

10.6: Semi-Empirical Methods- Extended Hückel

An electronic structure calculation from first principles (*ab initio*) presents a number of challenges. Many integrals must be evaluated followed by a self-consistent process for assessing the electron-electron interaction and then electron correlation effects must be taken into account. Semi-empirical methods do not proceed analytically in addressing these issues, but rather uses experimental data to facilitate the process. Several such methods are available. These methods are illustrated here by the approaches built on the work of Hückel.

Extended Hückel Molecular Orbital Method (EH)

One of the first semi-empirical methods to be developed was [Hückel Molecular Orbital Theory \(HMO\)](#). HMO was developed to describe molecules containing conjugated double bonds. HMO considered only electrons in π orbitals and ignored all other electrons in a molecule. It was successful because it could address a number of issues associated with a large group of molecules at a time when calculations were done on mechanical calculators.

The **Extended Hückel Molecular Orbital Method (EH)** grew out of the need to consider all valence electrons in a molecular orbital calculation. By considering all valence electrons, chemists could determine molecular structure, compute energy barriers for rotation about bonds, and even determine energies and structures of transition states for reactions. The computed energies could be used to choose between proposed transitions states to clarify reaction mechanisms.

In the EH method, only the n valence electrons are considered. The total valence electron wavefunction is described as a product of the one-electron wavefunctions.

$$\psi_{valence} = \psi_1(1)\psi_2(2)\psi_3(3)\psi_3(3) \dots \psi_j(n) \quad (10.6.1)$$

where n is the number of electrons and j identifies the molecular orbital. Each molecular orbital is written as an linear combination of atomic orbitals (LCAO).

$$\psi_j = \sum_{r=1}^N c_{jr} \varphi_j \quad (10.6.2)$$

where now the φ_j are the valence atomic orbitals chosen to include the 2s, 2p_x, 2p_y, and 2p_z of the carbons and heteroatoms in the molecule and the 1s orbitals of the hydrogen atoms. These orbitals form the *basis set*. Since this basis set contains only the atomic-like orbitals for the valence shell of the atoms in a molecule, it is called a *minimal basis set*.

Each ψ_j , with $j = 1 \dots N$, represents a molecular orbital, i.e. a wavefunction for one electron moving in the electrostatic field of the nuclei and the other electrons. Two electrons with different spins are placed in each molecular orbital so that the number of occupied molecular orbitals N is half the number of electrons, n , i.e. $N = n/2$.

The number of molecular orbitals that one obtains by this procedure is equal to the number of atomic orbitals. Consequently, the indices j and r both run from 1 to N . The c_{jr} are the weighting coefficients for the atomic orbitals in the molecular orbital. These coefficients are not necessarily equal, or in other words, the orbital on each atom is not used to the same extent to form each molecular orbital. Different values for the coefficients give rise to different net charges at different positions in a molecule. This charge distribution is very important when discussing spectroscopy and chemical reactivity.

The energy of the j^{th} molecular orbital is given by a one-electron Schrödinger equation using an effective one electron Hamiltonian, h_{eff} , which expresses the interaction of an electron with the rest of the molecule.

$$h_{\text{eff}}\psi_j = \epsilon_j\psi_j \quad (10.6.3)$$

is the energy eigenvalue of the j^{th} molecular orbital, corresponding to the eigenfunction ψ_j . The beauty of this method, as we will see later, is that the exact form of h_{eff} is not needed. The total energy of the molecule is the sum of the single electron energies.

$$E_{\pi} = \sum_j n_j \epsilon_j \quad (10.6.4)$$

where n_j is the number of electrons in orbital j .

The expectation value expression for the energy for each molecular orbital is used to find and then E_{π}

$$\epsilon_j = \frac{\int \psi_j \times h_{eff} \psi_j d\tau}{\int \psi_j \times \psi_j d\tau} = \frac{\langle \psi_j | h_{eff} | \psi_j \rangle}{\langle \psi_j | \psi_j \rangle} \quad (10.6.5)$$

The notation $\langle || \rangle$, which is called a bra-ket, just simplifies writing the expression for the integral. Note that the complex conjugate now is identified by the left-side position and the bra notation $\langle |$ and not by an explicit $*$.

