HOPPING CONDUCTION IN DISORDERED POLYPEPTIDE CHAINS

A. K. BAKHSHI
Department of Chemistry, ARSD College, (University of Delhi), New Delhi 110 021, India.

ABSTRACT

Recent results of the investigation of hopping conduction in disordered polypeptide chains are reviewed. The electronic density of states of multicomponent polypeptide chains has been determined using the theory of disordered systems. Aperiodic chains are found to have larger regions of allowed energy states with fewer gaps in between than the corresponding periodic chains. Due to the large values of the energy gap, both periodic and aperiodic chains are predicted to be insulators in their intrinsic state. To explore the possibility of extrinsic conduction, the localization properties (Anderson localization) of the lowest unoccupied energy levels of the aperiodic polypeptide chain have been investigated using inverse iteration technique. The results indicate these states to be highly localized, thereby making charge transport through hopping mechanism rather probable in these chains. Using a hopping model and assuming charge transfer from DNA to the polypeptide chains, the hopping frequencies have been calculated for the aperiodic polypeptide chains and the results are found to compare very well with those for amorphous semiconductors. Using the results of hopping frequencies, the possibilities for calculating frequency dependence of a.c. conductivity for aperiodic polypeptide chains on the basis of continuous time random walk and coherent medium approximation methods are also discussed.

INTRODUCTION

THE question of the possibility of electronic conduction in proteins (and DNA) has remained unsettled since Szent-Györgyi[1] postulated in 1941 that various biological phenomena can be explained on the basis of the fact that proteins (and DNA) become conductors, rather than insulators, of electricity under certain conditions. He also emphasized[2] that easy energy and charge transport in DNA and proteins are necessary for normal cell functioning. He pointed out that if the flow of electric charges in these macromolecules is hindered it can lead to the cancerous state[2]. Since that time, there have been numerous theoretical and experimental investigations aimed at the electronic structure of proteins and to explain the possible pathways for electron delocalization in these chains. The earlier conductivity measurements on proteins[3,4] showed a weak semiconductivity in the dark which is possibly (but not necessarily) due to electron transport. Since the materials used in these studies were native proteins with an unknown amount of inorganic and organic impurities, it was not possible to interpret these experimental results correctly. The same is true for the transport studies carried out on proteins[5,6]. Apart from these studies, the existence of electronic conduction in proteins is also indicated by electron spin resonance[7], pulse radiolysis[8] and flash photolysis[9] studies. There is also evidence to suggest that the electrical properties of proteins may be involved in preventing the initiation of adverse effects on blood components and coagulation[10,11] and in their various other biological functions[12–15].

The quantum-mechanical investigation of the electronic structure and conduction properties of proteins is a formidable task because of the complexity of these biopolymers. Proteins consist of one or more polypeptide chains that for parts of their lengths can be folded in an apparently random way or form regular β-pleated sheets or α-helical structures. A polypeptide chain is made up from 20 different amino acid residues and the sequence of these residues, is random. The sequence of amino acids in a large number of proteins is known, though the conformation of only a few smaller protein molecules has been determined with the aid of X-ray diffraction. Further, under biological conditions, there are ions and water molecules, which make the determination of the electronic structure of proteins even more difficult. In view of all this it is not possible to determine the electronic structure of proteins and investigate electronic conduction in them in one step. One has,

therefore, to proceed step-wise using a combination of various techniques with rather large-scale computations.

As a first step, the calculations have been performed for periodic models of proteins using both *ab initio* and semi-empirical crystal orbital methods. The band structure calculations have been performed for two possible pathways for electron delocalization in proteins: (i) along hydrogen-bonded network[16–25] –C=O . . . H–N–C=O . . . H–N, which runs perpendicular to α-helical and the antiparallel β-pleated sheet structures of proteins (figure 1), and (ii) along the main polypeptide chain[26–33]. In one of the subsequent calculations[34], interactions along both main polypeptide chain and along hydrogen-bonded network have been simultaneously taken into account and the results show that the most favourable pathway of electronic transport in proteins is the main polypeptide chain rather than the hydrogen-bonded π-electron network.

Recently[35] we have performed band structure calculations for all the 20 homopolypeptides on the basis of *ab initio* Hartree–Fock LCAO SCF crystal orbital method[36,37] using Clementi's minimal basis set[38]. The secondary structure of the elementary unit cell has been taken to be anti-parallel β-pleated sheet structure[39], the exception being polyproline, for which the structural parameters of poly-L-proline I and II have been applied[40]. The energy gap values of these homopolypeptides are found to range from 8.329 eV [poly (lys)] to 15.776 eV [poly(gly)]. These large values of the energy gap, though obtained using minimal basis set and without considering correlation effects, suggest that homopolypeptides in their intrinsic state are expected to be insulators. Similar conclusions are obtained in the case of polydipeptides in both α-helical and β-pleated sheet configurations. The effect of water and ions on the band structure of periodic α-helical[41] and β-pleated sheet[42] polypeptides has also been the subject of recent investigations and the results show that changes in the band gap values and band widths in the presence of water and ions are too small to change conduction properties significantly.

As a next step towards more realistic models of proteins, aperiodicity in proteins has been treated using the theory of disordered systems. The electronic density of states (DOS) of 4-, 5- and 6-component aperiodic polypeptide chains has been determined[43,44] using *ab initio* matrix block negative factor counting technique and the possibilities of electronic conduction in these aperiodic chains have been investigated. This study involves three steps: (i) determination of electronic DOS of aperiodic polypeptide chains, (ii) investigation of localization properties of the wave functions, (iii) investigation of hopping conduction in aperiodic polypeptide chains.

