

ON THE HMO TREATMENT OF SYSTEMS, BUILT OF REPEATING UNITS

O. Castaño and P. Karadakov

Department for Physical Chemistry, Faculty of Chemistry of the
Sofia State University, A. Ivanov Boul. 1, Sofia 1126, Bulgaria

(Received January 1981)

ABSTRACT

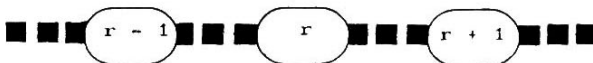
The paper proposes a development of the method of finite differences for systems with periodic structure. It is shown, that the electron wave functions and energy levels in the Hückel approximation can be derived, solving a system of first order linear homogeneous finite difference equations. The general relations have been made concrete on an example: the p-polyphenyls.

INTRODUCTION

There is constant interest in quantum chemistry towards systems, constructed of repeating units. Different approaches to the subject from the standpoint of the Hückel Molecular Orbital (HMO) theory have been advanced [1,2,3]. We show, that the method of finite differences [4,5] allows a relatively simple derivation of the HMO energy levels and wave functions for periodic systems, incorporating easily the most widely encountered boundary conditions: cyclic or Born-Karman conditions and conditions for an open chain. The derivation of the wave functions is a particular advantage of the method, allowing the calculation of a number of molecular quantities, e.g. the elements of the bond-order matrix, etc.

GENERAL FORMULATION OF THE METHOD

The secular equations of a periodic system, consisting of N elementary units:



in the frame of the HMO theory can be written as:

$$\widetilde{\underline{B}} \underline{c}_{r-1} + \underline{H} \underline{c}_r + \underline{B} \underline{c}_{r+1} = \underline{0}, \quad r=1, \dots, N \quad (1)$$

where \underline{H} is the Hückel matrix of the elementary unit (if there are M atoms in one unit, it is a $M \times M$ matrix), \underline{B} is the matrix, describing the interaction between the r -th and the $(r+1)$ -th unit - \underline{B} is also a $M \times M$ matrix with L non-zero elements - L is the number of bonds between the r -th and the $(r+1)$ -th unit cells, \underline{c}_r is a M -dimensional column vector of the coefficients for the atoms in the r -th cell and $\underline{0}$ is a M -dimensional zero column vector. $\widetilde{\underline{B}}$ is the transposed of \underline{B} .

The boundary conditions can be represented as:

1) Born-Karman or "cyclic" boundary conditions

$$\underline{c}_{r+N} = \underline{c}_r \quad (2)$$

2) Conditions, describing an "open" system

$$\widetilde{\underline{B}} \underline{c}_0 = \underline{B} \underline{c}_{N+1} = \underline{0} \quad (3)$$

When $M > 2L$, which is often encountered, (1) can be reduced to a system of $2L$ first order homogeneous linear finite difference equations by excluding the coefficients of the atoms, which do not participate in bonding between neighbouring cells. However, the derivation below shows, that such an operation is not necessary and it is easier to solve directly (1) for an arbitrary r . It should be noted, that there may be cases, in which in the system (1) appear one or more second order finite difference equations. These cases can be handled in the way described below, taking a doubled unit cell, which reduces the system to a system of first order equations.

In consistence with the general theory of finite difference equations [4], the particular solutions of (1) are given by:

$$\underline{c}_r = \lambda^r \underline{u}, \quad (4)$$

where λ is a complex number (in order to obtain the non-trivial solutions, it is assumed that $\lambda \neq 0$) and \underline{u} is a complex M -dimensional column vector, determined to a constant.

Substituting (4) in (1) it is obtained that

$$(\lambda^{-1} \widetilde{\underline{B}} + \underline{H} + \lambda \underline{B}) \underline{u} = \underline{0} \quad (5)$$

The condition for the existence of a non-zero \underline{u} leads to the characteristic equation for (1):

$$|\underline{P}| = |\lambda^{-1} \widetilde{\underline{B}} + \underline{H} + \lambda \underline{B}| = 0 \quad (6)$$

