Chapter II

Approximate Molecular Orbital Theories

Although ab initio calculations are successful in calculating small-sized molecular systems, for larger systems they will lead to large C.P.U. times.

For this reason more simplifications are needed, and they lead to a computational framework usually refered to as "Semiempirical MO Calculations". There are many types of these approximate molecular orbital theories, for example CNDO/1, CNDO/2, CNDO/S, MINDO, and INDO. In this work we will deal with the most universal CNDO/2 method, which was developed by Pople, Santry and Segal(10), and which will be referred to as "CNDO" in this text. A general feature of all of these methods is the consideration of valence-shell electrons only.

Before discussing the details of the CNDO approximation, we should consider the important invariant properties of the SCF equation, which any approximate molecular orbital theories must maintain.

SCF equation and transformation properties.

It is well known that the molecular wave functions are invariant with respect to an orthogonal (or Unitary) transformation of the occupied molecular orbitals. The molecular wave functions formed from an antisymmetrized product of LCAO-MO's and the corresponding energies have the further property of being invariant with respect to an orthogonal transformation of the atomic orbitals (basis set).

To investigate the effect of approximations on this invariance,

we need to study this invariance in some detail.

If a new basis set of functions t_1 is chosen related to the original set ϕ_k by the matrix equation

$$T = O \Psi \qquad\qquad 2.1$$

where O is an orthogonal transformation matrix, any square matrices M acquire the new values.

$$M' = O M O^{-1} \qquad\qquad 2.2$$

Considering the Roothaan equation where we separate the Fock matrix into one-electron and two-electron terms,

$$F C = (H + G) C = S C E \qquad\qquad 2.3$$

can be written as

$$(O^{-1}H'O + O^{-1}G'O) C = O^{-1}S'O C E \qquad\qquad 2.4$$

where H', G' and S' correspond to the new basis functions T. Multiplying equation 2.4 from the left by O gives

$$[H' + G'] (O C) = S' (O C) E \qquad\qquad 2.5$$

indicating that (OC) are the orbital coefficients for the solution of the Roothaan equation using the new basis set. The diagonal matrix E is the same as in equation 2.3 using the basis Ψ and trace E is

therefore invariant.

The essential feature of this invariance proof is that the one and two electron integrals transform according to:

$$H'_{uv} = \sum_k \sum_l O_{uk} O_{vl} H_{kl} \qquad\qquad 2.6$$

$$\langle uv | st \rangle ' = \sum_k \sum_l \sum_m \sum_n O_{uk} O_{vl} O_{sm} O_{tn} \langle kl | mn \rangle \qquad 2.7$$

and for the overlap matrix

$$S'_{uv} = \sum_k \sum_l O_{uk} O_{vl} S_{kl} \qquad\qquad 2.8$$

where u, v, s, t are used for the new basis functions. Any approximate LCAO-MO SCF calculation will only be invariant in so far as they satisfy these three transformation conditions. Any possible transformation O may be classified in order of increasing complexity as follows.

    1. Transformations which only mix $2p_x$, $2p_y$, $2p_z$ atomic orbitals entered on the same atom (the rotation of the local axes).

    2. Transformations which only mix 2s and 2p orbitals on the same atom (the atomic hybrid orbitals).

    3. Transformations which mix atomic orbitals on different atoms. (leading to nonatomic basis sets).

Transformations of type 1 and 2 are requried to be invariant for any of the approximate LCAO-MO SCF calculations.

Approximation with complete neglect of differential overlap (CNDO).

The complete neglect of differential overlap method (CNDO)

consists of 3 main approximations. They are the Neglect of Overlap (NO), the Core-Hamiltonian approximation, and the Zero-Differential-Overlap approximation (ZDO). As the ZDO approximation is not generally invariant under transformation, a further step to restore this invariance must be applied.

The details of the approximation above are :

1. The neglect of overlap (NO)

$$S_{kl} = \delta_{kl} \qquad\qquad 2.9$$

so the Roothaan equation will be

$$F\,C = S\,C\,E \longrightarrow F\,C = C\,E \qquad\qquad 2.10$$

2. The zero-differential-overlap (ZDO) approximation

The second main approximation of CNDO is the zero differential-overlap (ZDO) approximation. The ZDO approximation applies to the two-electron integrals of the Roothaan equation:

$$\langle kl \,|\, mn \rangle = \gamma_{km}\,\delta_{kl}\,\delta_{mn} \qquad\qquad 2.11$$

where δ_{kl} and δ_{mn} are the Kronecker delta functions.

