Quantum States of π-Electrons in Polyacetylene

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1 LCAO Approach to Linear π-Conjugated Systems

A simple MO treatment to a linear chain of N sp^2-hybridized carbon atoms describes the π molecular orbitals as a set of linear combinations of the constituing p_z atomic orbitals, the members of the basis set.

$$\Phi_i = \sum_j c_{ij}\psi_{ij}, \quad \text{with} \quad i, j = 1 \ldots N \tag{1}$$

This results in a set of linear equations that can be written in matrix form and solved from the secular determinant:

$$\begin{vmatrix} \alpha_{11} - E & \beta_{21} - ES_{21} & . \; . \; . & \beta_{N1} - ES_{N1} \\ \beta_{12} - ES_{12} & \alpha_{22} - E & . \; . \; . & . \\ . & . & . \; . \; . & . \\ \beta_{1N} - ES_{1N} & . & . \; . \; . & \alpha_{NN} - E \end{vmatrix} = 0 \tag{2}$$

In the case of molecule where $N > 2$, the full MO treatment becomes more difficult to solve manually as the secular determinant becomes large but can be straightforwardly done using mathematical software.

2 The Electron in a 1D Box Model

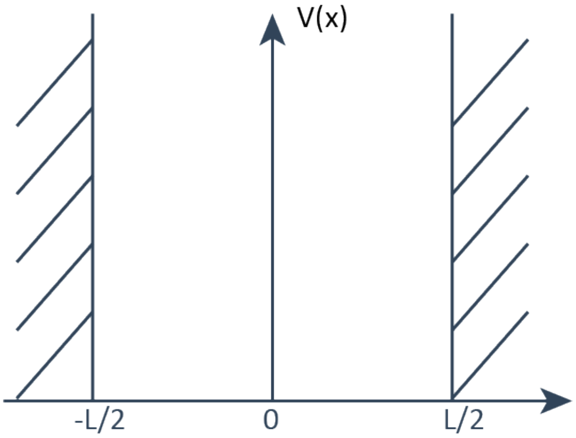

Figure 1: Schematic representation of the potential of a particle in a one-dimensional box with infinite boundary potential

In a first approximation, a polyacetylene molecule can be considered as a one-dimensional chain of carbons. An electron in this molecule contributing to its π-bonding can be regarded as free to roam along this one-dimensional segment in space, but is not allowed to leave the segment boundaries. With this approximation, one can reason that the quantum states in the poly(acetylene) molecule with N atoms can be approximated by the quantum states of an electron in a potential well of size $L = (N-1)a$ with infinite boundary potential, where a is the interactomic distance assumed to be equal between all carbons of the molecule We can define such a potential well as a function of a spatial coordinate which lies along the molecule axis (Figure 1).

The probability of finding the electron outside of the well is 0, i.e. $|\Psi|^2 = 0$. The boundary conditions are as follows:

$$\Psi(\frac{L}{2}) = \Psi(-\frac{L}{2}) = 0 \tag{3}$$

because

$$\Psi(x) = 0 \quad \forall \quad \frac{L}{2} \leq x \quad \& \quad x \leq -\frac{L}{2} \tag{4}$$

So we are looking for $\Psi(x)$ such that

$$-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\Psi(x) = E(x)\Psi(x) \quad \forall \quad x \in]-\frac{L}{2}, \frac{L}{2}[\tag{5}$$