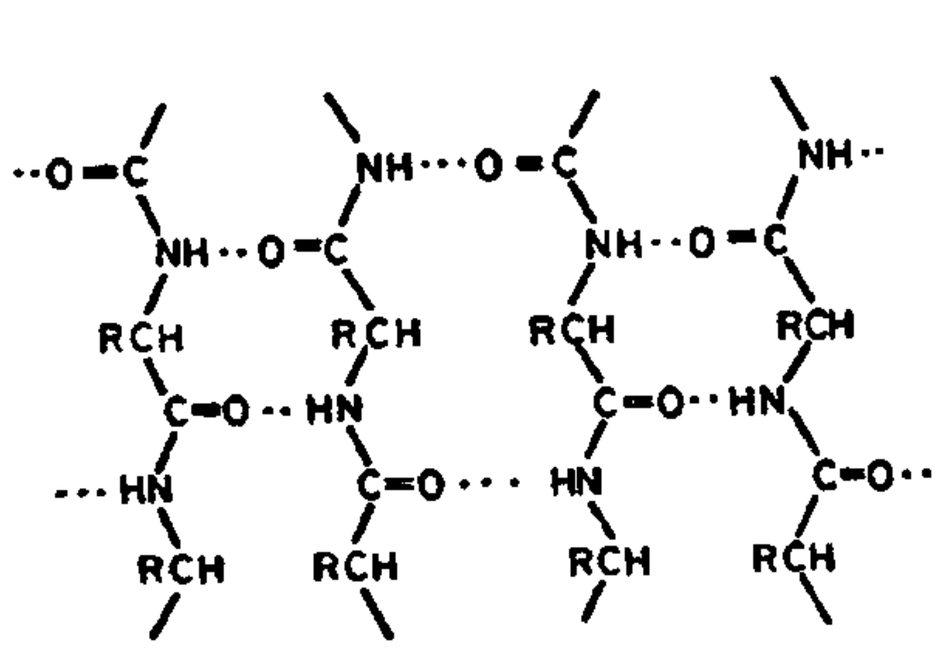

Figure 1. The antiparallel β-pleated polypeptide structure.

DETERMINATION OF ELECTRONIC DOS OF APERIODIC POLYPEPTIDE CHAINS

Matrix block negative factor counting technique

Aperiodic proteins are too large to be treated by direct SCF method. Under these circumstances, the electronic DOS of quasi-one-dimensional aperiodic protein chains can be determined using negative factor counting (NFC) technique based on Dean's negative energy eigenvalue theorem[45]. Dean's method was first used by Pumpernick *et al*[46] to determine the electronic structure of a bundle of short disordered alloy chains. Seel[47] used the simple tight-binding NFC method to determine the DOS of valence bonds of binary glycine–alanine chains on the basis of MINDO results for homopolypeptides. Using the more sophisticated matrix block NFC method, Day *et al*[48] performed model calculations on two-component nucleotide base stacks and on three-component (glycine, alanine, serine) polypeptide chains.

The NFC method can be applied in two ways: (i) simple NFC method, which assumes one orbital per unit of the chain and by which one obtains the DOS for a single band at a time, and (ii) matrix block NFC method, which is more sophisticated and can be applied to the case of any number of orbitals per unit of the chain. This method gives the total DOS coming from all the bands (both valence and conduction bands). In this method, in order to determine the electronic DOS of a multicomponent

quasi-one-dimensional polypeptide chain consisting of N units, one writes the secular determinant

$$|M(\lambda)| = |F - \lambda S|$$

$$= \begin{bmatrix} A_1 - \lambda S_1 & B_{1,2} - \lambda Q_{1,2} & 0 \ldots\ldots 0 \\ B_{1,2}^T - \lambda Q_{1,2}^T & A_2 - \lambda S_2 & B_{2,3} - \lambda Q_{2,3} \ldots 0 \\ 0 & \ddots & \vdots \\ \vdots & & \vdots \\ 0 \ldots\ldots\ldots\ldots\ldots\ldots & & A_N - \lambda S_N \end{bmatrix} = 0. \quad (1)$$

The determinant is triblock diagonal when only first neighbour interaction approximation is taken into account. Here A_i and $B_{i,i+1}$ are the diagonal and off-diagonal blocks of the Fock matrix and S_i and $Q_{i,i+1}$ are the corresponding blocks of the overlap matrix. The superscript T denotes the transpose of the matrix block. It can be shown that (1) can be brought into the form

$$|M(\lambda)| = \det S \,.\, \det(\bar{F} - \lambda 1)$$

$$= \left(\prod_{i=1}^{n} s_i \right) \prod_{j=1}^{n} (\lambda_j - \lambda), \quad (2)$$

where $\bar{F} = S^{-\frac{1}{2}} F S^{\frac{1}{2}}$. The s_i are the eigenvalues of S and the λ_j are the roots of the generalized eigenvalue equation

$$Fc_j = \lambda_j S c_j. \quad (3)$$

The triblock diagonal determinant $|F - \lambda S|$ can be brought into a didiagonal form by applying the successive Gaussian elimination procedure. One then obtains for the new diagonal blocks

$$u_i(\lambda) = A_i - \lambda S_i - (B_{i,i+1}^T - \lambda Q_{i,i+1}^T) U_{i-1}^{-1} \times (B_{i,i+1} - \lambda Q_{i,i+1}), \quad (4)$$

with

$$U_1(\lambda) = A_1 - \lambda S_1. \quad (5)$$

Now if $u_{ik}(\lambda)$ stands for the kth eigenvalue of diagonal matrix block $U_i(\lambda)$ defined by (4) and l_i is its dimension, then

$$|M(\lambda)| = |F - \lambda S| = \left(\prod_{i=1}^{n} s_i \right) \left(\prod_{j=1}^{n} (\lambda_j - \lambda) \right)$$

$$= \prod_{i=1}^{N} \left(\prod_{k=1}^{l_i} u_{ik}(\lambda) \right), \quad n = \sum_{i=1}^{N} l_i. \quad (6)$$

The matrices $U_i(\lambda)$ can be easily diagonalized for a given value of λ. The number of negative $u_{ik}(\lambda)$ values has to be equal to the number of those eigenvalues λ_j that are smaller than the chosen λ value. Thus by changing λ, the whole spectrum can be scanned again and in this way the total DOS of the aperiodic chain can be obtained for all the bands to any desired accuracy.