The ZDO approximation which is used for atomic orbitals must satisfy the invariance of transformation which was discussed previously. Considering the monatomic differential overlap ψ_k, ψ_l involving the product of two different orbitals on the same atom, we will find that an arbitary transformation of them will not be

invariant. For example a rotation of 45° about the Z axis of the $2s_A$ and $2p_A$ atomic orbitals leading to the new cartensian coordinates.

$$2\ s_A' \quad = \quad 2^{-1/2}\ (\ x + y\ ) \qquad\qquad 2.12$$

$$2\ p_A' \quad = \quad 2^{-1/2}\ (\ x - y\ ) \qquad\qquad 2.13$$

leads to a product of $2s_A$ and $2p_A$ atomic orbitals given by:

$$(\ 2\ s_A'\ )\ (\ 2\ p_A'\ ) \ = \ 1/2\ [\ (\ x,\ x\ ) - (\ y,\ y\ )\ ] \qquad\qquad 2.14$$

When the ZDO approximation is applied the left hand side is neglected but the right hand side is not. Therefore the product is not invatiance to transformation.

To restore the invariance to transformation , we assume that the interaction between electrons belonging to orbitals of one atom depends only on the nature of the atom and not on the nature of the orbitals involved. Thus the two electron-integrals will be set

$$\gamma_{km} \quad = \quad \langle\ kk|\ mm\ \rangle \ = \ \gamma_{AB} \qquad\qquad 2.15$$

where k is an orbital of atom A and m is an orbital of atom B.

3 The core hamiltonian approximation.

In the Fock matrix elements the first part is the one-electron term H_{kl} representing the interaction of each valence shell electron with the effective cores of the various atoms and its kinetic energy.

$$H_{k1} = \langle \phi_k(1)| - 1/2 \, \nabla^2 - \sum_A V_A(r)| \phi_1(1) \rangle \qquad 2.16$$

We distinguish three cases, depending on whether k is equal to 1 or not, and whether they are located on the same atom or not.

3.1 $k=1$: In this case no term is cancelled by the approximation. We group together the terms representing the attraction of an electron in the orbital k by its own core A and its kinetic energy, and the attraction of the electron by the cores of all other atoms B :

$$H_{kk} = \langle \phi_k(1)| - 1/2 \, \nabla^2 - V_A(r)| \phi_k(1) \rangle$$

$$- \sum_{A \neq B} \sum \langle \phi_k(1)| \, V_B| \phi_k(1) \rangle \qquad 2.17$$

or, in short notation,

$$H_{kk} = U_{kk}^A - \sum_{A \neq B} \sum V_{kk}^B \qquad 2.18$$

3.2 $k \neq 1$ and $k, 1 \in A$:   In this case, in analogy to the ZDO approximation the matrix elements H_{k1} will be set at zero.

$$H_{k1} = 0 \, , \, \phi_k \neq \phi_1 \qquad \text{(both on A)} \qquad 2.19$$

3.3 $k \neq 1$ and $k \in A, 1 \in B$:   In this case, where ϕ_k and ϕ_1 are on different atoms A and B, the NO approximation does not apply. On the contrary these elements correspond to the basic bonding capacity due to the overlap between the orbitals. We may seperate the

case of atoms A, B, and all other C, and write

$$H_{kl} = \left\langle \phi_k(i) \,\middle|\, -\,1/2\, \nabla^2 - V_A - V_B \,\middle|\, \phi_l(i) \right\rangle$$

$$- \sum_{C \neq A,B} \left\langle \phi_k(i) \,\middle|\, V_C \,\middle|\, \phi_l(i) \right\rangle \qquad\qquad 2.20$$

where the second part gives the interaction of the distribution with the cores of third atoms C. These integrals will be neglected. The first part then depends only on the local environment and is a measure of the possible lowering of energy levels by an electron interacting with two nuclei simultaneously. It is commonly refered to as a "resonance integral" and is denoted by the symbol B_{kl}.

$$H_{kl} = B_{kl} \qquad\qquad 2.21$$

The B_{kl} terms are then approximated according to Mulliken (11) and Wolfsberg and Helmholtz (12) by:

$$B_{kl} = S_{kl}\, B_{AB} \qquad\qquad 2.22$$

where B_{AB} consists of the atom specific parameters B_A and B_B. Defining the total electronic density of atom A as

$$P_{AA} = \sum_{k \in A} P_{kk} \qquad\qquad 2.23$$

where the summation applies to all valence orbitals k of atom A and

$$P_{BB} = \sum_{m \in B} P_{mm} \qquad\qquad 2.24$$

The Fock matrix elements will become

$$F_{kk} = U_{kk}^A + (P_{AA} - 1/2\, P_{kk}) \; \gamma_{AA} + \sum_{B \neq A} \sum (P_{BB} \; \gamma_{AB} - V_A^B) \qquad 2.25$$

$$F_{kl} = H_{kl} - 1/2\, P_{kl} \; \gamma_{AB} \qquad 2.26$$

The total energy derived from CNDO can be expressed in terms of the energies associated with monatomic contributions and that associated with diatomic contributions

