Qualitative Orbital Picture and Semi-Empirical Methods F

Some of the material contained in the early parts of this Appendix appears, in condensed form, near the end of Chapter 7. For the sake of completeness and clarity of presentation, this material is repeated and enhanced here.

In the simplest picture of chemical bonding, the valence molecular orbitals ϕ_i are constructed as linear combinations of valence atomic orbitals χ_μ according to the LCAO-MO formula:

$$\phi_i = \Sigma_\mu C_{i\mu} \chi_\mu .$$

The core electrons are not explicitly included in such a treatment, although their effects are felt through an electrostatic potential V as detailed below. The electrons that reside in the occupied MO's are postulated to experience an effective potential V that has the following properties:

1. V contains contributions from all of the nuclei in the molecule exerting coulombic attractions on the electron, as well as coulombic repulsions and exchange interactions exerted by the other electrons on this electron;

2. As a result of the (assumed) cancellation of attractions from distant nuclei and repulsions from the electron clouds (i.e., the core, lone-pair, and valence orbitals) that surround these distant nuclei , the effect of V on any particular MO ϕ_i depends primarily on the atomic charges and local bond polarities of the atoms over which ϕ_i is delocalized.

As a result of these assumptions, qualitative molecular orbital models can be developed in which one assumes that each MO ϕ_i obeys a one-electron Schrödinger equation

$$h \phi_i = \varepsilon_i \phi_i .$$

Here the orbital-level hamiltonian h contains the kinetic energy of motion of the electron and the potential V mentioned above:

$$[- \hbar^2/2m_e \quad {}^2 + V] \phi_i = \varepsilon_i \phi_i .$$

Expanding the MO ϕ_i in the LCAO-MO manner, substituting this expansion into the above Schrödinger equation, multiplying on the left by χ^*_ν, and integrating over the coordinates of the electron generates the following orbital-level eigenvalue problem:

$$\Sigma_\mu <\chi_\nu|- \hbar^2/2m_e \quad {}^2 + V|\chi_\mu> C_{i\mu} = \varepsilon_i \Sigma_\mu <\chi_\nu|\chi_\mu> C_{i\mu} .$$

If the constituent atomic orbitals $\{\chi_\mu\}$ have been orthonormalized as discussed in Chapter 7, the overlap integrals $<\chi_\nu|\chi_\mu>$ reduce to $\delta_{\mu,\nu}$.

In all semi-empirical models, the quantities that explicitly define the potential V are not computed from first principles as they are in so-called ab initio methods. Rather, either experimental data or results of ab initio calculations are used to determine the parameters in terms of which V is expressed. The various semi-empirical methods discussed below differ in the sophistication used to include electron-electron interactions as well as in the manner experimental data or ab initio computational results are used to specify V.

If experimental data is used to parameterize a semi-empirical model, then the model should not be extended beyond the level at which it has been parameterized. For example, orbitals obtained from a semi-empirical theory parameterized such that bond energies, excitation energies, and ionization energies predicted by theory agree with experimental data should not subsequently be used in a configuration interaction (CI) calculation. To do so would be inconsistent because the CI treatment, which is designed to treat dynamical correlations among the electrons, would duplicate what using the experimental data (which already contains mother nature's electronic correlations) to determine the parameters had accomplished.

Alternatively, if results of ab initio theory at the single-configuration orbital level are used to define the parameters of a semi-empirical model, it would be proper to use the semi-empirical orbitals in a subsequent higher-level treatment of electron correlations.

A. The Hückel Model

In the most simplified embodiment of the above orbital-level model, the following additional approximations are introduced:

1. The diagonal values $\langle\chi_\mu|- \hbar^2 /2m_e \quad {}^2 + V|\chi_\mu\rangle$, which are usually denoted α_μ, are taken to be equal to the energy of an electron in the atomic orbital χ_μ and, as such, are evaluated in terms of atomic ionization energies (IP's) and electron affinities (EA's):

$$\langle\chi_\mu|- \hbar^2/2m_e \quad {}^2 + V\, |\chi_\mu\rangle = -IP_\mu,$$

for atomic orbitals that are occupied in the atom, and

$$\langle\chi_\mu|- \hbar^2/2m_e \quad {}^2 + V\, |\chi_\mu\rangle = -EA_\mu,$$

for atomic orbitals that are not occupied in the atom.

These approximations assume that contributions in V arising from coulombic attraction to nuclei other than the one on which χ_μ is located, and repulsions from the core, lone-pair, and valence electron clouds surrounding these other nuclei cancel to an extent that $\langle\chi_\mu|\, V\, |\, \chi_\mu\rangle$ contains only potentials from the atom on which χ_μ sits.

It should be noted that the IP's and EA's of valence-state orbitals are not identical to the experimentally measured IP's and EA's of the corresponding atom, but can be obtained from such information. For example, the 2p valence-state IP (VSIP) for a Carbon atom is the energy difference associated with the hypothetical process

$$C(1s^2 2s 2p_x 2p_y 2p_z) \text{ ==> } C^+(1s^2 2s 2p_x 2p_y).$$

If the energy differences for the "promotion" of C

$$C(1s^2 2s^2 2p_x 2p_y) \text{ ==> } C(1s^2 2s 2p_x 2p_y 2p_z) \;;\; \Delta E_C$$

and for the promotion of C^+

$C^+(1s^2 2s^2 2p_x) \Longrightarrow C^+(1s^2 2s 2p_x 2p_y)$; ΔE_{C^+}

are known, the desired VSIP is given by:

$$IP_{2p_z} = IP_C + \Delta E_{C^+} - \Delta E_C .$$

The EA of the 2p orbital is obtained from the

$$C(1s^2 2s^2 2p_x 2p_y) \Longrightarrow C^-(1s^2 2s^2 2p_x 2p_y 2p_z)$$

energy gap, which means that $EA_{2p_z} = EA_C$. Some common IP's of valence 2p orbitals in eV are as follows: C (11.16), N (14.12), N^+ (28.71), O (17.70), O^+ (31.42), F^+ (37.28).

2. The off-diagonal elements $<\chi_\nu|- \hbar^2/2m_e \;\; {}^2 + V |\chi_\mu>$ are taken as zero if χ_μ and χ_ν belong to the same atom because the atomic orbitals are assumed to have been constructed to diagonalize the one-electron hamiltonian appropriate to an electron moving in that atom. They are set equal to a parameter denoted $\beta_{\mu,\nu}$ if χ_μ and χ_ν reside on neighboring atoms that are chemically bonded. If χ_μ and χ_ν reside on atoms that are not bonded neighbors, then the off-diagonal matrix element is set equal to zero.

3. The geometry dependence of the $\beta_{\mu,\nu}$ parameters is often approximated by assuming that $\beta_{\mu,\nu}$ is proportional to the overlap $S_{\mu,\nu}$ between the corresponding atomic orbitals:

$$\beta_{\mu,\nu} = \beta^o_{\mu,\nu} S_{\mu,\nu} .$$

Here $\beta^o_{\mu,\nu}$ is a constant (having energy units) characteristic of the bonding interaction between χ_μ and χ_ν; its value is usually determined by forcing the molecular orbital energies obtained from such a qualitative orbital treatment to yield experimentally correct ionization potentials, bond dissociation energies, or electronic transition energies.

The particular approach described thus far forms the basis of the so-called Hückel model. Its implementation requires knowledge of the atomic α_μ and $\beta^0_{\mu,\nu}$ values, which are eventually expressed in terms of experimental data, as well as a means of calculating the geometry dependence of the $\beta_{\mu,\nu}$'s (e.g., some method for computing overlap matrices $S_{\mu,\nu}$).

B. The Extended Hückel Method

It is well known that bonding and antibonding orbitals are formed when a pair of atomic orbitals from neighboring atoms interact. The energy splitting between the bonding and antibonding orbitals depends on the overlap between the pair of atomic orbitals. Also, the energy of the antibonding orbital lies higher above the arithmetic mean $E_{ave} = E_A + E_B$ of the energies of the constituent atomic orbitals (E_A and E_B) than the bonding orbital lies below E_{ave} . If overlap is ignored, as in conventional Hückel theory (except in parameterizing the geometry dependence of $\beta_{\mu,\nu}$), the differential destabilization of antibonding orbitals compared to stabilization of bonding orbitals can not be accounted for.

By parameterizing the off-diagonal Hamiltonian matrix elements in the following overlap-dependent manner:

$$h_{\nu,\mu} = <\chi_\nu|- \hbar^2/2m_e \quad {}^2 + V |\chi_\mu> = 0.5\ K\ (h_{\mu,\mu} + h_{\nu,\nu})\ S_{\mu,\nu}\ ,$$

and explicitly treating the overlaps among the constituent atomic orbitals $\{\chi_\mu\}$ in solving the orbital-level Schrödinger equation

$$\Sigma_\mu <\chi_\nu|- \hbar^2/2m_e \quad {}^2 + V|\chi_\mu> C_{i\mu} = \varepsilon_i\ \Sigma_\mu <\chi_\nu|\chi_\mu> C_{i\mu},$$

Hoffmann introduced the so-called extended Hückel method. He found that a value for K= 1.75 gave optimal results when using Slater-type orbitals as a basis (and for calculating the $S_{\mu,\nu}$). The diagonal $h_{\mu,\mu}$ elements are given, as in the conventional Hückel method, in terms of valence-state IP's and EA's. Cusachs later proposed a variant of this parameterization of the off-diagonal elements:

$$h_{\nu,\mu} = 0.5\ K\ (h_{\mu,\mu} + h_{\nu,\nu})\ S_{\mu,\nu}\ (2-|S_{\mu,\nu}|).$$

For first- and second-row atoms, the 1s or (2s, 2p) or (3s,3p, 3d) valence-state ionization energies (α_μ's), the number of valence electrons (#Elec.) as well as the orbital exponents (e_s , e_p and e_d) of Slater-type orbitals used to calculate the overlap matrix elements $S_{\mu,\nu}$ corresponding are given below.

Atom	# Elec.	e_s=e_p	e_d	α_s(eV)	α_p(eV)	α_d(eV)
H	1	1.3		-13.6		
Li	1	0.650		-5.4	-3.5	
Be	2	0.975		-10.0	-6.0	
B	3	1.300		-15.2	-8.5	
C	4	1.625		-21.4	-11.4	
N	5	1.950		-26.0	-13.4	
O	6	2.275		-32.3	-14.8	
F	7	2.425		-40.0	-18.1	
Na	1	0.733		-5.1	-3.0	
Mg	2	0.950		-9.0	-4.5	
Al	3	1.167		-12.3	-6.5	
Si	4	1.383	1.383	-17.3	-9.2	-6.0
P	5	1.600	1.400	-18.6	-14.0	-7.0
S	6	1.817	1.500	-20.0	-13.3	-8.0
Cl	7	2.033	2.033	-30.0	-15.0	-9.0

In the Hückel or extended Hückel methods no explicit reference is made to electron-electron interactions although such contributions are absorbed into the V potential, and hence into the α_μ and $\beta_{\mu,\nu}$ parameters of Hückel theory or the $h_{\mu,\mu}$ and $h_{\mu,\nu}$ parameters of extended Hückel theory. As electron density flows from one atom to another (due to electronegativity differences), the electron-electron repulsions in various atomic orbitals changes. To account for such charge-density-dependent coulombic energies, one must use an approach that includes explicit reference to inter-orbital coulomb and exchange interactions. There exists a large family of semi-empirical methods that permit explicit treatment of electronic interactions; some of the more commonly used approaches are discussed below.

C. Semi-Empirical Models that Treat Electron-Electron Interactions

1. The ZDO Approximation

Most methods of this type are based on the so-called zero-differential overlap (ZDO) approximation. Their development begins by using an approximation to the atomic-orbital-based two-electron integrals introduced by Mulliken:

$$<\chi_a\chi_b|g|\chi_c\chi_d> = S_{a,c}S_{b,d} \{\lambda_{a,b} + \lambda_{a,d} + \lambda_{c,b} + \lambda_{c,d}\}/4,$$

where $S_{a,c}$ is the overlap integral between χ_a and χ_c , and

$$\lambda_{a,b} = <\chi_a\chi_b|g|\chi_a\chi_b>$$

is the coulomb integral between the charge densities $|\chi_a|^2$ and $|\chi_b|^2$.
Then, when the so-called zero-overlap approximation

$$S_{a,c} = \delta_{a,c}$$

is made, the general four-orbital two-electron integral given above reduces to its zero-differential overlap value:

$$<\chi_a\chi_b|g|\chi_c\chi_d> = \delta_{a,c}\,\delta_{b,d}\,\lambda_{a,b}.$$

This fundamental approximation allows the two-electron integrals that enter into the expression for the Fock matrix elements to be expressed in terms of the set of two-orbital coulomb interaction integrals $\lambda_{a,b}$ as well as experimental or ab initio values for valence-state IP's and EA's, as is now illustrated.

2. Resulting Fock Matrices

Using the ZDO approximation, the Fock matrix elements over the valence atomic orbitals (the cores are still treated through an effective electrostatic potential as above)

$$F_{\mu,\nu} = < \chi_\mu \,|\, h \,|\, \chi_\nu > + \Sigma_{\delta,\kappa} \,[\, \gamma_{\delta,\kappa} < \chi_\mu\, \chi_\delta \,|\, g \,|\, \chi_\nu\, \chi_\kappa >$$

$$- \;\gamma_{\delta,\kappa}{}^{ex} < \chi_\mu\, \chi_\delta \,|\, g \,|\, \chi_\kappa\, \chi_\nu >],$$

reduce, to:

$$F_{\mu,\mu} = < \chi_\mu \,|\, h \,|\, \chi_\mu > + \Sigma_\varepsilon\, \gamma_{\varepsilon,\varepsilon}\, \lambda_{\mu,\varepsilon} - \;\gamma_{\mu,\mu}{}^{ex}\, \lambda_{\mu,\mu},$$

for the diagonal elements and

$$F_{\mu,\nu} = < \chi_\mu \,|\, h \,|\, \chi_\nu > - \gamma_{\mu,\nu}{}^{ex}\, \lambda_{\mu,\nu}$$

for the off-diagonal elements. Here, h represents the kinetic energy $-\hbar^2\;\;{}^2/2m$ operator plus the sum of the attractive coulombic potential energies to each of the nuclei $-\Sigma_a Z_a e^2/|r-R_a|$ and the electrostatic repulsions of the core electrons (i.e., all those not explicitly treated as valence in this calculation) around each of the nuclei.

Further reduction of the diagonal $F_{\mu,\mu}$ expression is achieved by:

a. Combining terms in the sum Σ_ε involving orbitals χ_ε on atomic centers other than where χ_μ sits (atom a) together with the sum of coulomb attractions (which appear in h) over these same centers:

$$\Sigma_{\varepsilon(\text{not on atom a})}\; \gamma_{\varepsilon,\varepsilon}\, \lambda_{\mu,\varepsilon}$$

$$- \;\Sigma_{b(\text{not on atom a})} <\chi_\mu|\; Z_b e^2 |r-R_b|^{-1}\; |\chi_\mu>$$

$$= \Sigma_{b,\varepsilon(\text{not center a})}\, (\gamma_{\varepsilon,\varepsilon}\, \lambda_{\mu,\varepsilon} - V_{\mu,b}\;).$$

This combination represents the net coulombic interaction of $|\chi_\mu|^2$ with the total electron density (first sum) and the total attractive positive density (second sum) on atoms other than the atom on which χ_μ sits.

b. Recognizing

$$< \chi_\mu | -\hbar^2 \nabla^2/2m | \chi_\mu > + \Sigma_{\varepsilon \neq \mu (\text{ on center a })} \gamma_{\varepsilon,\varepsilon} \lambda_{\mu,\varepsilon}$$

$$- <\chi_\mu | Z_a e^2/|r-R_a| |\chi_\mu> = U_{\mu,\mu}$$

as the average value of the atomic Fock operator (i.e., kinetic energy plus attractive colomb potential to that atom's nucleus plus coulomb and exchange interactions with other electrons on that atom) for an electron in χ_μ on the nucleus a. As in Hückel theory, the values of these parameters $U_{\mu,\mu}$, which play the role of the Hückel α_μ, can be determined from atomic valence-state ionization potentials and electron affinities. These quantities, in turn, may be obtained either from experimental data or from the results of <u>ab initio</u> calculations.

As a result, the diagonal F matrix elements are given by

$$F_{\mu,\mu} = U_{\mu,\mu} + (\gamma_{\mu,\mu} - \gamma_{\mu,\mu}^{ex}) \lambda_{\mu,\mu} + \Sigma_{b,\varepsilon(\text{not center a})} (\gamma_{\varepsilon,\varepsilon} \lambda_{\mu,\varepsilon} - V_{\mu,b}).$$

The evaluation of the quantities entering into this expression and that for the off-diagonal $F_{\mu,\nu}$ elements differs from one semi-empirical method to another; this topic is covered late in this Appendix.

Reduction of the off-diagonal elements involving orbitals χ_μ and χ_ν on the <u>same</u> atom (a) is achieved by assuming that the atomic orbitals have been formed in a manner that makes the contributions to $F_{\mu,\nu}$ from atom a vanish

$$< \chi_\mu | -\hbar^2 \nabla^2/2m | \chi_\nu > - <\chi_\mu | Z_a e^2/|r-R_a| |\chi_\nu> - \gamma_{\mu,\nu}^{ex} \lambda_{\mu,\nu}$$

$$+ \Sigma_{\varepsilon(\text{on atom a})} \gamma_{\varepsilon,\varepsilon} <\chi_\mu \chi_\varepsilon | g | \chi_\nu \chi_\varepsilon> = 0,$$

and then neglecting, to be consistent with the ZDO assumption, the contributions from atoms other than atom a

$$- \Sigma_{b(\text{not center a})} <\chi_\mu | Z_b e^2/|r-R_b| |\chi_\nu> + \Sigma_{\varepsilon(\text{ not on atom a})} \gamma_{\varepsilon,\varepsilon}$$

$$<\chi_\mu \chi_\varepsilon | g | \chi_\nu \chi_\varepsilon> = 0.$$

Hence, the off-diagonal F matrix elements vanish, $F_{\mu,\nu} = 0$ for χ_μ and χ_ν both on the same atom (a).

The off-diagonal F matrix elements coupling orbitals from different atoms (a and b) are expressed as

$$F_{\mu,\nu} = < \chi_\mu | -\hbar^2 \nabla^2/2m | \chi_\nu > - <\chi_\mu | Z_a e^2/|r-R_a| |\chi_\nu>$$

$$- <\chi_\mu | Z_b e^2/|r-R_b| |\chi_\nu> - \gamma_{\mu,\nu}^{ex} \lambda_{\mu,\nu} = \beta_{\mu,\nu} - \gamma_{\mu,\nu}^{ex} \lambda_{\mu,\nu} .$$

Contributions to these elements from atoms other than a and b are neglected, again to be consistent with the ZDO approximation.

Unlike the Hückel and extended Hückel methods, the semi-empirical approaches that explicitly treat electron-electron interactions give rise to Fock matrix element expressions that depend on the atomic-orbital-based density matrix $\gamma_{\mu,\nu}$. This quantity is computed using the LCAO-MO coefficients $\{C_{i,\mu}\}$ of the occupied molecular orbitals from the previous iteration of the

$$\Sigma_\mu F_{\nu,\mu} C_{i\mu} = \varepsilon_i \Sigma_\mu <\chi_\nu|\chi_\mu> C_{i\mu}$$

equations. In particular,

$$\gamma_{\mu,\nu} = \Sigma_{i(\text{occupied})} n_i C_{i,\mu} C_{i,\nu},$$

$$\gamma_{\mu,\nu}^{ex} = \Sigma_{i(\text{occupied and of spin } \sigma)} C_{i,\mu} C_{i,\nu}.$$

Here, n_i is the number (0, 1, or 2) of electrons that occupy the ith molecular orbital, and spin σ denotes the spin (α or β) of the orbital whose Fock matrix is being formed. For example, when studying doublet radicals having K doubly occupied orbitals and one half-filled orbital (K+1) in which an α electron resides, σ is α. In this case, $n_i = 2$ for the first K orbitals and $n_i = 1$ for the last occupied orbital. Moreover, the Fock matrix elements $F_{\mu,\nu}^\beta$ for β orbitals contains contributions from $\gamma_{\mu,\nu}^{ex}$ that are of the form

$$\gamma_{\mu,\nu}^{ex} = \Sigma_{i=1,K} C_{i,\mu} C_{i,\nu},$$

while the Fock matrix elements $F_{\mu,\nu}^\alpha$ for α orbitals contains

$$\gamma_{\mu,\nu}^{ex} = \Sigma_{i=1,K} C_{i,\mu} C_{i,\nu} + C_{K+1,\mu} C_{K+1,\nu}.$$

For both $F_{\mu,\nu}^\alpha$ and $F_{\mu,\nu}^\beta$, coulomb contributions arise as

$$\gamma_{\mu,\nu} = 2 \Sigma_{i=1,K} C_{i,\mu} C_{i,\nu} + C_{K+1,\mu} C_{K+1,\nu}.$$

3. Various Semi-Empirical Methods

a. The Pariser-Parr-Pople (PPP) Method for π-Orbitals

In the PPP method, only the π- orbitals and the corresponding π-electrons are considered. The parameters included in the F matrix

$$F_{\mu,\mu} = U_{\mu,\mu} + (\gamma_{\mu,\mu} - \gamma_{\mu,\mu}^{ex}) \lambda_{\mu,\mu} + \Sigma_{b,\varepsilon(\text{not center a})} (\gamma_{\varepsilon,\varepsilon} \lambda_{\mu,\varepsilon} - V_{\mu,b}).$$

$$F_{\mu,\nu} = \beta_{\mu,\nu} - \gamma_{\mu,\nu}^{ex} \lambda_{\mu,\nu}$$

are obtained as follows:

i). The diagonal integrals $\lambda_{a,a}$, which represent the mutual coulomb repulsions between a pair of electrons in the valence-state orbital labeled a, can be estimated, as suggested by Pariser, in terms of the valence-state IP and EA of that orbital:

$$\lambda_{a,a} = IP_a - EA_a .$$

Alternatively, these one-center coulomb integrals can be computed from first principles using Slater or Gaussian type orbitals.

ii). The off-diagonal coulomb integrals $\lambda_{a,b}$ are commonly approximated either by the Mataga-Nishimoto formula:

$$\lambda_{a,b} = e^2/(R_{a,b} + x_{a,b}),$$

where

$$x_{a,b} = 2e^2 /(\lambda_{a,a} + \lambda_{b,b}),$$

or by the Dewar-Ohno-Klopman expression:

$$\lambda_{a,b} = \frac{e^2}{\sqrt{(R^2_{a,b} + 0.25\ e^4\ (1/\lambda_{a,a} + 1/\lambda_{b,b})^2)}} .$$

iii). The valence-state IP's and EA's, $U_{\mu,\mu}$ are evaluated from experimental data or from the results of ab initio calculations of the atomic IP's and EA's.

iv). The $\beta_{\mu,\nu}$ integrals are usually chosen to make bond lengths, bond energies, or electronic excitation energies in the molecule agree with experimental data. The geometry dependence of $\beta_{\mu,\nu}$ is often parameterized as in Hückel theory $\beta_{\mu,\nu} = \beta^o_{\mu,\nu} S_{\mu,\nu}$, and the overlap is then computed from first principles.

v). The $\Sigma_{b(\text{not center a})} V_{\mu,b}$ term, which represents the coulombic attraction of an electron in χ_μ to the nucleus at center b, is often approximated as $Z_b \lambda_{\mu,\varepsilon}$, where ε labels the one π orbital on center b, and Z_b is the number of π electrons contributed by center b. This parameterization then permits the attractive interaction for center b to be combined with the repulsive interaction to give
$\Sigma_{b,\varepsilon(\text{not center a})} (\gamma_{\varepsilon,\varepsilon} - Z_b) \lambda_{\mu,\varepsilon}$.

b. All Valence Electron Methods

The CNDO, INDO, NDDO, MNDO, and MINDO methods all are defined in terms of an orbital-level Fock matrix with elements

$$F_{\mu,\mu} = U_{\mu,\mu} + (\gamma_{\mu,\mu} - \gamma_{\mu,\mu}^{ex}) \lambda_{\mu,\mu} + \Sigma_{b,\varepsilon(\text{not center a})} (\gamma_{\varepsilon,\varepsilon} \lambda_{\mu,\varepsilon} - V_{\mu,b}).$$

$$F_{\mu,\nu} = \beta_{\mu,\nu} - \gamma_{\mu,\nu}^{ex} \lambda_{\mu,\nu} .$$

They differ among one another in two ways: (i) in the degree to which they employ the ZDO approximation to eliminate two-electron integrals, and (ii) in whether they employ experimental data (MINDO, MNDO, CNDO/S) or results of ab initio one-electron calculations (CNDO, INDO, NDDO) to define their parameters.

The CNDO and CNDO/S methods apply the ZDO approximation to all integrals, regardless of whether the orbitals are located on the same atom or not. In the INDO method, which was designed to improve the treatment of spin densities at nuclear centers and to handle singlet-triplet energy differences for open-shell species, exchange integrals $<\chi_a\chi_b|g|\chi_b\chi_a>$ involving orbitals χ_a and χ_b on the same atom are retained. In the NDDO approach, the ZDO approximation is applied only to integrals involving orbitals on two or more different atoms; that is, all one center integrals are retained. The text Approximate Molecular Orbital Theory by J. A. Pople and D. L. Beveridge, McGraw-Hill, New York (1970) gives a treatment of several of these semi-empirical methods beyond the introduction provided here.

To illustrate the differences among the various approaches and to clarify how their parameters are obtained, let us consider two specific and popular choices- CNDO/2 and MINDO.

i. The CNDO/2 and CNDO/S Models

In the CNDO/2 approach as originally implemented, ab initio (orbital-level) calculated values of the energies mentioned below are used in determining the requisite parameters. In the later CNDO/S method, experimental values of these energies are employed. Briefly, in any CNDO method:

1). The diagonal integrals $\lambda_{a,a}$, which represent the mutual coulomb repulsions between a pair of electrons in the valence-state orbital labeled a, are calculated in terms of the valence-state IP and EA of that orbital:

$$\lambda_{a,a} = IP_a - EA_a .$$

2). The valence-state IP's and EA's, and hence the $U_{\mu,\mu}$ are evaluated from the results of ab initio calculations (CNDO/2) or experimental measurement (CNDO/S) of the atomic IP's and EA's. The expressions used are:

$$-IP_A = U_{a,a} +(Z_A -1) \lambda_{a,a},$$

for orbitals χ_a, and

$$-EA_A = U_{b,b} + Z_A \lambda_{b,b},$$

for orbitals χ_b. Here Z_A is the effective core charge of atom A (the nuclear charge minus the number of "core" electrons not explicitly treated). For first row atoms, several $U_{a,a}$ and $\lambda_{a,a}$ values are tabulated below (all quantities are in eV).

	H	Li	Be	B	C	N	O	F
$U_{s,s}$	-13.6	-5.00	-15.4	-30.37	-50.69	-70.09	-101.3	-129.5
$U_{p,p}$		-3.67	-12.28	-24.7	-41.53	-57.85	-84.28	-108.9
$\lambda_{A,A}$	12.85	3.46	5.95	8.05	10.33	11.31	13.91	15.23

3). The off-diagonal coulomb integrals $\lambda_{a,b}$ are commonly approximated either by the Mataga-Nishimoto formula:

$$\lambda_{a,b} = e^2/(R_{a,b} + x_{a,b}),$$

where

$$x_{a,b} = 2e^2 /(\lambda_{a,a} + \lambda_{b,b}),$$

or by the Dewar-Ohno-Klopman expression:

$$\lambda_{a,b} = \frac{e^2}{\sqrt{(R^2_{a,b} + 0.25\ e^4\ (1/\lambda_{a,a} + 1/\lambda_{b,b})^2)}} \ .$$

4). As in PPP theory, the term $\Sigma_{b,\varepsilon(\text{not center a})} (\gamma_{\varepsilon,\varepsilon}\ \lambda_{\mu,\varepsilon} - V_{\mu,b})$ is approximated by $\Sigma_{b,\varepsilon(\text{not center a})} (\gamma_{\varepsilon,\varepsilon} - Z_b)\ \lambda_{\mu,\varepsilon}$, where Z_b is the number of valence electrons contributed by atom b, and χ_ε is one of the valence electrons on atom b.

