POLYMER SCIENCE

FUNDAMENTALS OF POLYMER SCIENCE

Electronic Structure of Polymers

Prof. A.K. Bakhshi
Department of Chemistry
University of Delhi
Delhi- 110007

(17.10.2007)

CONTENTS

Keywords
Electronic conduction, periodic polymer, aperiodic polymer, negative factor counting

Introduction

Why do we need to calculate the electronic properties of polymers theoretically? The most frequent task of practical polymer research is to find out among the members of a polymer family (the same ring or rings with given different substituents) those few which possess for a certain purpose usually unrelated optimal properties. In the experimental polymer research out of say 4000 possibilities they choose (on the basis of experience and chemical intuition) 200-400 polymers, they synthesize them and measure the properties in which they are interested in. Finally on the basis of their results they decide which polymers they try to apply for the given purpose. This procedure is obviously very expensive and it may happen that the polymer family does not consist of those polymers which have optimal properties for the prescribed purpose. Further, if the research has to find out polymers for a completely new purpose (which means several new optimal properties), the reduction of the number of polymers to be investigated (in our example from 4000 to a few hundred) may not work at all.

A much less expensive and safe procedure is to calculate the electronic structure in a good approximation (which means a good quality Hartree Fock (HF) band structure calculation and correction of the band structure for correlation) and calculate the desired properties of the chosen smaller pool of polymers (in the above example a few hundred polymers). On the basis of the theoretical results one can predict which 15-20 polymers should be synthesized and their properties measured to come up with the few polymers optimal for a given purpose. Though such calculations require very much CPU time, they certainly are orders of magnitudes cheaper than the conventional experimental approach.

How do we calculate the electronic structure of polymers? We start with the very familiar molecular orbital theory and solve the Schrodinger equation for molecules. Next we extend our treatment of molecules to polymers (thinking polymer as an infinite chain of repeating unit cells). A crystal orbital $\varphi_i(k)$, the polymer equivalent of molecular orbital is formed from linear combination of Bloch orbitals. The homopolymers have been studied using ab initio Hartree Fock crystal orbital method while the copolymers and biopolymers (both periodic and aperiodic) have been studied using negative factor counting (NFC) in the tight binding approximation. The method can be extended to include many neighbour interactions. Researchers have developed a computer code that calculates the electronic structure of polymers using these techniques.

Investigation of Electronic Conduction of Periodic Polymers

Quantum mechanics in principle makes it possible to calculate the properties of a polymer from the solution of its basic equation – the Schrodinger equation:

$$\hat{H}\Psi = E\Psi \qquad (1)$$

Where
$\hat{H}$ is the energy operator Hamiltonian,
ψ the wave function of the system and
E its total energy.

In the Hartree Fock theory, the solution of eqn. 1 is achieved through following assumptions.

i. Non relativistic motion: This ignores the change in the mass of particles with motion. This approximation breaks down for the innermost core electrons of the heavier electrons but is reasonable otherwise.

ii. Born Oppenheimer Approximation: This approximation separates electronic and nuclear motion in a molecule or solid. In these systems, it is common for the electrons to be moving at much higher speeds than the nuclei, due to the large differences in their masses. It is, therefore, reasonable to consider nuclei at rest relative to electrons.

iii. One electron Approximation (OEA): This approximation helps in reducing the many electron problems to the one-electron equation which is the starting point in the calculation of the electronic energies and wavefunctions for condensed matter. In this approximation, it is assumed that in a many electron system, the action on a given electron of all the nuclei and all the rest of the electrons of the system can be approximately replaced by the action of some average effective field in which the potential energy of electron the so called "effective one electron potential" V, depends only on the coordinates of the system. In different systems this V shall be different and thus the quantum mechanical investigation of different many electron systems under OEA is reduced to the much simpler investigation of the motion of one electron in fields with different potentials. The general form of the one electron Schrodinger equation in a multielectron system is

$$\left(-\frac{1}{2} \nabla^2 + V \right) \phi = \epsilon \phi \qquad (2)$$

iv. Hartree Fock Approximation: The form of the potential energy V for a many electron system under OEA depends upon how the total wavefunction of the system is expressed in terms of its one electron wavefunctions. In the Hartree Fock approximation the total wavefunction is represented by a Slater determinant wavefunction composed of one electron wavefunctions. The one electron equation for a system containing A nuclei and m electrons, then, reduces to the following form:

$$\left\{ \hat{h}_1 + \sum_{r=1}^{m/2} (2\hat{J}_r - \hat{K}_r) \right\} \phi_i (r_1) = \epsilon_i \phi_i (r_1) \qquad (3)$$

where $$\hat{h}_1 = -\frac{1}{2} \nabla^2_1 + \sum_{A=1}^{Y} \frac{Z_A}{r_{A1}}$$

This equation is known as the Hartree Fock (HF) equation for an electron occupying the space orbital in the Slater determinant. $\hat{J}_r$ and K_r are known as Coulomb and exchange operators.