After substituting Equation 10.6.2 into 10.6.5, we obtain for each molecular orbital

$$\epsilon_j = \frac{\left\langle \sum_{r=1}^N c_{jr} \psi_r | h_{eff} | \sum_{s=1}^N c_{js} \psi_s \right\rangle}{\left\langle \sum_{r=1}^N c_{jr} \psi_r | \sum_{s=1}^N c_{js} \psi_s \right\rangle} \quad (10.6.6)$$

which can be rewritten as

$$\epsilon = \frac{\sum_{r=1}^N \sum_{s=1}^N c_r^* c_s \langle \psi_r | h_{eff} | \psi_s \rangle}{\sum_{r=1}^N \sum_{s=1}^N c_r^* c_s \langle \psi_r | \psi_s \rangle} \quad (10.6.7)$$

where the index j for the molecular orbital has been dropped because this equation applies to any of the molecular orbitals.

Exercise 10.6.1

Consider a molecular orbital made up of three atomic orbitals, e.g. the three carbon $2p_z$ orbitals of the allyl radical, where the internuclear axes lie in the xy -plane. Write the LCAO for this MO. Derive the full expression, starting with Equation 10.6.5 and writing each term explicitly, for the energy expectation value for this LCAO in terms of h_{eff} . Compare your result with Equation 10.6.7 to verify that Equation 10.6.7 is the general representation of your result.

Exercise 10.6.2

Write a paragraph describing how the Variational Method could be used to find values for the coefficients c_{jr} in the linear combination of atomic orbitals.

To simplify the notation we use the following definitions. The integrals in the denominator of Equation 10.6.7 represent the overlap between two atomic orbitals used in the linear combination. The overlap integral is written as S_{rs} . The integrals in the numerator of Equation 10.6.7 are called either resonance integrals or coulomb integrals depending on the atomic orbitals on either side of the operator h_{eff} as described below.

- $S_{Rs} = \langle \psi_r | \psi_s \rangle$ is the overlap integral. $S_{rr} = 1$ because we use normalized atomic orbitals. For atomic orbitals r and s on different atoms, S_{rs} has some value between 1 and 0: the further apart the two atoms, the smaller the value of S_{rs} .
- $H_{rr} = \langle \psi_r | h_{eff} | \psi_r \rangle$ is the **Coulomb Integral**. It is the kinetic and potential energy of an electron in, or described by, an atomic orbital, ψ_r , experiencing the electrostatic interactions with all the other electrons and all the positive nuclei.
- $H_{rs} = \langle \psi_r | h_{eff} | \psi_s \rangle$ is the **Resonance Integral** or **Bond Integral**. This integral gives the energy of an electron in the region of space where the functions ψ_r and ψ_s overlap. This energy sometimes is referred to as the energy of the overlap charge. If r and s are on adjacent bonded atoms, this integral has a finite value. If the atoms are not adjacent, the value is smaller, and assumed to be zero in the Hückel model.

In terms of this notation, Equation 10.6.7 can be written as

$$\epsilon = \frac{\sum_{r=1}^N \sum_{s=1}^N c_r^* c_s H_{rs}}{\sum_{r=1}^N \sum_{s=1}^N c_r^* c_s S_{rs}} \quad (10.6.8)$$

We now must find the coefficients, the c 's. One must have a criterion for finding the coefficients. The criterion used is the *Variational Principle*. Since the energy depends linearly on the coefficients in Equation 10.6.8, the method we use to find the best set of coefficients is called the **Linear Variational Method**.