For the application of the matrix block NFC method in its *ab initio* form one requires, as a first step, the various Fock and overlap matrix blocks to construct the secular determinant. These matrix blocks are obtained from the corresponding cluster studies (a cluster in the first neighbour interaction approximation consists of two interacting molecules) using the *ab initio* Hartree–Fock SCF LCAO method. For a disordered chain containing P different components, one needs to perform P^2 cluster calculations (in the case of a binary chain of two components A and B, the four clusters AA, AB, BA and BB must be studied). From the results of a cluster, say AB (where AB stands for the helix direction $\overset{B}{\uparrow}_{A}$), the diagonal Fock and overlap matrix blocks representing interactions within unit A and the off-diagonal Fock and overlap matrix blocks representing interaction of molecule A with molecule B are extracted. Thus four matrix blocks are used from each cluster result. To be able to represent various orientations of the β-pleated sheet structure of the aperiodic polypeptide chains (helical angle 180°), the elements of the four matrix blocks obtained from each cluster must be rotated through 180°, thereby obtaining in all eight matrix blocks per cluster. Using these various matrix blocks one can construct the secular determinant for any periodic or aperiodic polypeptide chain and then solve it to obtain the electronic DOS.

The electronic DOS

The electronic DOS of 4-, 5- and 6-component periodic and aperiodic polypeptide chains in anti-parallel β-pleated sheet configuration have been recently determined[43,44] on the basis of *ab initio* matrix block NFC method. The six amino acid residues chosen for the study are glycine (gly), serine (ser), cysteine (cys), asparagine (asn), histidine (his) and aspartic acid (asp) in its neutral form and the necessary 36 clusters have been studied on the basis of *ab initio* Hartree-Fock SCF LCAO method using Clementi's minimal basis set[38]. In all the calculations of the DOS, a chain length of 300 units and an energy grid of 0.002 have been used consistently. The electronic DOS distributions for the conduction band regions of 4- and 6-component periodic

polypeptide chains are shown in figures 2 and 3 respectively. These results are for the sequences poly(ser-gly-cys-asn) and poly(ser-gly-cys-asn-his-asp) and in each chain the concentrations of all the components are equal. As is evident from these figures, for both chains, the conduction band regions consist of well-separated, very narrow peaks, most of them being of equal intensity. Similar curves were obtained for other periodic polypeptide chains and for the valence band regions and therefore we do not show them here. The fundamental band gap for all these multicomponent periodic polypeptide chains has been found to be very large (>13 eV) and therefore these chains are expected to be insulators. Further, since the peaks are very narrow, these chains are not likely to become conducting on doping with electron acceptors or electron donors.

In figures 4 and 5 are shown the DOS curves for the conduction band region of aperiodic 4- and 6-component polypeptide chains. In comparison with the corresponding curves for the periodic chains, the

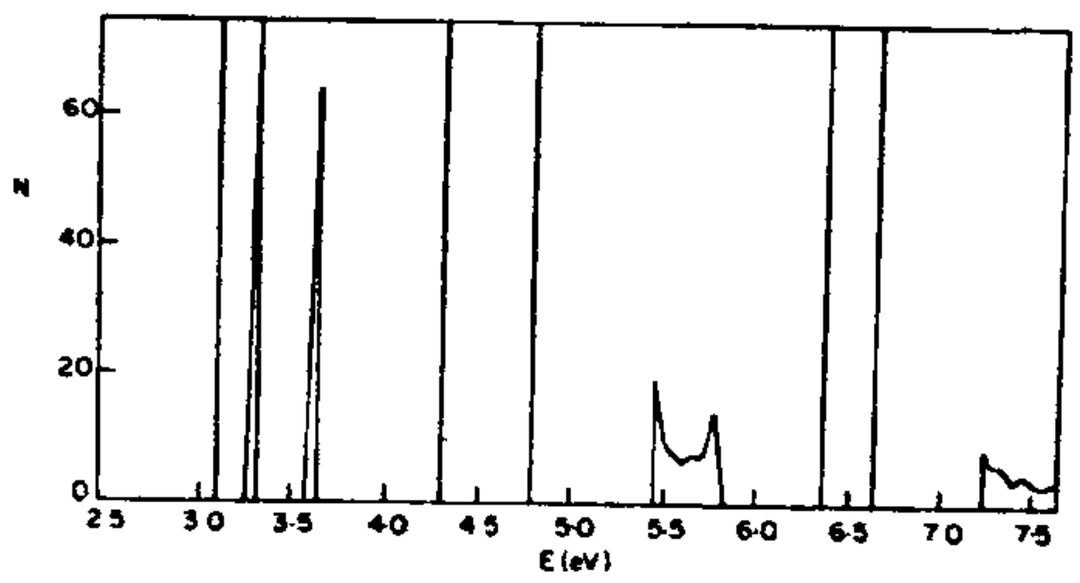

Figure 2. The electronic DOS distribution for the conduction band region of the periodic poly(ser-gly-cys-asn) chain.