In the case of molecules, the one electron orbitals are known as molecular orbitals and these, unlike atomic orbitals of atoms, are delocalized over the whole molecule and therefore the advantage of the spherical symmetry present in atoms is not there in molecular systems. Therefore, the HF one electron equation in the case of molecules is solved using LCAO approximation and the method is known as the Hartree Fock Roothaan (HFR) Method.

Viewing a polymer as a large molecule, it should be possible in principle to apply the HFR method to polymers. However, due to the very large size of the polymer, it is not possible to extend HFR equations to polymers (all the associated matrices become of infinite order). This problem in the case of polymers is overcome through the use of symmetry present in the polymer. The translational symmetry present in the polymer along with the Born-von-Karaman boundary condition is used to solve the one electron HF equation in the case of polymers. The corresponding method is known as Hartree Fock Rothaan crystal orbital method. In the ab initio version of this method, all integrals are calculated numerically. On the other hand, in the semiemperical techniques, some integrals are assigned zero values at the start and others approximated empirically. Some of the well known semiemperical formalisms are: CNDO (Complete Neglect of Differential overlap), INDO (Intermediate NDO), MINDO (Modified INDO), VEH (Valence Effective Hamiltonian) and DFT (Density Function Theory).

1. Ab initio Hartree Fock crystal orbital method

In this method, a crystal orbital $\phi_i(k)$, the polymer equivalent of a molecular orbital, is formed from the linear combination of Bloch orbitals.

$$\phi_i(k) = \sum_{\nu=1}^{s} C_{\nu i}(k)\Phi_\nu(k) \qquad (4)$$

The Bloch orbitals are formed from a linear combination of the atomic basis functions χ_ν^j thus

$$\Phi_\nu(k) = \frac{1}{(2N+1)^{1/2}} \sum_{j=-N}^{+N} \exp(ikaj)\chi_\nu^j \qquad (5)$$

where χ_ν^j is the ν^{th} basis function in the j^{th} cell and the normalization constant $(2N+1)^{-1/2}$ results from our considering the polymer to be made up of (2N+1) identical unit cells, s is the no. of basis functions per unit cell and a is the length of the unit cell.

By applying the variational theorem, the coefficients $C_{\nu i}(k)$ occurring in LCAO approximation of the crystal orbital $\phi_i(k)$ and the energy $\varepsilon_i(k)$ of this crystal orbital must satisfy the following set of simultaneous equations

$$\sum_{\nu=1}^{s} (F_{\mu\nu}(k) - S_{\mu\nu}(k)\varepsilon_i(k))C_{\mu i}(k) = 0 \qquad \mu = 1,2,.....s;\ i = 1,2,.....s \qquad (6)$$

In the matrix form, the equation may be written as

$$F(k)C(k) = S(k)C(k)\varepsilon(k) \tag{7}$$

where the matrices *F(k)* and *S(k)* are the Fock and overlap matrices between the Bloch orbitals. Both these matrices are complex Hermitian, while *C(k)* is complex and $\varepsilon(k)$ the real.

The elements of these matrices are expressed as:

$$S_{\mu\nu}(k) = \sum_{j=-N}^{+N} \exp(ikaj) S_{\mu\nu}^{j} \tag{8}$$

$$F_{\mu\nu}(k) = \sum_{j=-N}^{+N} \exp(ikaj) F_{\mu\nu}^{j} \tag{9}$$

where $S_{\mu\nu}^{j}$ is the overlap integral $\left\langle \chi_{\mu}^{0} \middle| \chi_{\nu}^{j} \right\rangle$ over the basis functions χ_{μ}^{0} in the zeroth cell and χ_{ν}^{j} in the j^{th} cell

