HUCKEL THEORY FOR SPECIAL SYSTEMS

1. The Hückel equation

Recall that the energy of a system is given by the expectation value of the Hamiltonian operator as

$$E = \frac{\langle\psi|\hat{H}|\psi\rangle}{\langle\psi|\psi\rangle} \tag{1}$$

The molecular orbital (MO) wavefunction, ψ, can be written as a linear combination of atomic orbitals, ϕ, as

$$\psi = \sum_r c_r \phi_r \tag{2}$$

where ϕ_r is atomic orbital on atom r, c_r is the accompanying coefficient.

Substituting the above into the energy expression Eq. (1) and expanding the sum, we obtain

$$E = \frac{\sum_{rs} c_r^* c_s H_{rs}}{\sum_{rs} c_r^* c_s S_{rs}} \tag{3}$$

$$= \frac{\sum_{rs} c_r c_s H_{rs}}{\sum_{rs} c_r c_s S_{rs}} \qquad \text{(real orbitals)} \tag{4}$$

where

$$H_{rs} = \langle\phi_r|\,\hat{H}\,|\phi_s\rangle = H_{sr} \tag{5}$$

$$S_{rs} = \langle\phi_r|\phi_s\rangle = S_{sr} \tag{6}$$

By the variational principle, we seek to minimize energy with respect to the coefficients c_r so that the first derivative with respect to c_r all vanish, i.e.,

$$\frac{\partial E}{\partial c_r} = 0 \tag{7}$$

After a fairly straightforward exercise in partial differentiation (try this!), we obtain the following matrix equation:

$$\sum_s (H_{rs} - E S_{rs}) c_s = 0 \tag{8}$$

Now, applying the following Hückel approximations

$$H_{rs} = \begin{cases} \alpha, & \text{if } r = s \\ \beta, & \text{if } r \neq s \\ 0, & \text{otherwise} \end{cases} \tag{9}$$

$$S_{rs} = \begin{cases} 1, & \text{if } r = s \\ 0, & \text{otherwise} \end{cases} \tag{10}$$

and we can immediately see that a row in the Hückel equation becomes (think of this by fixing *one* value of i and summing over all j values and applying the Hückel approximations in Eqs. (9) and (10)):

$$(\alpha - E_n)c_r^{(n)} + \beta(c_{r+1}^{(n)} + c_{r-1}^{(n)}) = 0 \tag{11}$$

where we have added a superscript n to denote the n^{th} number of molecular orbital that we are referring to.

2. Rings of arbitrary length

Consider a cyclic polyene ring of N atomic sites (Fig. 1). Note that site r is connected to sites $r-1$ and $r+1$. We now aim to solve a row in the Hückel equation Eq. (11).

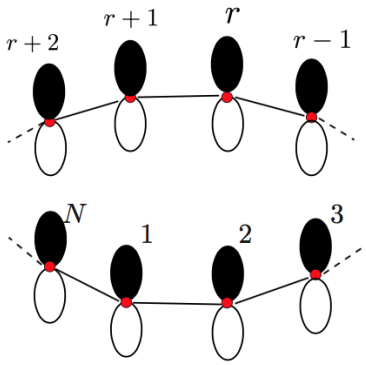

Figure 1. A cyclic polyene ring of N atomic sites.

For this particular system, the *cyclic* boundary condition is given by

$$c_r^{(n)} = c_{N+r}^{(n)}. \tag{12}$$

since the wavefunction must be *single-valued*.

We will proceed by guessing the following solution, which satisfies the boundary condition, to Eq. (11):

$$c_r^{(n)} = e^{i2\pi nr/N} \tag{13}$$

where we note again that, r denotes the atomic site and n the molecular orbital number.

