Quantum Chemistry

Lecture 13

Generalization of the variational approach to LCAO-MO

NC State University

The linear combination of atomic orbitals

We begin the discussion of the rigorous procedure for calculating molecular orbitals by defining a basis set. The basis set consists of a set of atomic orbitals located at specific points in space the we will refer to as the molecular geometry. We will show how a linear approach to molecular orbital theory provides leads to a system of linear equations that can be solved by matrix methods. We will consider the molecular orbitals as a linear combination of the atomic orbitals in the basis set that we have chosen:

$$\Psi = c_1\phi_1 + c_2\phi_2 + c_3\phi_3 + \cdots = \sum_{j=1}^{N} c_j\phi_j$$

In this formalism the c_{ij} are variational parameters that will be minimized.

Definition of the average energy

From this point forward, we will assume that all of the functions are real. Using this definition we can apply the variational principle to the average energy:

$$E = \frac{\int \Psi H \Psi d\tau}{\int \Psi \Psi d\tau}$$

We begin with the calculation of the denominator.

$$\int \Psi\Psi d\tau = \int \sum_{j=1}^{N} c_j \phi_j \sum_{k=1}^{N} c_k \phi_k \, d\tau = \sum_{j=1}^{N} \sum_{k=1}^{N} c_j c_k \int \phi_j \phi_k d\tau$$

Using the definition

$\int \phi_j \phi_k d\tau = S_{jk}$ we see that $\int \Psi\Psi d\tau = \sum_{j=1}^{N} \sum_{k=1}^{N} c_j c_k S_{jk}$

Expansion of the numerator in energy term

The basis functions, ϕ_i and ϕ_k are not necessarily orthogonal since they are hydrogen-like functions on different centers. The numerator is,

$$\int \Psi H \Psi d\tau = \int \sum_{j=1}^{N} c_j \phi_j \, H \sum_{k=1}^{N} c_k \phi_k \, d\tau = \sum_{j=1}^{N} \sum_{k=1}^{N} c_j c_k \int \phi_j H \phi_k d\tau$$

Using the abbreviation

$$\int \phi_j H \phi_k d\tau = H_{jk}$$

We can write

$$\int \Psi H \Psi d\tau = \sum_{j=1}^{N} \sum_{k=1}^{N} c_j c_k \, H_{jk}$$

Application of the variational principle

The variational energy integral is evaluated as

$$E = \frac{\sum_{j=1}^{N} \sum_{k=1}^{N} c_j c_k H_{jk}}{\sum_{j=1}^{N} \sum_{k=1}^{N} c_j c_k S_{jk}}$$

$$E \sum_{j=1}^{N} \sum_{k=1}^{N} c_j c_k S_{jk} = \sum_{j=1}^{N} \sum_{k=1}^{N} c_j c_k H_{jk}$$

The variational integral is a function of N independent variables, c_1, c_2, …., c_N. The partial derivatives with respect to each of the independent variables must vanish at the minimum point.

$$\frac{\partial E}{\partial c_i} = 0\ , i = 1,2,3, \ldots$$

Application of the variational principle

$$\frac{\partial E}{\partial c_i}\sum_{j=1}^{N}\sum_{k=1}^{N} c_j c_k S_{jk} + E\frac{\partial}{\partial c_i}\sum_{j=1}^{N}\sum_{k=1}^{N} c_j c_k S_{jk} = \frac{\partial}{\partial c_i}\sum_{j=1}^{N}\sum_{k=1}^{N} c_j c_k H_{jk}$$

$$\frac{\partial}{\partial c_i}\sum_{j=1}^{N}\sum_{k=1}^{N} c_j c_k S_{jk} = \sum_{j=1}^{N}\sum_{k=1}^{N}\left[\frac{\partial}{\partial c_i}(c_j c_k)\right] S_{jk}$$

$$= \sum_{j=1}^{N}\sum_{k=1}^{N}\left[c_k \frac{\partial c_j}{\partial c_i} + c_j \frac{\partial c_k}{\partial c_i}\right] S_{jk}$$

Application of the variational principle

The c_i's are all independent variables, and therefore

$$\frac{\partial c_j}{\partial c_i} = \delta_{ij}$$

We then have

$$\frac{\partial}{\partial c_i}\sum_{j=1}^{N}\sum_{k=1}^{N} c_j c_k S_{jk} = \sum_{j=1}^{N} c_j S_{ik} + \sum_{k=1}^{N} c_k S_{ij}$$

Note that

$$S_{ij} = S_{ji}$$

and therefore

$$\frac{\partial}{\partial c_i}\sum_{j=1}^{N}\sum_{k=1}^{N} c_j c_k S_{jk} = 2\sum_{k=1}^{N} c_k S_{jk}$$

Application of the variational principle

Using the same logic we can write

$$\frac{\partial}{\partial c_i}\sum_{j=1}^{N}\sum_{k=1}^{N} c_j c_k H_{jk} = 2\sum_{k=1}^{N} c_k H_{jk}$$

Thus,

$$\sum_{k=1}^{N}\left[\left(H_{jk} - ES_{jk}\right)c_k\right] = 0$$

This implies that we can determine the solution to this set of equations using an N x N determinant.

$$\det\left(H_{jk} - ES_{jk}\right) = 0$$

The secular determinant is:

$$\begin{matrix} H_{11} - ES_{11} & H_{12} - ES_{12} & H_{13} - ES_{13} & \ldots\ldots & H_{1N} - ES_{1N} \\ H_{21} - ES_{21} & H_{22} - ES_{22} & H_{23} - ES_{23} & \ldots\ldots & H_{2N} - ES_{2N} \\ H_{31} - ES_{31} & H_{32} - ES_{32} & H_{33} - ES_{33} & \ldots\ldots & H_{3N} - ES_{3N} \\ \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \\ H_{N1} - ES_{N1} & H_{N2} - ES_{N2} & H_{N3} - ES_{N3} & \ldots\ldots & H_{NN} - ES_{NN} \end{matrix}$$

There are N roots, which we can write as

$$E_1, E_2, E_3, \ldots\ldots E_N$$