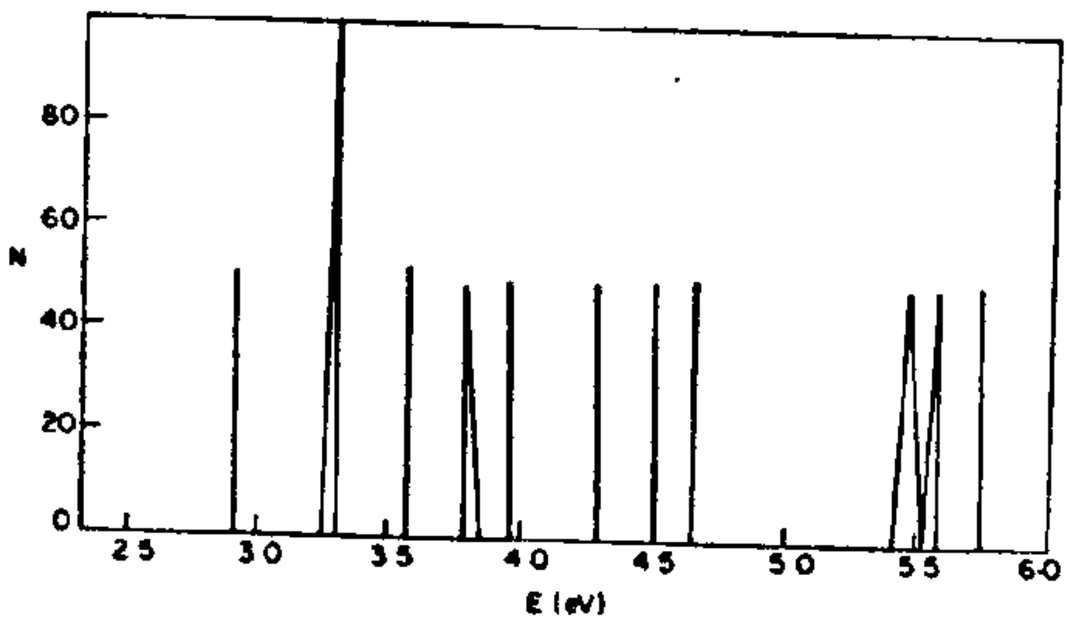

Figure 3. The electronic DOS distribution for the conduction band region of the periodic poly(ser-gly-cys-asn-his-asp) chain.

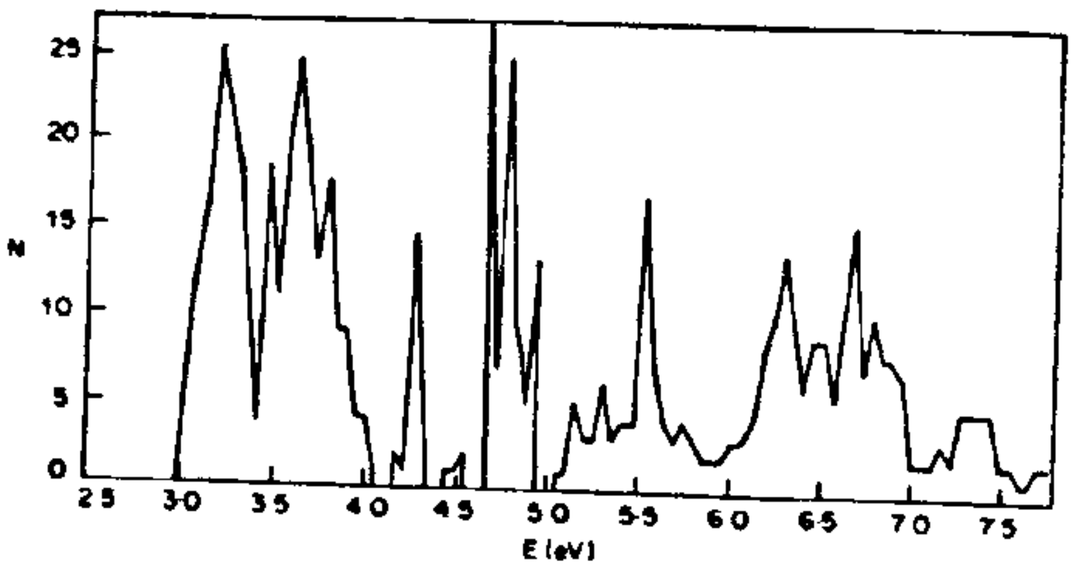

Figure 4. The electronic DOS distribution for the conduction band region of the aperiodic poly(ser, gly, cys, asn) chain in the composition (1:1:1:1).