By introducing the wave number k

$$k = \sqrt{\frac{2mE(x)}{\hbar^2}} \tag{6}$$

The equation becomes the equation of the harmonic oscillator

$$\Psi''(x) = -k^2\Psi(x) \tag{7}$$

This equation has the general solution

$$\Psi(x) = Asin(kx) + Bcos(kx) \tag{8}$$

which imposes the shape of the wavefunction. A mathematical consequence of the symmetry of the potential well is that $\Psi(x)$ must have a defined parity, i.e. the function must be either odd or even. We have then

$$A = 0 \quad \text{or} \quad B = 0 \tag{9}$$

$$\Psi(x) = Bcos(kx) \quad \text{or} \quad \Psi(x) = Asin(kx) \tag{10}$$

With $\Psi(\pm\frac{L}{2}) = 0$ we have

$$Bcos(k\frac{L}{2}) = 0 \quad \text{or} \quad Asin(k\frac{L}{2}) = 0 \tag{11}$$

$$\Rightarrow$$

$$kL = (2n+1)\pi \quad \text{or} \quad kL = 2n\pi \tag{12}$$

The wavenumber is thus quantified

$$k = \frac{n\pi}{L} \quad n \in \mathbb{N} \tag{13}$$

However, n cannot take all allowed values as some solutions would have no physical sense. Indeed, $n = 0$ is excluded because $\Psi(x) = 0$ everywhere and thus the probability to find the electron would be null, $|\Psi(x)|^2 = 0$. Moreover, Also n and $-n$ give rise to the same quantum states

$$\begin{cases} \text{If} \quad \Psi(x) \quad \text{is} \quad \text{even} \quad \Psi_{-n}(x) = \Psi_{+n}(x) \quad \forall x \\ \text{If} \quad \Psi(x) \quad \text{is} \quad \text{odd} \quad \Psi_{-n}(x) = e^{i\pi}\Psi_{+n}(x) \quad \forall x \end{cases} \tag{14}$$

In both cases

$$|\Psi_{+n}(x)|^2 = |\Psi_{-n}(x)|^2 \quad \forall x \tag{15}$$

Thus the quantum numbers $n \in \mathbb{N}^{+*}$, that is, $n \in \{1, +\infty\}$. With (6) and (13) we now know that k is quantified and we can conclude that E is independent of x but quantified, as well. Indeed,

$$\sqrt{\frac{2mE_n}{\hbar^2}} = \frac{n\pi}{L} \Leftrightarrow E_n = \frac{\pi^2\hbar^2}{2mL}n^2 = E_1 n^2 \tag{16}$$

Now that we have found an expression for E, we can also determine A and B. The probability that an electron, occupying the energy level n, is found anywhere in space is $|\Psi_n|^2$=1. With the consideration of (4),

$$|\Psi_n|^2 = \langle\Psi_n|\Psi_n\rangle \tag{17}$$

$$= \int_{-\infty}^{+\infty} \Psi_n^*(x)\Psi_n(x)dx \tag{18}$$

$$= \int_{-\frac{L}{2}}^{+\frac{L}{2}} \Psi_n^*(x)\Psi_n(x)dx \tag{19}$$

For the case where n is odd, because of the boundary conditions (3), $\Psi_n(x)$ will take the following form

$$\Psi_n(x) = Bcos(\frac{n\pi}{L}x) \tag{20}$$

Thus

$$|\Psi_n|^2 = \int_{-\frac{L}{2}}^{+\frac{L}{2}} B^*cos(\frac{n\pi}{L}x)Bcos(\frac{n\pi}{L}x)dx \tag{21}$$

$$= |B|^2 \int_{-\frac{L}{2}}^{+\frac{L}{2}} cos^2(\frac{n\pi}{L}x)dx \tag{22}$$

$$= |B|^2 \int_{-\frac{L}{2}}^{+\frac{L}{2}} (\frac{1}{2}cos(2\frac{n\pi}{L}x) + \frac{1}{2})dx \tag{23}$$

using

$$cos(x+y) = cos(x)cos(y) - sin(x)sin(y) \quad \text{and} \quad 1 = cos^2(x) + sin^2(x) \tag{24}$$

Continuing from (23)

$$= |B|^2 \left[\frac{1}{4}sin(\frac{2n\pi x}{L}) + \frac{x}{2} + c\right]_{-\frac{L}{2}}^{+\frac{L}{2}} = |B|^2\frac{L}{2} \tag{25}$$

