5.04 Principles of Inorganic Chemistry II
Fall 2008

5.04, Principles of Inorganic Chemistry II
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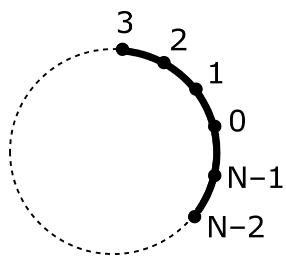
Lecture 8: N-Dimensional Cyclic Systems

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,

$$D_N(x) = \begin{vmatrix} x & 1 & & & & & & \\ 1 & x & 1 & & & & & \\ & 1 & x & \ddots & & & & \\ & & 1 & \ddots & \ddots & & & \\ & & & \ddots & \ddots & \ddots & & \\ & & & & \ddots & \ddots & \ddots & \\ & & & & & \ddots & \ddots & 1 \\ & & & & & & \ddots & x & 1 \\ & & & & & & & 1 & x \end{vmatrix} = 0 \quad \text{where} \quad x = \frac{\alpha - E}{\beta}$$

From a Laplace expansion one finds,

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

where

$$D_1(x) = x$$

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

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

$$D_3(x) = xD_2(x) - D_1(x) = x(x^2-1) - x = x(x^2-2)$$
$$D_4(x) = xD_3(x) - D_2(x) = x^2(x^2-2) - (x^2-1)$$
$$\vdots$$

and so on

The expansion of $D_N(x)$ has as its solution,

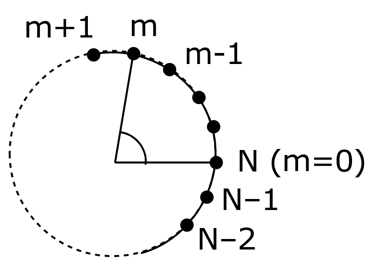
$$x = -2\cos\frac{2\pi}{N}j \qquad (j = 0, 1, 2, 3 \ldots N-1)$$

and substituting for x,

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

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,

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

$$= \sin\frac{c}{\lambda}\theta \bullet \cos\frac{c}{\lambda}2\pi + \sin\frac{c}{\lambda}2\pi \bullet \cos\frac{c}{\lambda}\theta = \sin\frac{c}{\lambda}\theta$$

$\cos\frac{c}{\lambda}2\pi$: must go to 1 $\qquad$ $\sin\frac{c}{\lambda}2\pi$: must go to 0

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 ψ_j at atom m is, (where $\frac{c}{\lambda} = j$ and $\theta = \frac{2\pi}{N}m$)

$$\psi_j(m) = \sin\frac{2\pi m}{N}j \qquad (j = 0, 1, 2 \ldots N-1)$$

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

$$\psi_j = \sum_{m=1}^{N} c_{jm}\phi_m$$

$$\text{where } c_{jm} = \sin\frac{2\pi m}{N}j \qquad (j = 0, 1, 2 \ldots N-1)$$

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

$$H\psi_j = E_j\psi_j$$

$$\left| H - E_j \right| \psi_j \rangle = 0$$

$$\left| H - E_j \right| \sum_{m}^{N} c_{jm}\phi_m \rangle = 0$$

The energy of the ϕ_m orbital is obtained by left–multiplying by ϕ_m,

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

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

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

$$+ \Big[c_{j(m-1)}\underset{\beta}{\langle\phi_m|H|\phi_{m-1}\rangle} - c_{j(m-1)}E_j\underset{0}{\langle\phi_m|\phi_{m-1}\rangle}\Big] = 0$$

Evaluating the integrals,

$$\alpha\, c_{jm} - c_{jm}\, E_j + \beta\left[c_{j(m+1)} + c_{j(m-1)}\right] = 0$$

$$\alpha\, c_{jm} + \beta\left[c_{j(m+1)} + c_{j(m-1)}\right] = c_{jm}E_j$$

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, $\kappa = \frac{2\pi}{N}j$

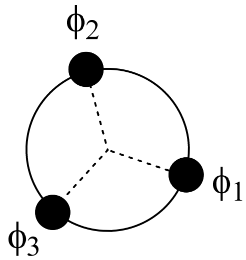
$$E_j = \alpha + \frac{\beta\left(\sin\kappa(m+1) + \sin\kappa(m-1)\right)}{\sin\kappa m}$$

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

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

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

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



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

$$E_0 = \alpha + 2\beta$$

$$E_1 = \alpha + 2\beta\cos\frac{2\pi}{3} = \alpha - \beta$$

$$E_2 = \alpha + 2\beta\cos\frac{4\pi}{3} = \alpha - \beta$$

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

$$\psi_j = \sum_m e^{ij\theta}\phi_m \qquad \text{for } j = 0, \pm 1, \pm 2 \ldots \begin{cases} \pm\dfrac{N}{2}\ \text{for N even} \\ \pm\dfrac{(N-1)}{2}\ \text{for N odd} \end{cases}$$

Using the general expression for ψ_j, 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,

$$\psi_0 = \phi_1 + \phi_2 + \phi_3 \rightarrow \qquad \psi_0 = \frac{1}{\sqrt{3}}\left(\phi_1 + \phi_2 + \phi_3\right)$$

$$\psi_{+1} + \psi_{-1} = 2\phi_1 - \phi_2 - \phi_3 \rightarrow \quad \psi_1 = \frac{1}{\sqrt{6}}\left(2\phi_1 - \phi_2 - \phi_3\right)$$

$$\psi_{+1} - \psi_{-1} = \phi_2 - \phi_3 \rightarrow \qquad \psi_2 = \frac{1}{\sqrt{2}}\left(\phi_2 - \phi_3\right)$$

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