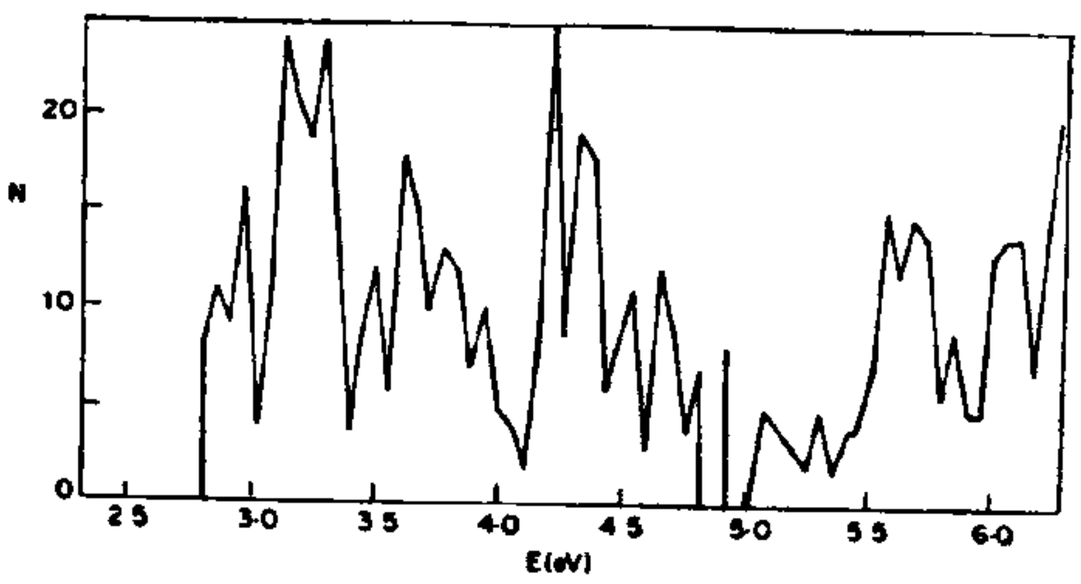

Figure 5. The electronic DOS distribution for the conduction band region of the aperiodic poly(ser, gly, cys, asn, his, asp) chain in the composition (1:1:1:1:1:1) (sequence 1).

DOS curves of aperiodic chains are strikingly different and consist of very broad regions of allowed energy states with a few small gaps in between. As a result of this broadening, the aperiodic chains have somewhat smaller band gaps than the corresponding periodic chains, though the value of this gap is still too large to permit semiconduction at physiological temperature. The broadening observed in the case of aperiodic chains is due to the continuously changing environment of a unit in the random sequence in contrast to the periodic sequence where the first neighbour of a unit throughout the chain remains the same (this broadening is also explicable on the basis of single- and many-environment molecular exciton theory). Similar broadening has been observed in the case of single-stranded aperiodic DNA base stacks[49], random copolymers of heterocyclic compounds[50], and random copolymers of acetylene with its nitrogen-containing analogues[51] and with its monofluoro and difluoro derivatives[52].

The effect of changing the sequence of units in both periodic and aperiodic chains has been investigated in the case of 6-component peptide chains. The DOS of periodic poly(ser-asn-asp-cys-gly-his) for the conduction band region are shown in figure 6. In comparison with the results for periodic poly(ser-gly-cys-asn-his-asp) (figure 3), it can be seen that the energy positions of the peaks are slightly shifted owing to the change in the environment of the units in the chain. In the case of two different aperiodic chains (figures 5 and 7), on the other hand, one notices that the two curves are very similar, except for very small differences. The reason why comparatively short chains of 300 units should be representative models lies in the strong localization of the electronic states. These localized states are relatively little affected by chain length. The requirement that chain length should meet is that the statistically possible different cluster arrangements should occur in the representative chain.

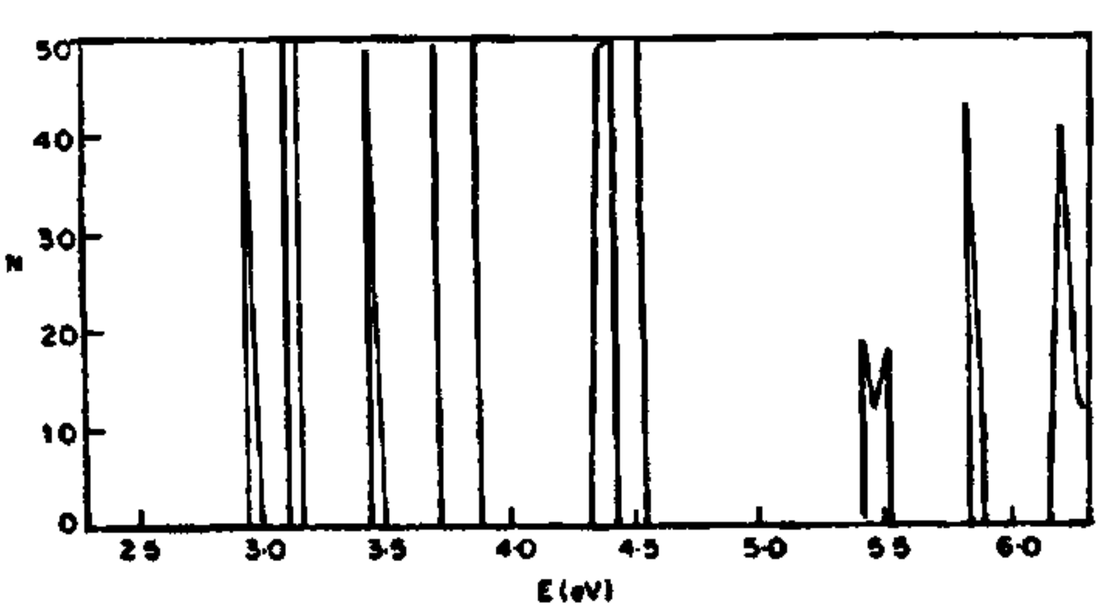

Figure 6. The electronic DOS distribution for the conduction band region of the periodic poly(ser-asn-asp-cys-gly-his) chain.