$$E^T = \sum_A E_A + \sum_{A<B} \sum E_{AB} \qquad 2.27$$

where

$$E_A = \sum_k^A P_{kk} \; U_{kk}^A + 1/2 \sum_k^A \sum_m^A (P_{kk} \; P_{mm} - 1/2\, P_{km}^2) \; \gamma_{AA} \qquad 2.28$$

and

$$E_{AB} = \sum_K^A \sum_l^B (2\, P_{kl} \; B_{AB} - 1/2\, P_{kl}^2 \; \gamma_{AB}) + (Z_A Z_B R_{AB}^{-1} - P_{AA} V_A^B$$

$$- P_{BB} V_B^A + P_{AA} P_{BB} \; \gamma_{AB}) \qquad 2.29$$

The CNDO parametrization

The CNDO/2 parametrization performed by Pople and Segal (13) tried to produce observed equilibium bond lengths and dipole moments. It contains the following elements:

1. The local core matrix element U_{kk}^A

The local core matrix element U_{kk} represents the attraction of an electron in the orbital k by its own core A and its kinetic energy. Due to the importance of the electronegativity in determining the relative ability of an atom to depart from neutrality by losing or

gaining electrons, the U_{kk}^A term was defined as the average of the experimental and calculated values of the ionization potential IP and electron affinity EA :

$$U_{kk}^A = 1/2 \left[-IP_k - (Z_A - 1) \gamma_{AA} - EA_k - Z_A \gamma_{AA} \right]$$

$$= -1/2 \left[IP_k + EA_k \right] - \left[Z_A - 1/2 \right] \gamma_{AA} \qquad 2.30$$

where from the Goeppert-Mayer and Sklar approximation we obtain

$$- IP_k = U_{kk}^A + (Z_A - 1) \gamma_{AA} \qquad 2.31$$

$$- EA_k = U_{kk}^A + Z_A \gamma_{AA} \qquad 2.32$$

2. The electron – core potential intergrals V_B^A —

This term, which represents the attraction of the electron of A by the other atom B, is set related to the electron repulsion integrals by

$$V_B^A = Z_B \gamma_{AB} \qquad 2.33$$

3. The bonding parameters B_{AB} —

$$B_{AB} = 1/2 (B_A + B_B) \qquad 2.34$$

where B_A and B_B are parameters characteristic of atoms A and B and determined empirically by comparing them with reference to ab initio calculations on some simple molecules.

The Fock matrix in this CNDO/2 frame work can now be written

$$F_{kk} = -1/2 \ (\ IP_k + EA_k) + [(\ P_{AA} - Z_A) - 1/2 \ (\ P_{kk} - 1 \ )] \ \gamma_{AA}$$

$$+ \ \underset{B \neq A}{\Sigma} \ (\ P_{BB} - Z_B) \ \gamma_{AB} \qquad\qquad 2.35$$

$$F_{kl} = B_{AB} \ S_{kl} - 1/2 \ P_{kl} \ \gamma_{AB} \qquad\qquad 2.36$$

The CNDO basis set

The CNDO basis set consists of Slater- type orbitals (STO) for the valence shell. These are:

$1S \ : \ (\ \zeta^3/ \ \pi \ ) \quad \exp \ (\ -\zeta r \ )$

$2S \ : \ (\ \zeta^5/ \ 96\pi \ ) \quad r \exp \ (\ -\zeta r/2 \ )$

$2P_Z \ : \ (\ \zeta^5/ \ 32\pi \ ) \quad r \cos \theta \exp \ (\ -\zeta r/2)$

For the 2s, 2p orbitals of Li, Be, B, C, N, O, and F the Slater exponents are 1.3, 1.95, 2.6, 3.25, 3.9, 4.55, and 5.2 . For hydrogen 1s orbitals 1.2 is used.

The overlap integrals S_{kl} are all calculated explicitly using formulas qiven by Mulliken, Ricke, and Orloff(14) . The electron repulsion integrals γ_{AB}, γ_{AA} and the potentials V_B^A, in order to maintain invariance, will involve valence s functions only.

The SCF procedure for CNDO

To solve the modified Roothaan equation in the CNDO approximation, the same iterative procedure is needed as in the ab initio method . The steps of solving are:

1. An initial set of molecular orbital coefficients C is obtained from a Huckel-type calculation in which F_{kk} is replaced by

the average of ionization potentials and electron affinities and F_{kl} are replaced by $B_{AB}S_{kl}$

2. Electrons are assigned in pairs to the molecular orbitals with lowest energies .

3. The charge density and the bond order matrix P is calculated and then used to form a new Fock matrix F .

4. New coefficients C are derived from this F and the process is repeated from step 2 until self consistency is achieved.