The expansion of $|\underline{P}|$, as defined in (6), leads to a polynomial equation for λ , in which the powers of λ range from $-L$ to $+L$. Having in mind, that $\lambda \neq 0$ and multiplying by λ^L one obtains a polynomial equation of degree $2L$ for λ . For every x ($x = (\alpha - e)/\beta_0$, e is one of the $M \times N$ energy levels of the polymer, $\beta_0 = -2,4 \text{ eV}$ is the standard resonance integral) this equation has $2L$ solutions $\{\lambda_j(x) \mid 1 \leq j \leq 2L\}$, not necessarily different. One should note, that (6) determines also the reverse dependence of x on λ . Solving (5) with respect to \underline{u} for every x and every $\lambda_j(x)$, the corresponding system of vectors $\{\underline{u}_j(x) \mid 1 \leq j \leq 2L\}$ is obtained. $\underline{u}_j(x)$ can be obtained only with a precision to a complex constant. Finally, for every x one can construct $2L$ particular solutions of the type (4):

$$\underline{e}_{rj}(x) = \lambda_j^r(x) \underline{u}_j(x) \quad , \quad j=1, \dots, 2L \quad (7)$$

Using the fact, that the determinant of a transposed matrix $|\widetilde{\underline{P}}| = |\underline{P}|$, it can be obtained that:

$$\begin{aligned} |\underline{P}| &= |\widetilde{\underline{P}}| = |\lambda^{-1} \widetilde{\widetilde{\underline{B}}} + \widetilde{\underline{H}} + \lambda \widetilde{\underline{B}}| = |\lambda \widetilde{\underline{B}} + \underline{H} + \widetilde{\lambda^{-1} \underline{B}}| = \\ &= |(\lambda^{-1})^{-1} \widetilde{\underline{B}} + \underline{H} + \lambda^{-1} \underline{B}| = 0 \end{aligned} \quad (8)$$

The comparison between (6) and (8) shows, that λ^{-1} satisfies the same equation as λ . Hence, if λ is a root of (6), λ^{-1} is also a root of (6). As a direct consequence, the roots $\{\lambda_j(x) \mid 1 \leq j \leq 2L\}$ can be ordered in couples:

$$\begin{aligned} \lambda_{2k-1}(x) &= \exp(i\vartheta_k(x)) \quad , \\ \lambda_{2k}(x) &= \exp(-i\vartheta_k(x)) \quad ; \quad k = 1, \dots, L \end{aligned} \quad (9)$$

where $\vartheta_k(x)$ is generally a complex number.

Using (9), the expression (5) can be written as:

$$\begin{aligned} (\exp(-i\vartheta_k(x)) \underline{B} + \underline{H} + \exp(i\vartheta_k(x)) \underline{B}) \underline{u}_{2k-1}(x) &= \underline{0} \\ (\exp(i\vartheta_k(x)) \underline{B} + \underline{H} + \exp(-i\vartheta_k(x)) \underline{B}) \underline{u}_{2k}(x) &= \underline{0} \end{aligned} \quad (10)$$

for $k = 1, \dots, L$.

Hence:

$$\underline{u}_{2k-1}(x) = \underline{u}_{2k}^*(x) = \underline{u}_k(x) \quad (11)$$

(we assume, that $\underline{u}_{2k-1}(x)$ and $\underline{u}_{2k}^*(x)$ are determined with a precision to one and the same complex constant).

The general solution of (1) can be represented as a linear combination of particular solutions (7):

$$\underline{c}_r(x) = \sum_{k=1}^L a_{2k-1}(x) \exp(ir\vartheta_k(x)) \underline{u}_k(x) + a_{2k}(x) (\exp(ir\vartheta_k(x)) \underline{u}_k(x))^* \quad (12)$$

The coefficients in the expansion $\{a_j(x) \mid 1 \leq j \leq 2L\}$ have to be determined from the boundary conditions (2) or (5) and from the normalization condition:

$$\sum_{r=1}^N \underline{c}_r^+(x) \underline{c}_r(x) = M.N \quad (13)$$

BORN-KARMAN OR "CYCLIC" BOUNDARY CONDITIONS

The condition (2), applied to (12), requires that:

$$\exp(i(r+N)\vartheta_k(x)) = \exp(ir\vartheta_k(x)) \quad (14)$$

As a consequence, there are N different values of $\vartheta_k(x)$,

$$\vartheta_k(x) = 2m\pi/N = \vartheta_m; \quad m = 1, \dots, N \quad (15)$$

leading to different values of $\{\lambda_{2k}(x) \mid 1 \leq k \leq L\}$ as defined by (9) (x also varies).

Up to now the discussion proceeded as if we knew the energy values e and consequently - the spectrum of x . The fact is that we do not know them, but we know the spectrum of $\vartheta_k(x)$ (see (15)). As it was already mentioned, (6) determines not only the dependence of λ on x , but also the reverse dependence of x on λ , resp. ϑ . Introducing λ as defined by (8) and (15) in (6), one obtains:

$$\left| \exp(-i\vartheta_m) \widetilde{B} + \underline{H} + \exp(i\vartheta_m) \underline{B} \right| = 0 \quad (16)$$

(16) represents a polynomial equation of degree M in respect to x . Solving this equation for the values of ϑ_m from (15), the spectrum of x is obtained:

$$\{\{x_{mn} \mid 1 \leq m \leq N\} \mid 1 \leq n \leq M\}$$

The index n denotes the roots of (16) for a fixed m.