$$F_{\mu\nu}^{j} = T_{\mu\nu}^{j} + V_{\mu\nu}^{j} + \sum_{h=-N}^{+N} \sum_{l=-N}^{+N} \sum_{\lambda=1}^{s} \sum_{\sigma=1}^{s} D_{\lambda\sigma}^{hl} \left\{ 2\left\langle \chi_{\mu}^{0} \chi_{\nu}^{j} \middle| \chi_{\lambda}^{h} \chi_{\sigma}^{l} \right\rangle - \left\langle \chi_{\mu}^{0} \chi_{\lambda}^{h} \middle| \chi_{\nu}^{j} \chi_{\sigma}^{l} \right\rangle \right\} \tag{10}$$

$$\text{where } T_{\mu\nu}^{j} = \left\langle \chi_{\mu}^{0} \middle| -\frac{1}{2}\nabla^{2} \middle| \chi_{\nu}^{j} \right\rangle \tag{11}$$

$$V_{\mu\nu}^{j} = \sum_{h=-N}^{+N} \sum_{A=1}^{Y} \left\langle \chi_{\mu}^{0} \middle| -\frac{Z_{Ah}}{r_{Ah}} \middle| \chi_{\nu}^{j} \right\rangle \tag{12}$$

The density matrix terms $D_{\lambda\sigma}^{hl}$ depends on *h-l*. So we write

$$D_{\lambda\sigma}^{hl} = D_{\lambda\sigma}^{j}$$
$$\text{where } j = h - l$$

$$\text{and } D_{\lambda\sigma}^{j} = \frac{a}{2\pi} \int_{BZ} \sum_{i=1}^{w/2} C_{\lambda i}(k) C_{\sigma i}(k) \exp(ikaj) dk \tag{13}$$

Of the *s* values of $\varepsilon(k)$, that is, the band structure associated with equation (7), the *w/2* bands of lowest energy, corresponding to the energies of the doubly occupied bands, are known as valence bands while the remaining *s-w/2* are known as conduction bands. The summation in equations (8), (9), (10) and (12) are truncated after second neighbours (N =

2). It should however be noted that the HF approach, though only a first approximation to the many practical problem, has many advantages both from practical and theoretical points of view. Some of them are:

1. The HF total energy per elementary cell in the crystal is variationally determined and admits quite realistic geometry optimizations:

2. The electronic charge distributions obtained by the HF method are very accurate and suitable not only for qualitative but also for quantitative discussions and interpretations of the properties related to them.

3. The one determinantal wave function of the method is precisely defined, therefore, it can serve as a reasonable starting point for the investigation of effects lying beyond the capabilities of the one particle approach (correlation corrections, optical properties etc.)

Finally it should be mentioned that the HFR-CO formalism is valid not only for the translational symmetry operation but also for the case of repeated combined symmetry operation (for example helix operation).

A crucial part of all HF CO studies in configuration space is the calculating and handling of the two electron integral contribution to the flock matrix. In principle, the number of these integrals is proportional to $N_3 \times s_4$ (s is the number of orbitals per unit cell and N is the number of neighbour interactions considered). This relation holds in practicle, however only for a few nearest neighbouring cells in the crystal and goes over very quickly into an $N \times V^2$ relation (the translation depends of curse, on the lattice parameters and basis set. The feasibility of correct computations depends now basically on whether the non-necessary two electron integrals lying at an absolute value between certain thresholds (usually 10^{-6} to 10^{-7} Hartree) can be picked out one basis of an approximation before they are actually calculated. Various groups have developed different strategies for cut off procedures. One procedure commonly employed is based on the basis of Mulliken's approximation to four center integrals. This procedure, as well as the efficient use of symmetry in both the upper and lower indices of the two electron integrals, makes it possible that extended systems with many atoms in the elementary cell can also be investigated.

