

7.4: 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:

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

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

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

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:

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

For first- and second-row atoms, the 1s or (2s, 2p) or (3s, 3p, 3d) valence-state ionization energies (α'_μ), 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 $S_{m,n}$ 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

Table 7.4.1: Insert caption here!

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 in Appendix F.

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