(16) can be shown to hold also when the system (1) contains linear homogeneous equations of order, higher than 1.

Equation (16) has been derived also in [3], using the theory of the infinite Jacobi matrices, and in [6] - using the properties of rotographs.

As it was noted before, equation (6) in respect to λ has for every x 2L roots, coupled as shown in (9). If the root $x_{m',n'}$ is non-degenerate, it is obvious that when $x = x_{m',n'}$, (6), resp. (16), is satisfied by only one value of $\mathcal{V}_m: \mathcal{V}_m = \mathcal{V}_{m'}$. (15) implies, that \mathcal{V}_m changes only with the variation of m , which means, that for a non-degenerate $x_{m',n'}$, it must be fulfilled:

$$\mathcal{V}_k(x_{m',n'}) = \mathcal{V}_{m'} \quad ; \quad k = 1, \dots, L$$

As a consequence, the expression (12) is simplified to:

$$\begin{aligned} \underline{c}_r(x_{m',n'}) = & A(x_{m',n'}) \exp(ir\mathcal{V}_{m'}) \underline{u}(x_{m',n'}) + \quad (17) \\ & + B(x_{m',n'}) (\exp(ir\mathcal{V}_{m'}) \underline{u}(x_{m',n'}))^* \end{aligned}$$

(here $\underline{u}(x_{m',n'}) = \underline{u}_k(x_{m',n'})$, $A(x_{m',n'}) = L \cdot a_{2k-1}(x_{m',n'})$, $B(x_{m',n'}) = L \cdot a_{2k}(x_{m',n'})$; $k=1, \dots, L$).

It is convenient to choose $B(x_{m',n'}) = 0$ and one obtains:

$$\underline{c}_r(x_{m',n'}) = A(x_{m',n'}) \exp(ir\mathcal{V}_{m'}) \underline{u}(x_{m',n'}) \quad (18)$$

When the discussed eigenvalue is K-fold degenerate, one obtains in (12) a linear combination of K expressions like (17), corresponding to the different values of m, n for the degenerate levels. The coefficients in this linear combination must be chosen so as to produce K linearly independent wave functions for the degenerate levels. A possible choice, when the degenerate levels correspond to different values of m (for example, consider the pairs $\mathcal{V}_s, \mathcal{V}_{N-s}$; $s=1, \dots, E((N-1)/2)$) is indicated by (18). However, the degeneracy of levels within a constant m (for different values of n) complicates the treatment and requires generally the existence of more than one acceptable solution for $\underline{u}(x_{mn})$. We shall not discuss this case further here, but it is possible to show that a solution in the form (18) is again satisfactory.

Summarizing, the wave function in the case of Born-Karman boundary conditions is characterized by:

$$\underline{c}_r(x_{mn}) = A(x_{mn}) \exp(ir\mathcal{V}_m) \underline{u}(x_{mn}) \quad (19)$$

$A(x_{mn})$ is determined from the normalization condition (13), which in this case simplifies to:

$$A^2(x_{mn}) \underline{u}^+(x_{mn}) \underline{u}(x_{mn}) = N \quad (20)$$

CONDITIONS, DESCRIBING AN "OPEN SYSTEM"

Applying (3) to (12), one obtains:

$$\underline{B} \underline{c}_0(x) = \sum_{k=1}^L a_{2k-1}(x) \widetilde{\underline{B}} \underline{u}_k(x) + a_{2k}(x) \widetilde{\underline{B}} \underline{u}_k^*(x) = \underline{0} \quad (21)$$

$$\begin{aligned} \underline{B} \underline{c}_{N+1}(x) = & \sum_{k=1}^L a_{2k-1}(x) \exp(i(N+1)\vartheta_k(x)) \underline{B} \underline{u}_k(x) + \\ & + a_{2k}(x) \exp(-i(N+1)\vartheta_k(x)) \underline{B} \underline{u}_k^*(x) = \underline{0} \quad (22) \end{aligned}$$

(21) and (22) form a system of $2L$ equations for $\{a_j(x) \mid 1 \leq j \leq 2L\}$. Let us introduce the L -dimensional column vectors

$$\begin{aligned} \underline{f}_k(x) &= (\widetilde{\underline{B}} \underline{u}_k(x))_c \\ \underline{h}_k(x) &= \exp(i(N+1)\vartheta_k(x)) (\underline{B} \underline{u}_k(x))_c \quad (23) \\ k &= 1, \dots, L \end{aligned}$$

where by c -contracted we mean the vectors (L -dimensional), obtained from the M -dimensional $\widetilde{\underline{B}} \underline{u}_k(x)$, resp. $\underline{B} \underline{u}_k(x)$ by crossing out all the elements, equal to zero.