2. Semiemperical Formalisms

As in the case of molecular quantum chemistry, semiemperical versions of the LCAO crystal orbital formalism have been developed by substituting into the general formalism the corresponding Hamiltonian matrix elements. Their range of applicability is also very similar to those of original molecular methods. The simple π electron only methods as that of Huckel and Pariser, Paar and Pople(PPP) have been applied to conjugated chains or other polymers. In the simple Huckel method, only nearest neighbour interactions are taken into account and hence only the first translation is retained in the secular system and determinant. As a consequence simple k- dependence of the π energy bands are produced. Practicle calculations in this method are even easier since atomic Huckel basis

is assumed to be orthogonal. Next in sophistication comes the extended Huckel theory (EHT). In this method which can be applied to σ bonded systems, only valence orbitals are considered. One center interactions are estimated from electron affinities and ionization potentials. Two center integrals are computed from one center integral by Mulliken's approximation and calibrated by a scale factor. The integrals vary exponentially with distance so that Bloch sums are generally extended over 10 or 15 unit cells in secular systems. Due to non orthogonality, diagonalisation procedures are more involved and sophisticated band structures can be generated. Since the procedure does not take into account the explicit electron electron interactions, the method is non interactive and directly produces a stable band structure.

Investigation of Electronic conduction of aperiodic polymers

Negative Factor Counting Method

To investigate the density of states (DOS) distribution of quasi 1-D system, multicomponent polymer system, and negative factor counting technique (NFC) based on Dean's negative eigenvalue theorem has proven to be the most accurate and fast method (though for a general case of a disordered system, the coherent potential approximation (CPA) with an energy and k-dependent self energy seems to be the relatively most accurate method to obtain the DOS). This method is related to the Givens-Householder-Wilkinson method for matrix diagonalization. It is based on Sturms theorem and determines the eigenvalues of a matrix as the changes of sign of its secular determinant as a function of λ. Evaluation of the secular determinant for a given value of λ is efficiently done by the Gaussian algorithm. There are two versions of this method: simple NFC (tight binding approximation) and matrix block NFC (taking into account the more neighbours' interactions).

1 Simple Negative Factor Counting (NFC) Method: In this method, electronic DOS of a quasi-one dimensional copolymer chain is obtained by writing down the Hückel determinant of a copolymer chain consisting of N units.

$$|\mathrm{H}(\lambda)| = \begin{vmatrix} \alpha_1 - \lambda & \beta_2 & 0 & .... & 0 \\ \beta_2 & \alpha_2 - \lambda & \beta_3 & .... & 0 \\ 0 & \beta_3 & \alpha_3 - \lambda & \beta_4 & 0 \\ 0 & 0 & \beta_4 & .... & \beta_N \\ 0 & 0 & 0 & .... & \alpha_N - \lambda \end{vmatrix} = 0 \qquad (14)$$

The determinant is only tridiagonal because calculations are carried out under tight binding approximation, i.e., only first neighbour interaction is taken into account. In this determinant, α's are diagonal elements, β's are off diagonal elements and λ's are eigenvalues, of an effective one-electron Hamiltonian. The α and β values and obtained from the corresponding band structures of the polymers. The tridiagonal determinant can be easily transformed into a didiagonal one with the help of successive Gaussian eliminations.

Thus the equation

$$|H(\lambda)| = \prod_{i=1}^{N} (\lambda_i - \lambda) \tag{15}$$

can be written as

$$|H(\lambda)| = \prod_{i=1}^{N} \varepsilon_i(\lambda) \tag{16}$$

where the diagonal elements of the didiagonal determinant are given by the simple relation

$$\varepsilon_i(\lambda) = (\alpha_i - \lambda) - \frac{\beta_j^2}{\varepsilon_{i-1}(\lambda)} \tag{17}$$

$$\varepsilon_1(\lambda) = \alpha_1 - \lambda \tag{18}$$

Since eqn. (15) and (16) are equal, it is easy to see that for a given λ value the number of eigenvalues λ_i smaller than λ ($\lambda_i < \lambda$) has to be equal to the number of negative ($\varepsilon_i(\lambda)$) factors in eqn. (17). The computation of all the eigenvalues λ_i for a long polymer chain (~ N = 10^3 – 10^4 units) by directly solving eqn. (14) is almost impossible but the computation of $\varepsilon_i(\lambda)$ values from (17) and (18) is very fast. By giving λ different values throughout the spectrum and taking the difference of the number of negatives belonging to consecutive $\varepsilon_i(\lambda)$ values, one can obtain the DOS for any copolymer chain to any desired accuracy.