Thus

$$|B|^2\frac{L}{2} = 1 \Leftrightarrow B = \pm\sqrt{\frac{2}{L}} \tag{26}$$

Proceeding in the same way for an even n, we obtain

$$A = \pm\sqrt{\frac{2}{L}} \tag{27}$$

As for $+n$ and $-n$ we obtain the same quantum states, we can just take the positive value and we have thus obtained the solutions to the quantum states of a particle in a box in an infinite potential well of length L

$$\begin{cases} \Psi_n(x) = \sqrt{\frac{2}{L}}cos(\frac{n\pi}{L}x) & \forall \text{ odd } n \in \mathbb{N}^{+*} \\ \Psi_n(x) = \sqrt{\frac{2}{L}}sin(\frac{n\pi}{L}x) & \forall \text{ even } n \in \mathbb{N}^{+*} \end{cases} \tag{28}$$

Each associated with the energies

$$E_n = E_1 n^2 \quad , \quad E_1 = \frac{\pi^2\hbar^2}{2mL^2} \tag{29}$$

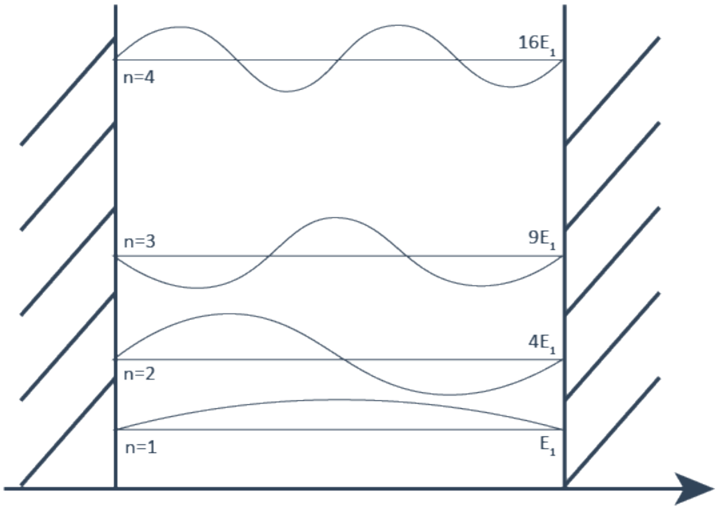

Figure 2: Wavefunctions and energy levels of a particle in a one-dimensional box

For the quantum states of a linear molecule with N carbon atoms, we noted $L = (N-1)a$. Moreover, we know that there are as many MO quantum states as there are constituting members of the basis set, so in this case N $2p_z$ atomic orbitals. The final solution is thus

$$\begin{cases} \Psi_n(x) = \sqrt{\frac{2}{(N-1)a}}cos(\frac{n\pi}{(N-1)a}x) & \forall \text{ odd } n \in \{1, ..., N\} \\ \Psi_n(x) = \sqrt{\frac{2}{(N-1)a}}sin(\frac{n\pi}{(N-1)a}x) & \forall \text{ even } n \in \{1, ..., N\} \end{cases} \tag{30}$$

Each associated with the energies

$$E_n = E_1 n^2 \quad , \quad E_1 = \frac{\pi^2\hbar^2}{2m(N-1)^2a^2} \tag{31}$$

3 The Hückel Method

While the electron in a 1D box model correctly accounts for quantization, the obtained energy levels significantly deviate from experimental values. A somewhat more rigorous approach is given by the Hückel Method, which is a further simplification of the LCAO approach. This method is specific to the case of π-conjugated molecules and aims to describe only the π molecular orbitals resulting from an interaction of the constituting $2p_z$ orbitals, independently of the framework of σ bonds. Then, it is assumed that there is no overlap between distinct $2p_z$ orbitals as well as that any Hamiltonian integral vanishes if it involves atoms i and j that are not nearest neighbours. Furthermore, it states that all similar interactions are equal for all orbitals, ie. $\forall i \in [\![1, N]\!] \quad \alpha_{ii} = \alpha \quad and \quad \beta_{i,i+1} = \beta$

