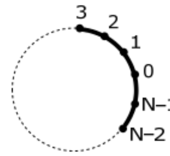
# 1.8: N-dimensional cyclic systems

This lecture will provide a derivation of the LCAO eigenfunctions and eigenvalues of N total number of orbitals in a cyclic arrangement. The problem is illustrated below:




There are two derivations to this problem.

## Polynomial Derivation

The Hückel determinant is given by,

$$D_N(x)=\begin{vmatrix} x & 1 & & & & & & & \\ 1 & x & 1 & & & & & & \\ & 1 & x & \ddots & & & & & \\ & & 1 & \ddots & \ddots & & & & \\ & & & \ddots & \ddots & \ddots & & & \\ & & & & \ddots & \ddots & \ddots & & \\ & & & & & \ddots & \ddots & 1 & \\ & & & & & & \ddots & x & 1 \\ & & & & & & 1 & x & \end{vmatrix}=0 \tag{1.8.1}$$

where

$$x=\frac{\alpha-E}{\beta} \tag{1.8.2}$$

From a Laplace expansion one finds,

$$D_N(x)=xD_{n-1}(x)-D_{N-2}(x) \tag{1.8.3}$$

Where

$$\begin{aligned} D_1(x) &= x \\ D_2(x) &= \begin{vmatrix} x & 1 \\ 1 & x \end{vmatrix} = x^2-1 \end{aligned}$$

With these parameters defined, the polynomial form of $D_N(x)$ for any value of N can be obtained,

$$\begin{gathered} D_3(x)=xD_2(x)-D_1(x)=x\left(x^2-1\right)-x=x\left(x^2-2\right) \\ D_4(x)=xD_3(x)-D_2(x)=x^2\left(x^2-2\right)-\left(x^2-1\right) \\ \vdots \\ \text{and so on} \end{gathered}$$

The expansion of DN(x) has as its solution,

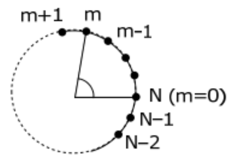
$$x=-2\cos\frac{2\pi}{N}j(j=0,1,2,3\ldots N-1)$$

and substituting for x,

$$E = \alpha + 2\beta \cos \frac{2\pi}{N} j (j = 0, 1, 2, 3 \ldots N-1)$$

## Standing Wave Derivation

An alternative approach to solving this problem is to express the wavefunction directly in an angular coordinate, θ




For a standing wave of λ about the perimeter of a circle of circumference c,

$$\psi_j = \sin \frac{c}{\lambda} \theta$$

The solution to the wave function must be single valued ∴ a single solution must be obtained for ψ at every 2nπ or in analytical terms,

$$\psi = \sin\frac{c}{\lambda}(\theta + 2\pi) = \sin\frac{c}{\lambda}\theta$$

$$= \sin\frac{c}{\lambda}\theta \cdot \underbrace{\cos\frac{c}{\lambda}2\pi}_{\text{must go to 1}} + \underbrace{\sin\frac{c}{\lambda}2\pi}_{\text{must go to 0}} \cdot \cos\frac{c}{\lambda}\theta = \sin\frac{c}{\lambda}\theta$$

$$\text{iff } \frac{c}{\lambda}2\pi = 2\pi j \; (j = 0, 1, 2 \ldots N-1)$$

$$\therefore \frac{c}{\lambda} = j$$ condition for an integral number of λ's about the circumference of a circle

Thus the amplitude of $\psi_j$ at atom m is, (where c/λ = j and θ = (2π/N)m)

$$\psi_j(m) = \sin 2m\pi N j (j = 0, 1, 2, 3 \ldots N-1)$$

Within the context of the LCAO method, $\psi_j$ may be rewritten as a linear combination in $\varphi_m$ with coefficients $c_{jm}$. Thus the amplitude of $\psi_j$ at m is equivalent to the coefficient of $\varphi_m$ in the LCAO expansion,

$$\psi_j = \sum_{k=1}^{N} C_{jm\phi m} \tag{1.8.4}$$

Where

$$C_{jm} = \sin 2\pi m N j (j = 0, 1, 2, 3 \ldots N-1)$$

The energy of each MO, $\psi_j$, may be determined from a solution of Schrödinger's equation,

$$\begin{aligned} \mathrm{H}\psi_j &= \mathrm{E}_j \psi_j \\ |\mathrm{H} - \mathrm{E_j}| \, \psi_j\rangle &= 0 \\ |\mathrm{H} - \mathrm{E}_j| \textstyle\sum_m^{\mathrm{N}} \mathrm{c}_{jm} \phi_m \Big\rangle &= 0 \end{aligned}$$