As mentioned earlier the α_i and β_j matrix elements of the secular determinant are determined from the corresponding band structures of each component constituting the copolymer chain. For a given band, α_i of a component is taken to be the middle point (or weighted middle point) of the corresponding band. Assuming the dispersion of the band to be given by the simple relation

$$\varepsilon_A(k) = \alpha_A + 2\beta_{A,A}\cos(ka) \tag{19}$$

where a is the translation length, $\beta_{A,A}$ is taken to be one fourth of the band width if the same component is repeated. If on the other hand, one component (say A) is followed by other component (say B), then the off-diagonal matrix element becomes $\beta_{A,B}$ and is given by a simple relation

$$\beta_{AB} = \frac{1}{2}(\beta_{A,A} + \beta_{B,B}) \tag{20}$$

2 Matrix Block NFC method: This method can be applied to disordered quasi one dimensional systems with an arbitrary number of orbitals per unit. In this case one has the secular determinant instead of a tridiagonal in a triblock-diagonal form,

$$
\begin{aligned}
|M(\lambda)| &= |F - \lambda S| \\
&= \begin{vmatrix}
F_{11} - \lambda S_{11} & F_{12} - \lambda S_{12} & & & & & \\
F_{12}^{\mathrm{tr}} - \lambda S_{12}^{\mathrm{tr}} & F_{22} - \lambda S_{22} & F_{23} - \lambda S_{23} & & & & \\
0 & F_{23}^{\mathrm{tr}} - \lambda S_{23}^{\mathrm{tr}} & F_{33} - \lambda S_{33} & F_{34} - \lambda S_{34} & & & \\
 & & & \ddots & & & \\
 & & & & \ddots & & \\
 & & & & & F_{N,N} & - \lambda S_{N,N}
\end{vmatrix} = 0 .
\end{aligned}
$$

Here the $\boldsymbol{F}_{ii}$'s are the diagonal and the $\boldsymbol{F}_{i,j}$'s the off-diagonal blocks of the Fock matrix, respectively (belonging to the ith unit and to its interaction with the jth unit, further N is the number of units in the chain).

We can rewrite the matrix $M(\lambda)$ in the form

$$M(\lambda) = F - \lambda S = S^{1/2}[S^{-1/2}FS^{-1/2} - \lambda \mathbf{1}]S^{1/2} = S^{1/2}[\tilde{F} - \lambda \mathbf{1}]S^{1/2}$$

or in determinantal form

$$
\begin{aligned}
\det M(\lambda) &= \det S^{1/2} \det(\tilde{F} - \lambda \mathbf{1}) \det S^{1/2} \\
&= \det S^{1/2} \det S^{1/2} \det(\tilde{F} - \lambda \mathbf{1}) = \det S \det(\tilde{F} - \lambda \mathbf{1}) .
\end{aligned}
$$

The determinant $|F - \lambda S|$ can be brought to a diblockdiagonal form with the help of a successive Gaussian elimination [110]. In this way one obtains for the diagonal blocks (as it could be shown easily) the recursion formula

$$U_i(\lambda) = F_{i+i} - \lambda S_{ii} - (F_{i,i+1}^{\mathrm{tr}} - \lambda S_{i,i+1}^{\mathrm{tr}}) U_{i-1}^{-1} (F_{i,i+1} - \lambda S_{i,i+1}) ,$$

$$U_1(\lambda) = F_{11} - \lambda S_{11} .$$

Therefore we can write

$$\det(F - \lambda S) = \left(\prod_{i=1}^{n} s_i \right) \left[\prod_{j=1}^{n} (\lambda_j - \lambda) \right] = \prod_{i=1}^{N} \left[\prod_{k=1}^{l_i} u_{ik}(\lambda) \right] \left(n = \sum_{i=1}^{N} l_i \right) .$$

Here the s_i's are the eigenvalues of S and the λ_j's are the roots of the generalized eigenvalue equation

$$Fc_j = \lambda_j S c_j .$$

Further N is again the number of units, l_i the dimension (number of basis functions) of the ith unit and $u_{ik}(\lambda)$ denotes the kth eigenvalue of the matrix block $U_i(\lambda)$. The latter matrix block can be easily diagonalized for a given trial value of λ.

it follows that for a given $\lambda^{(1)}$ the number of negative $u_{ik}(\lambda^{(1)})$ factors has to be

equal to the number of eigenvalues λ_j which are smaller than the chosen $\lambda^{(1)}$. Taking another trial $\lambda^{(2)}$ value one can determine the number of negative $u_{ik}(\lambda^{(2)})$'s again. The difference of the negative u_{ik} factors gives immediately the number of eigenvalues λ_j which lie between $\lambda^{(2)}$ and $\lambda^{(1)}$:

$$\lambda^{(1)} > \lambda_j > \lambda^{(2)} .$$

Taking a fine grid in the trial λ's and scanning the whole eigenvalue spectrum one obtains immediately the total DOS.