Therefore, in this model the secular equation in the case of the poly(acetylene) molecule with N atoms becomes

$$\begin{vmatrix} \alpha - E & \beta & 0 & \cdots & 0 \\ \beta & \ddots & \ddots & \ddots & \vdots \\ 0 & \ddots & \ddots & \ddots & 0 \\ \vdots & \ddots & \ddots & \ddots & \beta \\ 0 & \cdots & 0 & \beta & \alpha - E \end{vmatrix} = 0 \tag{32}$$

With N rows and N columns in the determinant. Solving this secular equation, that is, finding the E_n for which it is fulfilled, is equivalent to solving the system of equations from which the determinant was actually deduced, which involve the coefficients $(c_1, ..., c_N)$ in the LCAO describing the MO. This system can be rewritten in matrix form as the following eigenvalue equation

$$\begin{pmatrix} \alpha & \beta & 0 & \cdots & 0 \\ \beta & \ddots & \ddots & \ddots & \vdots \\ 0 & \ddots & \ddots & \ddots & 0 \\ \vdots & \ddots & \ddots & \ddots & \beta \\ 0 & \cdots & 0 & \beta & \alpha \end{pmatrix} \begin{pmatrix} c_1 \\ \vdots \\ \\ \\ c_N \end{pmatrix} = E \begin{pmatrix} c_1 \\ \vdots \\ \\ \\ c_N \end{pmatrix} \Leftrightarrow \mathbf{TC} = E\mathbf{C} \tag{33}$$

By construction of the MO, we have $c_0 = c_{N+1} = 0$ as boundary conditions. With $j \in [\![1, N]\!]$, the product of j^{th} row of $\mathbf{T}$ with the vector $\mathbf{C}$, the j^{th} component of the vector $E\mathbf{C}$, corresponds to

$$Ec_j = \beta c_{j-1} + \alpha c_j + \beta c_{j+1} \tag{34}$$

Then, $(c_1, ..., c_N)$ are the terms from 1 to N of the sequence $(c_j)_{j \in \mathbb{N}}$ fulfilling

$$c_0 = 0 \quad \& \quad c_{N+1} = 0 \quad \forall j \in \mathbb{N}, \quad \beta c_j + (\alpha - E)c_{j+1} + \beta c_{j+2} = 0 \tag{35}$$

We have a linearly recursive sequence of order two and it is known from that the general term of such sequence can be expressed as a function of the roots of the characteristic polynomial associated to the sequence, which is in this case

$$\beta + (\alpha - E)r + \beta r^2 = 0 \tag{36}$$

If the characteristic polynomial admits two distinct roots, the general term would be

$$c_k = \lambda r_1^k + \mu r_2^k \tag{37}$$

while if there is a double root $r_0 = r_1 = r_2$, it would be

$$c_k = (\lambda + \mu k) r_0^k \tag{38}$$

with λ and $\mu \in \mathbb{C}$.

The solution of the characteristic polynomial cannot be the double root 0, as it would give $(c_j)_{j\in\mathbb{N}} \equiv (\mathbf{0})_{\mathbf{j}\in\mathbb{N}}$. However, if $(\mathbf{0})_{\mathbf{j}\in[\![\mathbf{1},\mathbf{N}]\!]}$ is the only solution of (35) it means that E is not an Eigenvalue. Indeed, an Eigenvalue is, by definition, associated to a non-null Eigenvector. If the solution would be a non-null double root, according to the boundary conditions (36) and (37), we would find by injecting them in (41)

$$\lambda = 0 \quad \text{and} \quad \mu = 0 \tag{39}$$

then, we would also have $(c_j)_{j\in\mathbb{N}} \equiv (\mathbf{0})_{\mathbf{j}\in\mathbb{N}}$. Therefore, the characteristic polynomial must admit two distinct roots.