The energy of the $\varphi_m$ orbital is obtained by left–multiplying by $\varphi_m$,

$$\left\langle \phi_m \, | H - E_j | \sum_m^N c_{jm} \phi_m \right\rangle = 0$$

but the Hückel condition is imposed; the only terms that are retained are those involving $\varphi_m$, $\varphi_{m+1}$, and $\varphi_{m-1}$. Expanding,

$$\left[c_{jm}\left\langle\phi_m\right|\overset{\alpha}{\cancel{H}}\left|\phi_m\right\rangle - c_{jm}E_j\left\langle\phi_m\right|\overset{1}{\cancel{\phi_m}}\rangle\right] + \left[c_{j(m+1)}\left\langle\phi_m\right|\overset{\beta}{\cancel{H}}\left|\phi_{m+1}\right\rangle - c_{j(m+1)}E_j\left\langle\phi_m\right|\overset{0}{\cancel{\phi_{m+1}}}\rangle\right]$$
$$+\left[c_{j(m-1)}\left\langle\phi_m\right|\underset{\beta}{\cancel{H}}\left|\phi_{m-1}\right\rangle - c_{j(m-1)}E_j\left\langle\phi_m\right|\underset{0}{\cancel{\phi_{m-1}}}\rangle\right] = 0$$

Evaluating the integrals,

$$\begin{aligned} &\alpha c_{jm} - c_{jm}E_j + \beta\left\lfloor c_{j(m+1)} + c_{j(m-1)}\right\rfloor = 0 \\ &\alpha c_{jm} + \beta\left\lfloor c_{j(m+1)} + c_{j(m-1)}\right\rfloor = c_{jm}E_j \end{aligned} \quad \backslash\mathrm{no}tag \tag{1.8.5}$$

Substituting for $c_{jm}$,

$$\alpha \sin\frac{2\pi m}{N}j + \beta\left(\sin\frac{2\pi(m+1)}{N}j + \sin\frac{2\pi(m-1)}{N}j\right) = E_j \sin\frac{2\pi m}{N}j$$

Dividing by $\sin\frac{2\pi m}{N}j$,

$$\alpha + \frac{\beta\left(\sin\frac{2\pi(m+1)}{N}j + \sin\frac{2\pi(m-1)}{N}j\right)}{\sin\frac{2\pi m}{N}j} = E_j$$

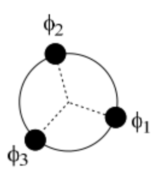
Making the simplifying substitution, $\kappa = \frac{2\pi}{N}j$

$$E_j = \alpha + \beta\left(\frac{\sin\kappa m\cdot\cos\kappa + \sin\kappa\cdot\cos\kappa m + \sin\kappa m\cdot\cos\kappa - \sin\kappa\cdot\cos\kappa m}{\sin\kappa m}\right)$$

$$E_j = \alpha + 2\beta\cos k$$

$$E_j = \alpha + 2\beta\cos\frac{2\pi}{N}j(j = 0, 1, 2, 3 \ldots N-1)$$

Let's look at the simplest cyclic system, N = 3




$N = 3$, so $E_j = \alpha + 2\beta\cos\frac{2\pi}{N}j$ where $j = 0, 1, 2$

$$\begin{aligned} E_0 &= \alpha + 2\beta \\ E_1 &= \alpha + 2\beta\cos\frac{2\pi}{3} = \alpha - \beta \\ E_2 &= \alpha + 2\beta\cos\frac{4\pi}{3} = \alpha - \beta \end{aligned}$$

Continuing with our approach (LCAO) and using Ej to solve for the eigenfunction, we find…

$$\psi_j = \sum_m e^{ij\theta}\phi_m \quad \text{for } j = 0, \pm1, \pm2\ldots\begin{cases} \pm\frac{N}{2} \text{ for } N \text{ even} \\ \pm\frac{(N-1)}{2} \text{ for } N \text{ odd} \end{cases} \tag{1.8.6}$$

Using the general expression for ψj, the eigenfunctions are:

$$\psi_0 = e^{i(0)0}\phi_1 + e^{i(0)\frac{2\pi}{3}}\phi_2 + e^{i(0)\frac{4\pi}{3}}\phi_3$$

$$\psi_1 = e^{i(1)0}\phi_1 + e^{i(1)\frac{2\pi}{3}}\phi_2 + e^{i(1)\frac{4\pi}{3}}\phi_3$$

$$\psi_{-1} = e^{i(-1)0}\phi_1 + e^{i(-1)\frac{2\pi}{3}}\phi_2 + e^{i(-1)\frac{4\pi}{3}}\phi_3$$

Obtaining real components of the wavefunctions and normalizing,

$$\begin{aligned} \psi_0 = \phi_1 + \phi_2 + \phi_3 \rightarrow & \qquad \psi_0 = \tfrac{1}{\sqrt{3}}(\phi_1 + \phi_2 + \phi_3) \\ \psi_{+1} + \psi_{-1} = 2\phi_1 - \phi_2 - \phi_3 \rightarrow & \qquad \psi_1 = \tfrac{1}{\sqrt{6}}(2\phi_1 - \phi_2 - \phi_3) \\ \psi_{+1} - \psi_{-1} = \phi_2 - \phi_3 \rightarrow & \qquad \psi_2 = \tfrac{1}{\sqrt{2}}(\phi_2 - \phi_3) \end{aligned} \tag{1.8.7}$$

Summarizing on a MO diagram where α is set equal to 0,