For the application of matrix block NFC method we require various flock and overlap matrix blocks to construct a secular determinant .these matrix blocks are obtained from the corresponding cluster studies using the ab initio HF SCF LCAO method. For a disordered chain containing p different components one has to study p^2 different clusters. For example, in a binary chain of two components A and B the four clusters to be studied are AA, AB, BA, BB. From the results of each cluster (say AB), the diagonal flock and overlap matrix blocks and the off diagonal flock and overlap matrix blocks representing interactions of molecule A and B are extracted. Thus 4 matrix blocks are used from each cluster.

3. Negative Factor Counting (NFC) Method - With More Neighbours' Interactions

Here the simple NFC method have extended to the case of more neighbours' interactions and developed a program for this. In this method one first fits the energy band dispersion $\varepsilon_i(k)$ of the two periodic polymers to the one-band expression

$$\varepsilon_i(k) = \alpha_i + 2\sum_{y=1}^{neig} \beta_i^{(y)} \cos(yka) \qquad (21)$$

where α_i, β_i^y are the fitting parameters, a the translation length, *neig*, which is the number of neighbours up to which interactions are taken into account, has to be chosen appropriately (in our study we went upto *neig* = 6). Eqn. (21) describes the band dispersion of the following matrix

$$H_i = \begin{pmatrix} \alpha_i & \beta_i^{(1)} & \beta_i^{(2)} & \beta_i^{(3)} & \ldots \\ . & \alpha_i & \beta_i^{(1)} & \beta_i^{(2)} & \ldots \\ . & & \alpha_i & \beta_i^{(1)} & \ldots \\ . & & & & \ldots \\ . & & & & \ldots \\ . & & & & \ldots \end{pmatrix} \qquad (22)$$

In the above matrix, α_i and $\beta_i^{(y)}$ of each component are obtained by fitting the corresponding *ab initio* Hartree-Fock band structure results in equation (21). Our study showed that the DOS calculated from the above matrix with $\beta_i^{(y)}$ with $y = 6$ (the $\beta_i^{(y)}$ with $y > 6 = 0$ were taken to be zero) exactly reproduce the *ab initio* results.

In the case of a copolymer chain of length N and consisting of two types of components A and B, the secular determinant depends upon the sequence of the units A and B in the

copolymer chain. For the following periodic sequence,

ABABABAB…

the secular determinant $H(\lambda)$ for a given value of energy λ, is of order 2N x 2N (since both valence and conduction bands of each component are taken into consideration) and is given by

$$H(\lambda) = \left(\begin{array}{cc|cc|cc|c} \alpha_{A1}-\lambda & 0 & \beta^{(1)}_{A1B1} & \beta^{(1)}_{A1B2} & \beta^{(2)}_{A1A1} & \beta^{(2)}_{A1A2} & \cdots\cdots \\ 0 & \alpha_{A2}-\lambda & \beta^{(1)}_{A2B1} & \beta^{(1)}_{A2B2} & \beta^{(2)}_{A2A1} & \beta^{(2)}_{A2A2} & \cdots\cdots \\ \hline & & \alpha_{B1}-\lambda & 0 & \beta^{(1)}_{B1A1} & \beta^{(1)}_{B1A2} & \cdots\cdots \\ & & 0 & \alpha_{B2}-\lambda & \beta^{(1)}_{B2A1} & \beta^{(1)}_{B2A2} & \cdots\cdots \\ \hline & & & & \alpha_{A1}-\lambda & 0 & \cdots\cdots \\ & & & & 0 & \alpha_{A2}-\lambda & \cdots\cdots \\ \hline & & & & & & \end{array}\right) \qquad (23)$$

where the numerals 1, 2 refer to the valence and the conduction bands respectively. α_{A1}, for example, is the diagonal element for the valence band of component A. $\beta^{(1)}_{A1B2}$ is the off-diagonal element or the interaction parameter for the valence band of component A and conduction band of component B when they are first neighbour to each other. Similarly $\beta^{(2)}_{A1A2}$ is the interaction parameter for the valence and conduction bands of component A when they are second neighbour to each other. The elements $\beta^{(y)}_{AiAi} = \beta^{(y)}_{Ai}$ but the element $\beta^{(y)}_{AiBj}$ for $A_i \neq B_j$ is obtained using the following ansatz.

$$\beta^{(y)}_{AiBj} = 0.5(\beta^{(y)}_{Ai} + \beta^{(y)}_{Bj}) y^{-p} \exp\left(-c\left|\alpha_{Ai} - \alpha_{Bj}\right|\right) \qquad (24)$$

where $p = 2$ and $c = 0.1$ eV^{-1}.