Linear Variational Method

The task is to minimize the energy with respect to all the coefficients by solving the N simultaneous equations produced by differentiating Equation 10.6.8 with respect to each coefficient.

$$\frac{\partial \epsilon}{\partial c_t} = 0 \quad (10.6.9)$$

for $t = 1, 2, 3, \dots, N$

Actually we also should differentiate Equation 10.6.8 with respect to the c_t^* , but this second set of N equations is just the complex conjugate of the first and produces no new information or constants.

To carry out this task, rewrite Equation 10.6.8 to obtain Equation 10.6.10 and then take the derivative of Equation 10.6.10 with respect to each of the coefficients.

$$\epsilon \sum_r \sum_s c_r^* c_s S_{rs} = \sum_r \sum_s c_r^* c_s H_{rs} \quad (10.6.10)$$

Actually we do not want to do this differentiation N times, so consider the general case where the coefficient is. Here t represents any number between 1 and N .

This differentiation is relatively easy, and the result, which is shown by Equation 10.6.12 is relatively simple because some terms in Equation 10.6.10 do not involve and others depend linearly on. The derivative of the terms that do not involve c_t is zero (e.g.

$$\frac{\partial c_3^* c_4 H_{34}}{\partial c_2} = 0. \quad (10.6.11)$$

The derivative of terms that contain is just the constant factor that multiplies the, (e.g. $\frac{\partial c_3^* c_2 H_{32}}{\partial c_2} = c_3^* H_{32}$). Consequently, only terms in Equation 10.6.10 that contain contribute to the result, and whenever a term contains, that term appears in Equation 10.6.12 without the because we are differentiating with respect to. The result after differentiating is

$$\epsilon \sum_r c_r^* S_{rt} = \sum_r c_r^* H_{rt} \quad (10.6.12)$$

If we take the complex conjugate of both sides, we obtain

Since

$$\epsilon = \epsilon^*, S_{rt}^* = S_{tr} \quad (10.6.13)$$

and

$$H_{rt}^* = H_{tr}, \quad (10.6.14)$$

then Equation ??? can be reversed and written as

$$\sum_r c_r H_{tr} = \epsilon \sum_r c_r S_{tr} \quad (10.6.15)$$

or upon rearranging as

$$\sum_r c_r (H_{tr} - S_{tr} \epsilon) = 0 \quad (10.6.16)$$

There are N simultaneous equations that look like this general one; N is the number of coefficients in the LCAO. Each equation is obtained by differentiating Equation 10.6.10 with respect to one of the coefficients.

Exercise 10.6.3

Explain why the energy $\epsilon = \epsilon^*$, show that $S_{rt}^* = S_{tr}$ (write out the integral expressions and take the complex conjugate of , and show that $H_{rt}^* = H_{tr}$ (write out the integral expressions, take the complex conjugate of , and use the Hermitian property of quantum mechanical operators).

Exercise 10.6.4

Rewrite your solution to Exercise 10.6.3 for the 3-carbon π system found in the allyl radical in the form of Equation 10.6.10 and then derive the set of three simultaneous equations for the coefficients. Compare your result with Equation 10.6.16 to verify that Equation 10.6.16 is a general representation of your result.

This method is called the **linear variational method** because the variable parameters affect the energy linearly unlike the shielding parameter in the wavefunction that was discussed in Chapter 9. The shielding parameter appears in the exponential part of the wavefunction and the effect on the energy is nonlinear. A nonlinear variational calculation is more laborious than a linear variational calculation.

Equations 10.6.15 and 10.6.16 represent a set of homogeneous linear equations. As we discussed for the case of **normal mode analysis** in Chapter 6, a number of methods can be used for solving these equations to obtain values for the energies, ϵ 's, and the coefficients, the c_r 's.