Inserting this into Eq. (11), we have

$$\begin{aligned} 0 &= (\alpha - E_n)e^{i2\pi nr/N} + \beta(e^{i2\pi n(r+1)/N} + e^{i2\pi n(r-1)/N}) \\ &= (\alpha - E_n)e^{i2\pi nr/N} + \beta e^{i2\pi nr/N}(e^{i2\pi n/N} + e^{-i2\pi n/N}) \\ &= (\alpha - E_n) + \beta(2\cos(2\pi n/N)) \end{aligned}$$

Thus, giving

$$\boxed{E_n = \alpha + 2\beta\cos(2\pi n/N)} \tag{14}$$

where $n = 0, \pm 1, \pm 2, \ldots, N/2$ for even-N or $n = 0, \pm 1, \pm 2, \ldots, \pm(N-1)/2$ for odd-N. There are always precisely N molecular orbitals. Since $\cos(x)$ is an even function, this implies that, apart from $n = 0$ and $n = N/2$, the energy levels come in degenerate pairs.

We now apply the normalization condition

$$\sum_r (c_r^{(n)})^* c_r^{(n)} = 1 \tag{15}$$

to get the coefficients to the MOs

$$\boxed{c_r^{(n)} = \frac{1}{\sqrt{N}} e^{i2\pi nr/N}} \tag{16}$$

3. Linear polyene chains

Now, consider a lienar polyene chain of length N (Fig. 2). Again, we wish to solve Eq. (11).

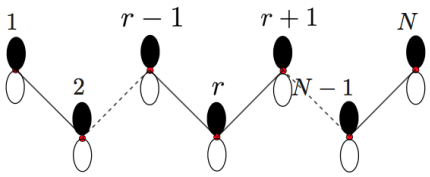

FIGURE 2. A linear polyene chain of N atomic sites.

The boundary condition is now given by

$$c_0^{(n)} = c_{N+1}^{(n)} = 0 \tag{17}$$

where we have set all the coefficients of all MOs "off-the-end" of the molecule to zero.

We now guess the following solution, again noting that it satisfies the boundary condition of the system:

$$c_r^{(n)} = sin(n\pi r/(N+1)) \tag{18}$$

Inserting this into Eq. (11), we have

$$\begin{aligned} 0 &= (\alpha - E_n)\sin(n\pi r/(N+1)) + \beta\left[\sin(n\pi(r+1)/(N+1)) + \sin(n\pi(r-1)/(N+1))\right] \\ &= (\alpha - E_n)\sin(n\pi r/(N+1)) + \beta\left[\sin(n\pi r/(N+1))\cos(n\pi/(N+1))\right. \\ &\qquad \left. + \sin(n\pi r/(N+1))\cos(n\pi/(N+1))\right] \\ &= (\alpha - E_n) + \beta(2\cos(n\pi/(N+1)) \end{aligned}$$

where we have used the trigonometric compound angle formula for the terms in the square brackets.

Thus, we have

$$\boxed{E_n = \alpha + 2\beta\cos(n\pi/(N+1))} \tag{19}$$

where n runs from 1 to N. Note that the linear chain does not have the doubly degenerate energy levels characteristic of the cyclic systems.

We now apply the normalization condition

$$\sum_r (c_r^{(n)})^* c_r^{(n)} = 1 \tag{20}$$

to get the coefficients to the MOs to obtain

$$\begin{aligned}\sum_r (c_r^{(n)})^* c_r^{(n)} &= \sum_r \sin^2\left(\frac{n\pi r}{N+1}\right) \\ &= \frac{1}{2}\sum_{r=1}^{N}(1-\cos\left(\frac{2n\pi r}{N+1}\right) \\ &= \frac{1}{2}\left[N - \sum_{r=1}^{N}\cos\left(\frac{2n\pi r}{N+1}\right)\right] \\ &= \frac{1}{2}\left[N+1 - \sum_{r=0}^{N}\cos\left(\frac{2n\pi r}{N+1}\right)\right] \\ &= \frac{N+1}{2}\end{aligned}$$

where the last summation goes to zero as the "corresponding bits" cancel. Therefore, we have, for linear chain, the coefficients of n^{th} MO is given by

$$\boxed{c_r^{(n)} = \sqrt{\frac{2}{N+1}}\,\sin(n\pi r/(N+1))} \tag{21}$$