The form of eqns. (23) and (24) has been constructed in such a way as to give back for the single component case (A = B) the exact DOS as obtained by eqns.(21 and 22).

The DOS of H(λ) from equation(23) was obtained, by the matrix block NFC method based on Dean's negative eigenvalue theorem which states that for any trial value of energy λ, the number of eigenvalues λ_i less than energy λ has to be equal to the number of negative factors. By giving different λ values throughout the whole spectrum and taking the differences of the number of negative values belonging to consecutive value of λ in the chosen grid, the distribution of eigenvalues of *H(λ)* can be obtained to any desired accuracy.

To calculate the number of eigenvalues for a given value of λ, one divides the matrix (23) into quadrants as shown below.

$$H(\lambda) = \begin{vmatrix} X_1 & Y_1 \\ Y_1' & Z_1 \end{vmatrix} \tag{25}$$

where (′) denotes transpose, X is of the order unity i.e. a scalar, Y is a row vector , Z is a square matrix of the order of *2N – i*, where *i* is the number of the row under consideration.

$$X_1 = H(1,1) \tag{26}$$

$$Y_1(j) = H(1, j+1) \tag{27}$$

$$Z_1(j,k) = H(j+1, k+1) \tag{28}$$

These are the initial quantities, which are then used in the following recursion relations

$$X_i = Z_{i-1}(1,1) - Y_{i-1}^2(1)/X_{i-1} \qquad i = 2,\ldots\ldots 2N \tag{29}$$

$$Y_i(j) = Z_{i-1}(1, j+1) - Y_{i-1}(1)Y_{i-1}'(j+1)/X_{i-1} \qquad j = 1,2,\ldots\ldots 2N - i \tag{30}$$

$$Z_i(j,k) = Z_{i-1}(j+1,k+1) - Y_{i-1}'(j+1)Y_{i-1}(k+1)/X_{i-1} \qquad j,k = 1,2,\ldots\ldots 2N - i \tag{31}$$

In the above equations, X_i is of particular interest because simply by counting the number of negative X_i (negative factors) as mentioned above, the number of eigenvalues λ_i can be determined. Thus by counting the number of negative *Xi* as a function of λ, one can construct the cumulative density of states (DOS) of any copolymer chain.

Suggested Reading:

1. Andre, J.M.,J.Delhalle and J.L.Bredas, Quantum Chemistry Aided Design of Organic Polymers, World Scientific, Singapore,1991

2. Ladik, J., Quantum Theory of Polymers as Solids, Plenum Press ,New York,1988

3. Bakhshi A.K., Investigation of Electronic Conduction in Proteins and DNA, Progress in Biophysical Molecular Biology 61(1994),187

4. Bakhshi A.K.,Quantum theory of Organic Polymers, Journal of Scientific and Industrial Research 52,407 (1993)

5. Bakhshi A.K., Electronic Structure of Conducting Polymers, Annual Reports on the Progress of Chemistry, Royal Society of Chemistry Section – C, Vol-89,147(1992)

6. Bakhshi A.K.,One Electron Approximation in Quantum Chemistry, Application to polymers, Chemistry Education 9(1),26(1992)

7. Duke B.J & Brian O'Leary, The Band Structure of Polymers, Journal of Chemical Education, Vol 65(4) April 1988

8.Levine,I.N., Allyn & Bacon, Quantum Chemistry 3rd edition, Newton ,MA (1983)

9.Mc Quarrie Quantum Chemistry,University Science (1983)

10.Atkins P.W. Molecular Quantum Chemistry, 2nd edition,, Oxford University,New York (1983)

11. Richards W.G. & J.A.Horsley, ab initio Molecular Orbital calculations for Chemists, Clarendon Press , Oxford - 1970