THE SECULAR EQUATIONS

1. Derivation of the secular equations

In Hückel theory, the molecular orbital (MO) wavefunction, ψ, can be written as a linear combination of atomic orbitals, ϕ, as

$$\psi = \sum_i c_i \phi_i \tag{1}$$

where ϕ_i is atomic orbital on atom i, c_i is the accompanying coefficient.

Now, we know that the energy of the system is given by the expectation value of the Hamiltonian operator as

$$E = \frac{\langle \psi | \hat{H} | \psi \rangle}{\langle \psi | \psi \rangle} \tag{2}$$

where we have used the Dirac notation. We now substitute Eq. 1 into Eq. 2 to get

$$E = \frac{\int (\sum_j c_j \phi_j)^* \hat{H} \sum_i c_i \phi_i d\tau}{\int (\sum_j c_j \phi_j)^* \sum_i c_i \phi_i d\tau} \tag{3}$$

Now, suppose we use real atomic orbitals with real coefficients, the above equation becomes

$$\begin{aligned} E &= \frac{\int \sum_j c_j \phi_j \hat{H} \sum_i c_i \phi_i d\tau}{\int \sum_j c_j \phi_j \sum_i c_i \phi_i d\tau} \\ &= \frac{\sum_j \sum_i c_j c_i \int \phi_j \hat{H} \phi_i d\tau}{\sum_j \sum_i c_j c_i \int \phi_j \phi_i d\tau} \\ &= \frac{\sum_{ij} c_j c_i \int \phi_j \hat{H} \phi_i d\tau}{\sum_{ij} c_j c_i \int \phi_j \phi_i d\tau} \end{aligned} \tag{4}$$

where in the last step, we have written the double summation using a shorthand notation.

We now define the following matrix elements:

$$H_{ji} = \int \phi_j \hat{H} \phi_i d\tau = \int \phi_i \hat{H} \phi_j d\tau = H_{ij} \tag{5}$$

$$S_{ji} = \int \phi_j \phi_i d\tau = \int \phi_i \phi_j d\tau = S_{ij} \tag{6}$$

where the first equation follows since the Hamiltonian operator $\hat{H}$ is Hermitian.

The energy expression in terms of these matrix elements now become

$$E = \frac{\sum_{ij} c_j c_i H_{ij}}{\sum_{ij} c_j c_i S_{ij}} \tag{7}$$

According to the variational principle, that the best approximate to the wavefunction is obtained when the energy of the system is minimised. Therefore, we now need to minimise E with respect to the coefficients c_i. We can first writen Eq. 7 as

$$E \sum_{ij} c_j c_i S_{ij} = \sum_{ij} c_j c_i H_{ij}$$

Taking partial derivative of the above with respect to the coefficients c_i and using product rule on the left hand side, we have

$$\begin{aligned} \frac{\partial}{\partial c_i}\left[E \sum_{ij} c_j c_i S_{ij}\right] &= \frac{\partial}{\partial c_i}\left[\sum_{ij} c_j c_i H_{ij}\right] \\ \frac{\partial E}{\partial c_i} \sum_{ij} c_j c_i S_{ij} + E \sum_{j} c_j S_{ij} &= \sum_{j} c_j H_{ij} \end{aligned} \tag{8}$$

Note that the derivative of a double summation returns a single summation. You can imagine this by thinking about the term-wise differentiation in the double summation.

We now set $\frac{\partial E}{\partial c_i} = 0$ in the above to obtain the coefficients for which the energy of the system is minimised. Thus, Eq. 8 becomes

$$E \sum_{j} c_j S_{ij} = \sum_{j} c_j H_{ij} \tag{9}$$

which can be equivalently written as

$$\sum_{j} (H_{ij} - E S_{ij}) c_j = 0 \tag{10}$$

or, in matrix form

$$(\mathbf{H} - E\mathbf{S})\mathbf{c} = \mathbf{0} \tag{11}$$

2. Hückel approximations for the secular equations

To simplify things, we write the matrix elements in the secular equations in terms of parameters α and β, where

$$\alpha_i = H_{ii} \tag{12}$$

$$\beta_{ij} = H_{ij} \tag{13}$$

These are negative parameters that are approcimately the energy of orbital i and the energy of the interaction of the adjecent orbitals i and j, respectively.

To simplify things further, the Hückel approximations futher assumes that

(1) the overlap between orbitals is neglected, $S_{ij} = 0$,
(2) the atomic orbitals are normalised, $S_{ii} = 1$, and
(3) only adjecent orbitals have interactions, $H_{ij} \neq 0$ only if i and j are adjecent to each other.

Eq. 11 , when written out in full, now has the form

$$\begin{pmatrix} \alpha_1 - E & \beta_{12} & \beta_{13} & \cdots & \beta_{1N} \\ \beta_{21} & \alpha_2 - E & \beta_{23} & \cdots & \beta_{2N} \\ \beta_{31} & \beta_{32} & \alpha_3 - E & \cdots & \beta_{3N} \\ \vdots & \vdots & \vdots & \vdots & \vdots \\ \beta_{N1} & \beta_{N2} & \beta_{N3} & \cdots & \alpha_N - E \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ c_3 \\ \vdots \\ c_N \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ 0 \\ \vdots \\ 0 \end{pmatrix} \tag{14}$$

To obtain non-trivial solutions of linear combinations of atomic orbitals of a system, we set the *secular determinants* to zero, viz.,

$$\begin{vmatrix} \alpha_1 - E & \beta_{12} & \beta_{13} & \cdots & \beta_{1N} \\ \beta_{21} & \alpha_2 - E & \beta_{23} & \cdots & \beta_{2N} \\ \beta_{31} & \beta_{32} & \alpha_3 - E & \cdots & \beta_{3N} \\ \vdots & \vdots & \vdots & \vdots & \vdots \\ \beta_{N1} & \beta_{N2} & \beta_{N3} & \cdots & \alpha_N - E \end{vmatrix} = 0 \tag{15}$$

This allows us to obtain N solutions of the *eigenvalues* E, each of which can be substituted back to Eq. 2 to obtain the coefficients (*eigenvectors*) that give the LCAO corresponding to the energy.