Using (23), (21) and (22) can be written as :

$$\begin{aligned} \underline{W}(x) \cdot \underline{a}(x) &= \underline{0} \quad \text{or} \\ \widetilde{\underline{a}}(x) \cdot \widetilde{\underline{W}}(x) &= \widetilde{\underline{0}} \quad (24) \end{aligned}$$

where

$$\begin{aligned} \underline{W}(x) &= \begin{pmatrix} \underline{f}_1(x) & \underline{f}_1^*(x) & \underline{f}_2(x) & \underline{f}_2^*(x) & \dots & \underline{f}_L(x) & \underline{f}_L^*(x) \\ \underline{h}_1(x) & \underline{h}_1^*(x) & \underline{h}_2(x) & \underline{h}_2^*(x) & \dots & \underline{h}_L(x) & \underline{h}_L^*(x) \end{pmatrix} \\ \widetilde{\underline{a}}(x) &= (a_1(x), a_2(x), \dots, a_{2L}(x)) \end{aligned}$$

$\underline{0}$ is here a $2L$ -dimensional zero column vector.

The condition for the existence of a non-zero solution of the system (24):

$$\left| \underline{W}(x) \right| = 0 \quad (25)$$

together with the equations, obtained from (6) for every λ , resp. ϑ , given by (10):

$$\left| \exp(-i\vartheta_k(x)) \widetilde{\underline{B}} + \underline{H} + \exp(i\vartheta_k(x)) \underline{B} \right| = 0 \quad (26)$$

$k = 1, \dots, L$

form a system of $L+1$ equations for x and ϑ_k , which allows the determination of the energy spectrum of the polymer. If after the solution of this system one finds $\underline{a}(x)$ from (24), after a normalization (13), (12) gives the values of the coefficients $\underline{c}_r(x)$.

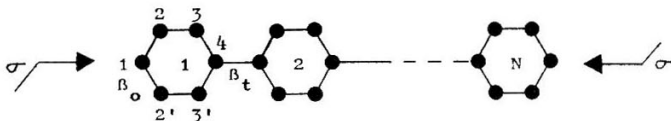
As it was already mentioned, $\psi_k(x)$ are generally complex numbers. The study of the conditions for the existence of complex $\psi_k(x)$, however, shall be the subject of another paper. We would like only to point out here that the existence of complex $\psi_k(x)$ is generally connected with the existence of local energy levels.

Other possible approaches to open systems are: the transfer matrix method [1], the polynomial matrix method [2], the perturbative treatment, proposed by [6]. In our opinion, the finite difference formalism, proposed here, is more expedient. The possibility for exact calculations of open systems of arbitrary length, having more than one bond between the elementary units, is another advantage of the method.

AN EXAMPLE - THE P-POLYPHENYLS

Our example will be centered on an "open" system, where the calculative difficulties are relatively graver.

It is useful to classify the MO's in the p-polyphenyls according to the plane of symmetry σ :



We shall begin with the MO's which are symmetric with respect to σ . Choosing a numeration of the atoms as shown above, it is obtained:

$$\underline{H}^S = \begin{pmatrix} x & 2 & 0 & 0 \\ 2 & 2x & 2 & 0 \\ 0 & 2 & 2x & 2 \\ 0 & 0 & 2 & x \end{pmatrix}, \quad \underline{B}^S = \begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ t & 0 & 0 & 0 \end{pmatrix}, \quad \underline{u}^S = \begin{pmatrix} u_1^S \\ u_2^S \\ u_3^S \\ u_4^S \end{pmatrix}$$

Here $x = (\alpha - e) / \beta_0$, $t = \beta_t / \beta_0$

From (6) we obtain:

$$\begin{aligned} |\underline{P}^S| &= |\lambda^{-1} \underline{B}^S + \underline{H}^S + \lambda \underline{B}^S| = & (27) \\ &= 4(x^4 - (5 + t^2)x^2 + t^2 - 2t(\lambda + 1/\lambda) + 4) = 0 \end{aligned}$$

