then **self-consistent**, hence the acronym SCF. The **Unrestricted Hartree-Fock** method (UHF) allows more freedom because it permits the spatial form of the orbital to depend upon whether the electron has an α or a β spin.

*B. PM3 method.*⁴

The two electron repulsion integrals $(\mu\sigma|\lambda\nu)$ and $(\mu\lambda|\sigma\nu)$ cause most of the trouble. These integrals are particularly difficult to evaluate if the atomic functions χ_μ , etc. are centered on different atoms. The central approximation to reduce the overall computation is to not permit the overlap of atomic orbitals residing on different atomic centers, for example, by assuming $(\mu\sigma|\lambda\nu) = \delta_{\mu\sigma}\delta_{\lambda\nu}(\mu\mu|\lambda\lambda)$. Here $\delta_{\mu\sigma}$ and $\delta_{\lambda\nu}$ (Kronecker's delta) equal 1 when the subscripts are equal; otherwise they are zero. Consequently, all three- and four-centers integrals are ignored, as well as two- and one-center integrals where different atomic orbitals are involved in either of two electrons. In other words, the central approximation to the reduce overall computation is to presume that atomic orbitals residing on different atomic centers do not overlap: $\int \chi_\mu \chi_\sigma dv = 0$.

A very popular semiempirical, MNDO (modified neglect of diatomic overlap) method was published in 1977 by Dewar and Thiel.⁵ The second generation of MNDO has been termed AM1 (Austin method #1)⁶, while the third generation MNDO-PM3, or in short PM3 (parametric method 3). PM3 includes atoms with d orbitals. Parameters for transition metals are based on reproducing known geometries.

C. Heat of formation calculation. (You'll use this in 5.32)

The heat of formation of any compound from its elements in their standard state is obtained by adding to the electronic plus nuclear energy, the calculated energy of formation of the gaseous atom A from its ion, $(E_{el}(A))$ and the experimental heat of formation for atom A, $\Delta H_f(A)$:

$$\Delta H_f = E_{ee} + E_{nr} + \sum_A E_{el}(A) + \sum_A \Delta H_f(A)$$

Calculation of the heat of formation: the case of the CH₂:

- Atomization energy is: $E_{atom} = -E_{totCH_2} + E_C + 2E_H = 151.586368 - 120.500606 - 2*11.906276 = 7.27321 \text{ eV} = 167.72 \text{ kcal mol}^{-1}$.

⁴ Stewart, J. J. P., *J. Computer-Aided Mol. Design* **1990**, 4, 1.

⁵ Dewar, M. J.; Thiel, W. *J. Am. Chem. Soc.* **1977**, 99, 4999.

⁶ Dewar, M. J.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, 107, 3902.

- Heat of formation: $\Delta H_{f(C)}^{\circ} + 2 * \Delta H_{f(H)}^{\circ}) - E_{atom} = 170.89 + 104.20 - 167.72 = 107.37 \text{ kcal mol}^{-1}$

D. Solutions of the self-consistent equations:

