

## Chapter 7

### *The Most Elementary Molecular Orbital Models Contain Symmetry, Nodal Pattern, and Approximate Energy Information*

#### I. The LCAO-MO Expansion and the Orbital-Level Schrödinger Equation

In the simplest picture of chemical bonding, the valence molecular orbitals  $\psi_i$  are constructed as linear combinations of valence atomic orbitals  $\phi_\mu$  according to the LCAO-MO formula:

$$\psi_i = \sum_{\mu} C_{i\mu} \phi_{\mu}$$

The core electrons are not explicitly included in such a treatment, although their effects are felt through an electrostatic potential  $V$  that has the following properties:

i.  $V$  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;

ii. 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 molecular orbital  $\psi_i$  depends primarily on the atomic charges and local bond polarities of the atoms over which  $\psi_i$  is delocalized.

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

$$\hat{h} \psi_i = \epsilon_i \psi_i$$

Here the orbital-level hamiltonian  $\hat{h}$  contains the kinetic energy of motion of the electron and the potential  $V$  mentioned above:

$$\left[ -\frac{\hbar^2}{2m_e} \nabla^2 + V \right] \psi_i = \epsilon_i \psi_i$$

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

$$\int \psi_i^* \left[ -\frac{\hbar^2}{2m_e} \nabla^2 + V \right] \sum_{\mu} C_{i\mu} \psi_{\mu} d\tau = E_i \int \psi_i^* \sum_{\mu} C_{i\mu} \psi_{\mu} d\tau.$$

If the constituent atomic orbitals  $\{\psi_{\mu}\}$  have been orthonormalized as discussed earlier in this chapter, the overlap integrals  $\int \psi_i^* \psi_{\mu} d\tau$  reduce to  $\delta_{i\mu}$ .

## II. Determining the Effective Potential $V$

In the most elementary models of orbital structure, the quantities that explicitly define the potential  $V$  are not computed from first principles as they are in so-called ab initio methods (see Section 6). Rather, either experimental data or results of ab initio calculations are used to determine the parameters in terms of which  $V$  is expressed. The resulting empirical or 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, experimental bond energies, excitation energies, and ionization energies may be used to determine molecular orbital energies which, in turn, are summed to compute total energies. In such a parameterization it would be incorrect to subsequently use these mos to form a wavefunction, as in Sections 3 and 6, that goes beyond the simple 'product of orbitals' description. To do so would be inconsistent because the more sophisticated wavefunction 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-product wavefunction level are used to define the parameters of a semi-empirical model, it would then be proper to use the semi-empirical orbitals in a subsequent higher-level treatment of electronic structure as done in Section 6.

### A. The Hückel Parameterization of $V$

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

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

$$\langle \mu | -\hbar^2/2m_e \nabla^2 + V | \mu \rangle = -IP_\mu,$$

for atomic orbitals that are occupied in the atom, and

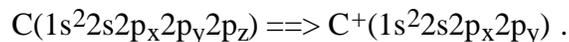
$$\langle \mu | -\hbar^2/2m_e \nabla^2 + V | \mu \rangle = -EA_\mu,$$

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  $\mu$  is located, and repulsions from the core, lone-pair, and valence electron clouds surrounding these other nuclei cancel to an extent that

$\langle \mu | V | \mu \rangle$  contains only potentials from the atom on which  $\mu$  sits.

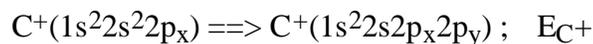
It should be noted that the IP's and EA's of valence-state orbitals are not identical to the experimentally measured IP's and EA's of the corresponding atom, but can be obtained from such information. For example, the 2p valence-state IP (VSIP) for a Carbon atom is the energy difference associated with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



If the energy differences for the "promotion" of C



and for the promotion of  $C^+$



are known, the desired VSIP is given by:

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

The EA of the 2p orbital is obtained from the

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

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<sup>+</sup> (28.71), O (17.70), O<sup>+</sup> (31.42), F<sup>+</sup> (37.28).

2. The off-diagonal elements  $\langle \mu | -\hbar^2/2m_e \nabla^2 + V | \nu \rangle$  are taken as zero if  $\mu$  and  $\nu$  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  $\mu_{\nu}$ , if  $\mu$  and  $\nu$  reside on neighboring atoms that are chemically bonded. If  $\mu$  and  $\nu$  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  $\mu_{\nu}$  parameters is often approximated by assuming that  $\mu_{\nu}$  is proportional to the overlap  $S_{\mu\nu}$  between the corresponding atomic orbitals:

$$\mu_{\nu} = \mu_0 S_{\mu\nu}.$$

Here  $\mu_0$  is a constant (having energy units) characteristic of the bonding interaction between  $\mu$  and  $\nu$ ; 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  $\mu$  and  $\mu_0$  values, which are eventually expressed in terms of experimental data, as well as a means of calculating the geometry dependence of the  $\mu_{\nu}$ '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  $S_{\mu, \nu}$ ), 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:

$$h_{\nu, \mu} = \langle \nu | -\hbar^2/2m_e \nabla^2 + V | \mu \rangle = 0.5 K (h_{\mu, \mu} + h_{\nu, \nu}) S_{\mu, \nu},$$

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

$$\mu \langle \nu | -\hbar^2/2m_e \nabla^2 + V | \mu \rangle C_{i\mu} = \epsilon_i \mu \langle \nu | \mu \rangle C_{i\mu},$$

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 ( $\mu$ '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.	$e_s=e_p$	$e_d$	s(eV)	p(eV)	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  $\mu$  and  $\mu$ , parameters of Hückel theory or the  $h_{\mu,\mu}$  and  $h_{\mu}$  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 in Appendix F.