Matrix methods are the most convenient and powerful. First we write more explicitly the set of simultaneous equations that is represented by Equation . The first equation has $t = 1$, the second $t = 2$, etc. N represents the index of the last atomic orbital in the linear combination.

$$\begin{aligned} c_1 H_{11} + c_2 H_{12} + \dots c_n H_{1N} &= c_1 S_{11} \epsilon + c_2 S_{12} \epsilon + \dots c_N S_{1N} \epsilon \\ c_1 H_{21} + c_2 H_{22} + \dots c_n H_{2N} &= c_1 S_{21} \epsilon + c_2 S_{22} \epsilon + \dots c_N S_{2N} \epsilon \\ &\vdots = \vdots \\ c_1 H_{N1} + c_2 H_{N2} + \dots c_n H_{NN} &= c_1 S_{N1} \epsilon + c_2 S_{N2} \epsilon + \dots c_N S_{NN} \epsilon \end{aligned} \quad (10.6.17)$$

This set of equations can be represented in matrix notation.

$$HC' = SC'\epsilon \quad (10.6.18)$$

Here we have square matrix \mathbf{H} and \mathbf{S} multiplying a column vector \mathbf{C}' and a scalar ϵ . Rearranging produces

$$HC' - SC'\epsilon = 0 \quad (10.6.19)$$

$$(H - S\epsilon)C' = 0 \quad (10.6.20)$$

Exercise 10.6.5

For the three atomic orbitals you used in Exercises ??? and ???, write the Hamiltonian matrix \mathbf{H} , the overlap matrix \mathbf{S} , and the vector \mathbf{C}' . Show by matrix multiplication according to Equation 10.6.18 that you produce the same Equations that you obtained in Exercise 10.6.21

The problem is to solve these simultaneous equations, or the matrix equation, and find the orbital energies, which are the ϵ 's, and the atomic orbital coefficients, the c_r 's, that define the molecular orbitals.

Exercise 10.6.6

Identify two methods for solving simultaneous equations and list the steps in each.

In the EH method we use an effective one electron Hamiltonian, and then proceed to determine the energy of a molecular orbital where $H_{rs} = \langle \psi_r | h_{eff} | \psi_s \rangle$ and $S_{rs} = \langle \psi_r | \psi_s \rangle$.

Minimization of the energy with respect to each of the coefficients again yields a set of simultaneous equations just like Equation 10.6.16

$$\sum_r c_r (H_{tr} - S_{tr} \epsilon) = 0 \quad (10.6.21)$$

As before, these equations can be written in matrix form in Equation 10.6.18

Equation 10.6.18 accounts for one molecular orbital. It has energy ϵ , and it is defined by the elements in the \mathbf{C}' column vector, which are the coefficients that multiply the atomic orbital basis functions in the linear combination of atomic orbitals.

We can write one matrix equation for all the molecular orbitals.

$$\mathbf{HC} = \mathbf{SCE} \quad (10.6.22)$$

where \mathbf{H} is a square matrix containing the H_{rs} , the one electron energy integrals, and \mathbf{C} is the matrix of coefficients for the atomic orbitals. Each column in \mathbf{C} is the \mathbf{C}' that defines one molecular orbital in terms of the basis functions. In extended Hückel theory, the overlap is not neglected, and \mathbf{S} is the matrix of overlap integrals. \mathbf{E} is the diagonal matrix of orbital energies. All of these are square matrices with a size that equals the number of atomic orbitals used in the LCAO for the molecule under consideration.

Equation 10.6.22 represents an eigenvalue problem. For any extended Hückel calculation, we need to set up these matrices and then find the eigenvalues and eigenvectors. The eigenvalues are the orbital energies, and the eigenvectors are the atomic orbital coefficients that define the molecular orbital in terms of the basis functions.

Exercise 10.6.7

What is the size of the \mathbf{H} matrix for HF? Write out the matrix elements in the \mathbf{H} matrix using symbols for the wavefunctions appropriate to the HF molecule. Consider this matrix and determine if it is symmetric by examining pairs of off-diagonal elements. In a symmetric matrix, pairs of elements located by reflection across the diagonal are equal, i.e. $H_{rc} = H_{cr}$ where r and c represent the row and column, respectively. Why are such pairs of elements equal? Write out the \mathbf{S} matrix in terms of symbols, showing the diagonal and the upper right portion of the matrix. This matrix also is symmetric, so if you compute the diagonal and the upper half of it, you know the values for the elements in the lower half. Why are pairs of \mathbf{S} matrix elements across the diagonal equal?