If one of the two distinct roots was, for instance, $r_2 = 0$, (40) would become

$$c_k = \lambda r_1^k \tag{40}$$

With the boundary conditions (36), we would then have $\lambda = 0$ and thus $(c_j)_{j\in\mathbb{N}} \equiv (\mathbf{0})_{\mathbf{j}\in\mathbb{N}}$. Hence, the characteristic polynomial must admits two distinct non-null roots.

Furthermore, by injecting the boundary conditions (36) and (37) in (40), we have

$$\begin{cases} c_0 = \lambda + \mu = 0 \\ c_{N+1} = \lambda r_1^{N+1} + \mu r_2^{N+1} = 0 \end{cases} \tag{41}$$

$$\Leftrightarrow$$

$$\begin{cases} \lambda = -\mu \\ (\frac{r_1}{r_2})^{N+1} = 1 \end{cases} \tag{42}$$

Then, $\frac{r_1}{r_2}$ is an $(N+1)$th root of unity, that is,

$$\frac{r_1}{r_2} = e^{i\frac{2n\pi}{N+1}} \text{ with } n \in [\![1, N]\!] \tag{43}$$

Thus,

$$|r_2| = |r_1| \tag{44}$$

Additionally, since the coefficients in the characteristic polynomial are real numberss, the roots are conjugated, that is,

$$\bar{r_2} = r_1 \tag{45}$$

It exists θ such that r_1 and r_2 can be written

$$\begin{cases} r_1 = |r_1|e^{i\theta} \\ r_2 = |r_1|e^{-i\theta} \end{cases} \tag{46}$$

Therefore,

$$\frac{r_1}{r_2} = e^{i2\theta} \tag{47}$$

Then, with (46)

$$\theta = \frac{n\pi}{(N+1)} \tag{48}$$

As r_1 and r_2 are the roots of the characteristic polynomial (39), their product and sum can be expressed as a function of the coefficients

$$\begin{cases} r_1 r_2 = \frac{\beta}{\beta} = 1 \\ r_1 + r_2 = -\frac{\alpha - E}{\beta} \end{cases} \tag{49}$$

but because r_1 and r_2 are conjugated we also have

$$r_1 r_2 = r_1 \bar{r}_1 = |r_1|^2 \tag{50}$$

$$\Rightarrow$$

$$|r_1| = 1 \tag{51}$$

and

$$\begin{aligned} r_1 + r_2 = r_1 + \bar{r}_1 &= 2\,\mathrm{Re}\{r_1\} && (52)\\ &= 2\,\mathrm{Re}\Big\{e^{i\frac{n\pi}{(N+1)}}\Big\} && (53)\\ &= 2\,\mathrm{Re}\Big\{\cos\big(\frac{n\pi}{(N+1)}\big) + i\sin\big(\frac{n\pi}{(N+1)}\big)\Big\} && (54)\\ &= 2\cos\big(\frac{n\pi}{(N+1)}\big) && (55)\\ &\Rightarrow \\ 2\cos\big(\frac{n\pi}{(N+1)}\big) &= -\frac{\alpha - E}{\beta} && (56) \end{aligned}$$

Therefore, E is quantified

$$E_n = \alpha + 2\beta\cos\big(\frac{n}{N+1}\pi\big) \text{ with } n \in [\![1, N]\!] \tag{57}$$

Each E_n is associated to the MO built from the LCAO of $2p_z$ orbitals with the coefficients

$$c_k = \lambda\big(e^{i\frac{kn\pi}{(N+1)}} + e^{-i\frac{kn\pi}{(N+1)}}\big) = \lambda 2i\sin\big(\frac{kn\pi}{N+1}\big) \text{ with } k \in [\![1, N]\!] \tag{58}$$

where λ can be determined using the normalization condition $\langle \Psi_n | \Psi_n \rangle = 1$.