# 7.3: The Hückel Parameterization

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

## Approximation 1: Diagonal Component

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

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

for atomic orbitals that are occupied in the atom, and

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

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 $\chi_\mu$ 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 $\chi_\mu$ 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

$$C(1s^2 2s 2p_x 2p_y 2p_z) \rightarrow C^+(1s^2 2s 2p_x 2p_y).$$

If the energy differences for the "promotion" of C

$$C(1s^2 2s^2 2p_x 2p_y) \rightarrow C(1s^2 2s 2p_x 2p_y 2p_z); \Delta E_C$$

and for the promotion of $C^+$

$$C^+(1s^2 2s^2 2p_x) \rightarrow C^+(1s^2 2s 2p_x 2p_y); \Delta E_C^+$$

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

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

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).

## Approximation 2: Nearest Neighbors Approximation

The off-diagonal elements $\langle \chi_\nu | \frac{-\hbar^2}{2m_e}\nabla^2 + V | \chi_\mu \rangle$ are taken as zero if $\chi_\mu$ and $\chi_n u$ 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 $\chi_\mu$ and $\chi_\nu$ reside on neighboring atoms that are chemically bonded. If $c_m$ and $c_n$ reside on atoms that are not bonded neighbors, then the off-diagonal matrix element is set equal to zero.

## Approximation 3: Off-Diagonal Component

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 $\chi_\mu$ and $\chi_\nu$; 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.

> It is sometimes assumed that the overlap matrix $S$ is the identity matrix. This means that overlap between the orbitals is neglected

The three approximations above form the basis of the so-called **Hückel model**. Its implementation requires knowledge of the atomic $\alpha_\mu$ 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 $S_{\mu,\nu}$ ).

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