The elements of the \mathbf{H} matrix are assigned using experimental data. This approach makes the extended Hückel method a *semi-empirical* molecular orbital method. The basic structure of the method is based on the principles of physics and mathematics while the values of certain integrals are assigned by using educated guesses and experimental data. The H_{rr} are chosen as valence state ionization potentials with a minus sign to indicate binding. The values used by R. Hoffmann when he developed the extended Hückel technique were those of H.A. Skinner and H.O. Pritchard (Trans. Faraday Soc. **49** (1953), 1254). These values for \mathbf{C} and \mathbf{H} are listed in Table 10.6.1. The values for the heteroatoms (N, O, and F) are taken from Pople and Beveridge (*Approximate Molecular Orbital Theory*, McGraw-Hill Book Company, New York, 1970).

Table 10.6.1: Ionization potentials of various atomic orbitals.

Atomic orbital	Ionization potential (eV)
H 1s	13.6
C 2s	21.4
C 2p	11.4
N 2s	25.58
N 2p	13.9
O 2s	32.38
O 2p	15.85
F 2s	40.20
F 2p	18.66

The H_{rs} values are computed from the ionization potentials according to

$$H_{rs} = \frac{1}{2}K(H_{rr} + H_{ss})S_{rs} \quad (10.6.23)$$

The rationale for this expression is that the energy should be proportional to the energy of the atomic orbitals, and should be greater when the overlap of the atomic orbitals is greater. The contribution of these effects to the energy is scaled by the parameter K . Hoffmann assigned the value of K after a study of the effect of this parameter on the energies of the occupied orbitals of ethane. The conclusion was that a good value for K is $K = 1.75$.

Exercise 10.6.8

Fill in numerical values for the diagonal elements of the Extended Hückel Hamiltonian matrix for HF using the ionization potentials given in Table 10.6.1.

The overlap matrix also must be determined. The matrix elements are computed using the definition $S_{rs} = \langle \psi_r | \psi_s \rangle$ where φ_k and ψ_s are the atomic orbitals. Slater-type orbitals (STO's) are used for the atomic orbitals rather than hydrogenic orbitals because integrals involving STO's can be computed more quickly on computers. Slater type orbitals have the form

$$\phi_{1s}(r) = 2\zeta^{3/2}\exp(-\zeta r) \quad (10.6.24)$$

$$\phi_{2s}(r) = \phi_{2p}(r) = \left(\frac{4\zeta^5}{3}\right)^{1/2} r \exp(-\zeta r) \quad (10.6.25)$$

where zeta, ζ , is a parameter describing the screened nuclear charge. In the extended Hückel calculations done by Hoffmann, the Slater orbital parameter ζ was 1.0 for the H_{1s} and 1.652 for the C_{2s} and C_{2p} orbitals.

Exercise 10.6.9

Describe the difference between Slater-type orbitals and hydrogenic orbitals.

Overlap integrals involve two orbitals on two different atoms or centers. Such integrals are called two-center integrals. In such integrals there are two variables to consider, corresponding to the distances from each of the atomic centers, r_A and r_B . Such integrals can be represented as

$$S_{A_2s, B_{2s}} = \left(\frac{4\zeta^5}{3}\right) \int r_A \exp(-\zeta r_A) r_B \exp(-\zeta r_B) d\tau \quad (10.6.26)$$

but elliptical coordinates must be used for the actual integration. Fortunately the software that does extended Hückel calculations contains the programming code to do overlap integrals. The interested reader will find sufficient detail on the evaluation of overlap integrals and the creation of the programmable mathematical form for any pair of Slater orbitals in Appendix B4 (pp. 199 - 200) of the book *Approximate Molecular Orbital Theory* by Pople and Beveridge. The values of the overlap integrals for HF are given in Table 10.6.2

Exercise 10.6.10

Using the information in Table 10.6.2 identify which axis (x, y, or z) has been defined as the internuclear axis. Fill in the missing values in Table 10.6.2 This requires no calculation, only insight.

Table 10.6.2: Overlap Integrals for HF

	F 2s	F 2p _x	F 2p _y	F 2p _z	H 1s
F 2s					0.47428
F 2p _x					0
F 2p _y					0.38434
F 2p _z					0
H 1s					

Exercise 10.6.11: Hydrogen Fluoride

Using the information in Tables 10.6.1 and 10.6.2, write the full Hückel H matrix and the S matrix that appears in Equation 10.6.22 for HF.

Our goal is to find the coefficients in the linear combinations of atomic orbitals and the energies of the molecular orbitals. For these results, we need to transform Equation 10.6.22

$$HC = SCE$$

into a form that allows us to use matrix diagonalization techniques. We are hampered here by the fact that the overlap matrix is not diagonal because the orbitals are not orthogonal. Mathematical methods do exist that can be used to transform a set of functions into an orthogonal set. Essentially these methods apply a transformation of the coordinates from the local coordinate system describing the molecule into one where the atomic orbitals in the LCAO are all orthogonal. Such a transformation can be accomplished through matrix algebra, and computer algorithms for this procedure are part of all molecular orbital programs. The following paragraph describes how this transformation can be accomplished.

If the matrix M has an inverse M^{-1} Then

$$MM^{-1} = 1 \quad (10.6.27)$$

and we can place this product in a matrix equation without changing the equation. When this is done for Equation 10.6.22 we obtain

$$HMM^{-1}C = SMM^{-1}CE \quad (10.6.28)$$

Next multiply on the left by M^{-1} and determine M so the product $M^{-1}SM$ is the identity matrix, i.e. a matrix that has 1's on the diagonal and 0's off the diagonal is the case for an orthogonal basis set.

$$M^{-1}HMM^{-1}C = M^{-1}SMM^{-1}CE \quad (10.6.29)$$

which then can be written as

$$H''C'' = C''E'' \quad (10.6.30)$$

where

$$C' = M^{-1}C \quad (10.6.31)$$

The identity matrix is not included because multiplying by the identity matrix is just like multiplying by the number 1. It doesn't change anything. The H'' matrix can be diagonalized by multiplying on the left by the inverse of C'' to find the energies of the molecular orbitals in the resulting diagonal matrix E .

$$E = C''^{-1}H''C'' \quad (10.6.32)$$

The matrix C'' obtained in the diagonalization step is finally back transformed to the original coordinate system with the M matrix, $C = MC''$ since $C'' = M^{-1}C$.

Fortunately this process is automated in some computer software. For example, in Mathcad, the command `genvals(H,S)` returns a list of the eigenvalues for Equation 10.6.22. These eigenvalues are the diagonal elements of E . The command `genvecs(H,S)` returns a matrix of the normalized eigenvectors corresponding to the eigenvalues. The i^{th} eigenvalue in the list goes with the i^{th} column in the eigenvector matrix. This problem, where S is not the identity matrix, is called a general eigenvalue problem, and *gen* in the Mathcad commands refers to *general*.

Exercise 10.6.12

Using your solution to Exercise 10.6.11, find the orbital energies and wavefunctions for HF given by an extended Hückel calculation. Construct an orbital energy level diagram, including both the atomic and molecular orbitals, and indicate the atomic orbital composition of each energy level. Draw lines from the atomic orbital levels to the molecular orbital levels to show which atomic orbitals contribute to which molecular orbitals. What insight does your calculation provide regarding the ionic or covalent nature of the chemical bond in HF?

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