5. The $\beta_{\mu,\nu}$ parameters are approximated as $\beta_{\mu,\nu} = S_{\mu,\nu}\ (\beta_a + \beta_b)$,
where $S_{\mu,\nu}$ is the overlap between the orbitals χ_μ and χ_ν , and β_a and β_b are atom-dependent parameters given below for first row atoms:

	H	Li	Be	B	C	N	O	F
β_a(eV)	-9	-9	-13	-17	-21	-25	-31	-39

ii. The INDO (and MINDO-Type) Methods

In these methods, the specification of the parameters entering into $F_{\mu,\nu}$ is carried out in the same fashion as in the CNDO/2 approach, except that:

1. The ZDO approximation is made only for two-center integrals; one-center coulomb $\lambda_{a,b} = <\chi_a\chi_b|g|\chi_a\chi_b>$ and exchange
$\lambda_{a,b}^{ex} = <\chi_a\chi_b|g|\chi_b\chi_a>$ integrals are retained. In the INDO approach, the values of these single-atom integrals are determined by requiring the results of the calculation, performed at the Fock-like orbital level, to agree with results of ab initio Fock-level calculations. In the MINDO approach, experimental electronic spectra of the particular atom are used to determine these parameters. The "diagonal" values $\lambda_{a,a}$ are determined, as indicated earlier, from valence-state energies (ab initio for INDO and experimental for MINDO) of the atom A on which χ_a resides.

2. The values of the $U_{a,a}$ parameters are determined according to the following equations:

$$U_{s,s} = -0.5\ (IP_H + EA_H)\ -0.5\ \lambda_{s,s}$$

for Hydrogen's 1s orbital;

$$U_{s,s} = -0.5(IP_s + EA_s) -(Z_A-0.5)\ \lambda_{s,s} +1/6\ (Z_A-1.5)\ G^1(s,s)$$

for Boron through Fluorine's 2s orbitals; and

$$U_{p,p} = -0.5(IP_p + EA_p) -(Z_A-0.5)\ \lambda_{p,p} +2/25\ (Z_A-1.5)\ F^2(p,p) + 1/3\ G^1(p,p).$$

Here, F^2 and G^1 represent the well known Slater-Condon integrals in terms of which the coulomb and exchange integrals can be expressed:

$$F^k(nl,n'l') = \int_0^\infty \int_0^\infty |R_{nl}(\mathbf{r})|^2\ |R_{n'l'}(\mathbf{r'})|^2\ 2\mathbf{r}_<{}^k/\mathbf{r}_>{}^{k+1}\ \mathbf{r}^2\mathbf{r'}^2\ \mathbf{dr}\ \mathbf{dr'}$$

$$G^k(nl,n'l') = \int_0^\infty \int_0^\infty |R_{nl}(\mathbf{r})R_{n'l'}(\mathbf{r})|^2\ 2\mathbf{r}_<{}^k/\mathbf{r}_>{}^{k+1}\ \mathbf{r}^2\mathbf{r'}^2\ \mathbf{dr}\ \mathbf{dr'}$$

and Z_A is the effective core charge (the nuclear charge minus the number of "core" electrons not explicitly treated in the calculation) of the atom A on which the orbitals in question reside. In the definitions of the integrals, $\mathbf{r}^<$ and $\mathbf{r}^>$ represent, respectively, the smaller and larger of $\mathbf{r}$ and $\mathbf{r'}$. Again, ab initio calculational data is used in the INDO method, and experimental data in the MINDO method to fix the parameters entering these expressions.

D. Summary

As presented, semi-empirical methods are based on a single-configuration picture of electronic structure. Extensions of such approaches to permit consideration of more than a single important configuration have been made (for excellent overviews, see Approximate Molecular Orbital Theory by J. A. Pople and D. L. Beveridge, McGraw-Hill, New York (1970) and Valence Theory, 2nd Ed., by J. N. Murrell, S. F. A. Kettle, and J. M. Tedder, John Wiley, London (1965)). Pople and co-workers preferred to use data from ab initio calculations in developing sets of parameters to use in such methods because they viewed semi-empirical methods as approximations to ab initio methods. Others use experimental data to determine parameters because they view semi-empirical methods as models of mother nature.