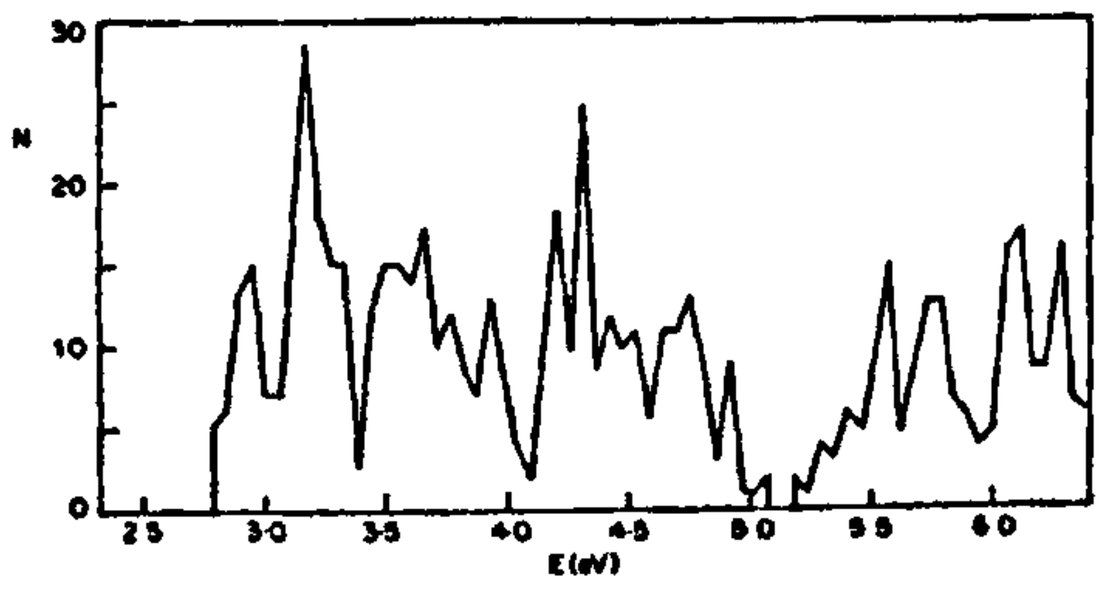

Figure 7. The electronic DOS distribution for the conduction band region of the aperiodic poly(ser, gly, cys, asn, his, asp) chain in the composition (1:1:1:1:1:1) (sequence 2).

INVESTIGATION OF LOCALIZATION PROPERTIES OF THE WAVE FUNCTIONS

To explore the possibility of extrinsic conductivity in aperiodic polypeptide chains, one needs to investigate the localization properties of one-electron wave functions corresponding to different energy levels in these chains. It is well known that any kind of disorder gives rise to localization of wave functions in one-dimensional systems[53,54]. In the case of quasi-one-dimensional multicomponent aperiodic polypeptide chains, the source of disorder is the random distribution of components in these chains and therefore it is expected that the corresponding wave functions are localized on the units of the chain. The localization properties of the wave functions can be investigated using inverse iteration technique[55,56] and the results of this study are important in determining whether the given polypeptide chain, even if it contains charge carriers, is able to show coherent Bloch-type conduction or only charge transport through hopping. For the investigation of charge transport phenomena in aperiodic polypeptide chains, the upper part of the valence band region or the lower part of the conduction band region are the physically interesting regions if one assumes a charge transfer *in vivo* due to the interaction of proteins with DNA or *in vitro* with electron acceptors or electron donors. The possibility of this type of charge transfer has also been suggested by Szent-Györgyi[57].

In the inverse iteration technique, one solves the trial equation.

$$(F-\lambda_a S)\, b_i = p \tag{7}$$

for the eigenvector b_i corresponding to the energy value λ_a. The matrix $(F-\lambda_a S)$ is a symmetric matrix and has a banded structure and it is therefore possible to transform it into a triangular one with the help of Gaussian elimination. One thus obtains from (7),

$$(F-\lambda_a S)b_i=(U^T D U)\, b_i = p, \tag{8}$$

where U is an upper triangular matrix (U^T is its transpose) with diagonal elements equal to one, and D is a diagonal matrix. Equation (8) can be split into three equations

$$U b_i = x \tag{9a}$$

$$D x = y \tag{9b}$$

$$U^T y = p. \tag{9c}$$

Assuming p to be a unit vector, one can solve (9c)

for y. Substituting it into (9b) one obtains x. Finally by putting x into (9a) one can compute b. Next one substitutes b_i obtained in this way for p in (9c) and repeats the iteration. One has to repeat this procedure till convergence is achieved (usually three or four iterations are sufficient).

The results of the study of the localization properties of the wave functions for the conduction band region of aperiodic 4-component (figure 4) and 6-component (figure 5) polypeptide chains calculated[43,44] using the inverse iteration technique are given in tables 1 and 2 respectively. Each table contains for the first 25 states the corresponding energies, the largest LCAO coefficient of the wave function, the corresponding number of the unit (between 1 and 300) on which the wave function is localized, and the amino acid residue in that unit. It is evident from these tables that for both chains the one-electron wave functions are highly localized, making charge transport through hopping rather probable.

Assuming a charge transfer of 0.1 e per unit of the aperiodic chain (which, *in vivo*, is rather probable), the Fermi level for the two chains lies at 3.06391 eV and 2.8090766 eV respectively (eigenvalues No. 15 in tables 1 and 2). It can also be seen from the tables that quite a few first-neighbour and second-neighbour excitations are possible in both chains. In the case of the 4-component chain, for example, the following excitations between first neighbours can be found (the numbers of the participating units are given in parentheses): from level 7 to level 9 (192, 193), from 8 to 9 (192, 193), from 27 to 31 and 32 (98, 97), from 16 to 51 (149, 150), from 12 to 37 (193, 194), etc. Possible excitations between second-neighbour pairs are excitations from level 13 to level 17 (249, 251) and from 26 to 37 (192, 194). Besides these, there are possible excitations within the same unit. These excitations can help to promote an electron to a higher level from which it can be excited in a subsequent step to an orbital localized on a different site. Likewise many such excitations are possible in the case of the 6-component chain