From (9):

$$\lambda_1 = \exp(i\vartheta) \quad , \quad \lambda_2 = \exp(-i\vartheta) \quad (28)$$

(ϑ stands for $\vartheta_1(x)$). Substituting (28) in (27):

$$x^4 - (5 + t^2)x^2 + t^2 - 4t \cos \vartheta + 4 = 0 \quad (29)$$

The next task is to find $\underline{u}_1^s(x)$, which we shall denote simply as \underline{u}^s ; $\underline{u}_2^s(x) = (\underline{u}_1^s(x))^* = (\underline{u}^s)^*$. Because \underline{u}^s is determined to a constant, it is convenient to choose $u_4^s = 1$. Solving (5) under this condition, it is obtained that:

$$\begin{aligned} u_1^s &= (t\lambda_1^{-1}(x^2 - 1) + 2)/(3x - x^3) \quad , \\ u_2^s &= (1 + t\lambda_1^{-1})/(x^2 - 3) \quad , \\ u_3^s &= (1 + t\lambda_1^{-1})/(3x - x^3) - 1/x \quad , \quad u_4^s = 1 \end{aligned} \quad (30)$$

Substituting (30) in the boundary conditions (21), (22), we obtain for (24):

$$\begin{aligned} \underline{\hat{a}}(x) &= (a_1(x) \quad , \quad a_2(x)) \\ \underline{\tilde{w}}(x) &= \begin{pmatrix} 1 & \frac{(t \exp(-i\vartheta)(x^2-1) + 2)\exp(i(N+1)\vartheta)}{3x - x^3} \\ 1 & \frac{(t \exp(i\vartheta)(x^2-1) + 2)\exp(-i(N+1)\vartheta)}{3x - x^3} \end{pmatrix} \end{aligned} \quad (31)$$

Hence, from (25):

$$\text{const.} \cdot \left| \underline{w}(x) \right| = \sin(N+1)\vartheta + t(x^2 - 1)\sin N\vartheta/2 = 0 \quad (32)$$

(24) allows to obtain also that

$$a_1(x) = -a_2(x) = a(x) \quad (33)$$

The system (29), (32) determines the energy levels, corresponding to symmetric MO's. The coefficients of the wave functions can be found from (12), (30) and (33):

$$\underline{c}_r(x) = \underline{b}(x) \begin{pmatrix} \frac{t(x^2 - 1)\sin(r-1)\vartheta}{3x - x^3} + 2\sin r\vartheta \\ \frac{t\sin(r-1)\vartheta + \sin r\vartheta}{x^2 - 3} \\ \frac{t\sin(r-1)\vartheta + \sin r\vartheta}{3x - x^3} - \frac{\sin r\vartheta}{x} \\ \sin r\vartheta \end{pmatrix}$$

$b(x) = 2ia(x)$ is determined trivially through normalization.

The solution for the orbitals, antisymmetric in respect to σ , leads to roots (here one does not need the finite difference method):

$$x_{m,\bar{m}}^a = \mp 1 \quad ; m = 1, \dots, N$$

and corresponding orbitals - any normalized linear combination of

$$\psi_r^a = \varphi_{2r} - \varphi_{2'r} + \varphi_{3r} - \varphi_{3'r} \quad , r=1, \dots, N$$

for the bonding antisymmetric MO's and of

$$\bar{\psi}_r^a = \varphi_{2r} - \varphi_{2'r} - \varphi_{3r} + \varphi_{3'r} \quad , r=1, \dots, N$$

for the antibonding antisymmetric MO's. In each of these cases the total number of linearly independent MO's that can be constructed is N .

[7] represents another example of application of the method, outlined in the present paper - to polyenes and annulenes.

ACKNOWLEDGEMENT

The authors would like to thank Prof. Dr. O. E. Polansky for his valuable critical remarks on the present paper.

REFERENCES

1. Y. Jido, T. Inagaki, H. Fukutome, Progr. Theor. Phys. 48 (1972), 808
2. M. V. Kaulgud, V. H. Chitgopkar, J. C. S. Faraday II 74 (1978), 951
3. I. V. Stankevich, Journ. Phys. Khimii 43 (1969), 3 (in Russian)
4. I. Gelfond, Ischislenie Konechnikh Raznostei (Moscow, 1967)
5. T. K. Rebane, in Voprosi Kvantovoi Khimii (Leningrad, 1963) p. 115
6. O. Polansky, N. Tyutyulkov, MATCH 3 (1977), 149
7. P. Karadakov, O. Castaño, F. Fratev, V. Enchev, to be published