Table 1 *Orbital energy E_i, the largest LCAO coefficient C_{imax} of the one-electron wave function, the corresponding number of the unit N_{unit} (between 1 and 300) on which the wave function is localized, and the type (amino acid residue) of the unit for the lowest 25 unoccupied states of aperiodic poly(ser, gly, cys, asn) chain whose DOS distribution is shown in figure 4*

i	E_i(eV)	C_{imax}	N_{unit}	Type
1	2.98441	0.939	252	ser
2	2.99009	0.755	207	asn
3	2.99577	0.687	101	asn
4	3.00145	0.797	63	ser
5	3.00713	0.871	63	ser
6	3.01280	0.902	24	ser
7	3.01848	0.693	192	gly
8	3.02416	0.890	192	gly
9	3.02984	0.802	193	gly
10	3.03552	0.873	108	gly
11	3.04119	0.792	227	asn
12	3.04688	0.896	193	gly
13	3.05255	0.893	249	ser
14	3.05823	0.775	210	ser
15	3.06391	1.230	81	asn
16	3.06959	0.762	149	gly
17	3.07527	0.647	251	asn
18	3.08085	0.901	108	gly
19	3.08662	0.708	63	ser
20	3.09231	0.902	108	gly
21	3.09799	0.901	108	gly
22	3.10366	0.749	134	asn
23	3.10934	0.795	192	gly
24	3.11502	0.904	192	gly
25	3.12070	0.905	192	gly

Table 2 *Orbital energy E_i, the largest LCAO coefficient C_{imax} of the one-electron wave function, the corresponding number of the unit N_{unit} (between 1 and 300) on which the wave function is localized, and the type (amino acid residue) of the unit for the lowest 25 unoccupied states of aperiodic poly(ser, gly, cys, asn, his, asp) chain whose DOS distribution is shown in figure 5*

i	E_i(eV)	C_{imax}	N_{unit}	Type
1	2.80687468	0.787	256	asn
2	2.80703196	0.856	264	asn
3	2.80718924	0.807	213	asn
4	2.80734652	0.680	166	asp
5	2.8075038	0.439	214	asn
6	2.80766108	0.863	26	asn
7	2.80781836	0.766	267	asn
8	2.80797564	0.636	285	asn
9	2.80813292	0.818	27	asn
10	2.80829020	0.950	242	ser
11	2.80844748	0.786	165	his
12	2.80860476	0.632	21	his
13	2.80876204	0.909	4	his
14	2.80891932	0.656	180	asn
15	2.80907660	0.677	299	ser
16	2.80923388	0.638	57	his
17	2.80939116	0.999	75	ser
18	2.80954844	0.967	242	ser
19	2.80970572	0.674	212	ser
20	2.8098630	0.635	212	ser
21	2.81002028	0.952	12	ser
22	2.81017756	0.684	162	ser
23	2.81033484	0.735	162	ser
24	2.81049212	0.485	198	ser
25	2.8106494	0.920	160	ser

also, and through hopping between them, it should be possible to transport charge in these chains.

INVESTIGATION OF HOPPING CONDUCTION IN APERIODIC POLYPEPTIDE CHAINS

Calculation of hopping frequencies

To describe hopping quantitatively one must know how the electron on one centre communicates with another centre. For this one must know the electronic wave functions and from them calculate hopping rates between typical centres. To calculate hopping frequencies or primary jump rates a hopping model is considered. In this model conduction is believed to take place through hopping between localized states with energies near the Fermi energy. The primary jump rate $W_{l,m}$ that is, the number of jumps from one localized state l to a given different state m per unit time of the phonon-assisted hopping at a given temperature T depends upon (i) the square of the overlap integral between the two exponentially localized wave functions at sites l and m, and (ii) the energy $\Delta E_{l,m}$ between the two sites, and is given to a good approximation[58-60] by

$$W_{l,m} = \nu_{\text{phonon}} [\exp(-\alpha|r_l - r_m|)]^2 \times \exp(-\Delta E_{l,m}/kT), \quad (10)$$

where $\Delta E_{l,m} = E_m - E_l$, r_l and E_l are the position and energy of the electron localized at site l, and r_m and E_m the position and energy of the electron localized at site m.

If an LCAO expression is used for the overlap integral and approximated by the dominant terms, then one obtains

$$W_{l,m} = \nu_{\text{phonon}} (\sum_{r,s} C_{l,r} C_{m,s} \langle \chi_r | \chi_s \rangle)^2 \times \exp(-\Delta E_{l,m}/kT), \quad (11)$$

where $C_{l,r}$ and $C_{m,s}$ are the dominant LCAO coefficients of the wave functions $\psi_l(\psi_m)$ which are localized at centres with energies E_l and E_m respectively.

Using the data given in table 1 and taking the phonon frequency ν_{phonon} for proteins to be $10^{-12}\,s^{-1}$ corresponding to the most acoustical modes[61], the primary jump rates have been calculated from (11). The results are given in table 3. The first two values refer to hopping between first neighbours and are 5×10^7 and $7 \times 10^8\,s^{-1}$ respectively. As the characteristic value for second-neighbour hopping, 10^5 jumps per second is obtained. The last three quantities give primary jump rates between orbitals localized in the same unit. The primary jump rates for these local excitations are between 7×10^{11} and $9 \times 10^{11}\,s^{-1}$—the small differences are due to differences in the overlap between the initial and final states. If a more realistic estimate of average excitation energy is taken into consideration, then the Boltzmann factor decreases by about 10^{-1} and therefore the physically most interesting first and third $W_{l,m}$ values in the table have to be decreased by this value. Comparison of these hopping jump rates for proteins calculated using *ab initio* one-electron wave functions with the ones obtained for non-crystalline solids[58,62] shows that the agreement between the two values is very good.

Table 3 *Characteristic primary jump rates $W_{l,m}$ (in s^{-1}) calculated from equation (11) for the aperiodic poly(ser, gly, cys, asn) chain (corresponding to its DOS distribution given in figure 4)*

l	m	i	j	$\Delta E_{l,m}$	$W_{l,m}$
193	192	12	23	0.062	5×10^7
192	193	8	9	0.006	7×10^8
192	194	26	37	0.062	1×10^5
192	192	7	8	0.006	7×10^{11}
108	108	18	20	0.011	7×10^{11}
108	108	20	21	0.006	9×10^{11}

$W_{l,m}$ are given for pairs of localization sites l and m, which have numbers of energy levels i and j; $\Delta E_{l,m}$ (in eV) is the energy difference entering the Boltzmann factor; ν_{phonon} was chosen to be $10^{-12}\,s^{-1}$; $kT = 2.67 \times 10^{-2}$ eV for $T = 310$ K.

Calculation of a.c. hopping conductivity

From the hopping jump rates calculated above, one can calculate the frequency dependence of a.c. hopping conductivity in aperiodic polypeptide chains. Since the hopping rate is a sensitive function of both the local separation and local energy fluctuation, the hopping transport will depend critically on the details of the statistical distribution of these parameters. Therefore even given a knowledge of the nature of the localized centres and their distribution, one needs to deal with the difficulties associated with the stochastic aspects of the site-to-site transport. To deal with the stochastic transport problem in the case of aperiodic polypeptide chains, it is possible to use the approach based on continuous time random walk[63] and coherent medium approximation[64] and thus calculate the frequency dependence of hopping

conductivity in these chains. There have already been several investigations[63-72] of hopping conduction in random one-dimensional systems using this scheme.

In this scheme one starts with the generalized Einstein relation for a.c. hopping conductivity

$$\sigma(\omega)=\frac{ne^2}{kT}D(\omega), \tag{12}$$

where n is the number density of carriers, e the charge of a carrier, ω the frequency, k the Boltzmann constant and T the absolute temperature. The diffusion constant $D(\omega)$ can be written in terms of the Laplace transform of the transition probability $P(x_m,t|x_0,0)$ as

$$D(\omega)=\frac{-\omega^2}{2}\sum_m\langle(x_m-x_0)^2\,\tilde{P}(x_m,i\omega|x_0)\rangle, \tag{13}$$

where

$$\tilde{P}(x_m,i\omega|x_0)=\int_0^\infty e^{-ut}\,P(x_m,t|x_0,0)\,dt, \quad (u=i\omega). \tag{14}$$

The transition probability $P(x_m,t|x_0,0)$ denotes the probability of finding a carrier at the mth localized centre x_m at time t if it was at x_0 at time $t=0$ and represents an ensemble average over the distribution of random quantities in the problem.

As is evident from the above equations, the key quantity to determine in a calculation of a.c. conductivity $\sigma(\omega)$ is the transition probability. It is generally difficult to evaluate it on the basis of first principles and therefore it is assumed to obey the random walk equation[63].

$$\frac{\delta P(x_m,t|x_0,0)}{\delta t}=-\Gamma_m P(x_m,t|x_0,0)+\sum_{l\neq m}W_{m,l}\,P(x_l,t|x_0,0), \tag{15}$$

where $\Gamma_m=\sum_l W_{l,m}$ and $W_{l,m}$ denotes the hopping frequency or jump rate of a carrier from localized centre m to l. For simplicity the jump rates are assumed to satisfy the condition $W_{l,m}=W_{m,l}$.

Equation (15) can be solved using the coherent medium approximation[64]. In this approximation the average transition probability is replaced by that of an average medium in which all jump rates are equal to the coherent jump rate $W_c(u)$ where u is the Laplace transform parameter introduced in (14). The explicit condition that determines the coherent jump rate can be shown[64] to be

$$\frac{1-u\bar{P}(x_0,u|x_0)}{2W_c(u)}\equiv\frac{1}{\xi+2W_c(u)}=\int\frac{P(W_{x,x+1})}{\xi+2W_{x,x+1}}dW_{x,x+1}, \tag{16}$$

where $\bar{P}(x_m,u|x_o)$ is the transition probability of the coherent medium and $P(W_{x,x+1})$ is the distribution function of the jump rates. In terms of the coherent jump rate $W_c(u)$ the a.c. conductivity $\sigma(\omega)$ is expressed as

$$\sigma(\omega)=\frac{ne^2a^2}{kT}W_c(i\omega), \quad (\because u=i\omega), \tag{17}$$

where a is the lattice constant of the chain.

ACKNOWLEDGEMENTS

The author thanks the Deutsche Akademischen Austauschdienst (DAAD) for the grant of a fellowship which enabled him to work in Erlangen, West Germany; Prof. J. Ladik for introducing him to quantum chemistry of polymers; and Prof. E. Clementi (IBM, Kingston) for his interest and support for this work. The author acknowledges his collaboration with Prof. P. Otto and Dr M. Seel. He also thanks IBM Kingston, IBM Germany, IBM Italy and Kraftwerk Union AG for providing free computer time. Financial support from the National Foundation for Cancer Research, USA, and from the Fond der Chemischen Industrie, West Germany, are also gratefully acknowledged.

19 February 1988; Revised 16 September 1988

1. Szent-Györgyi, A., *Nature (London)*, 1941, **148**, 157; *Science*, 1941, **93**, 609.
2. Szent-Györgyi, A., *Bioenergetics*, Academic Press, New York, 1957; *Introduction to submolecular biology*, Academic Press, New York, 1960; *Bioenergitics*, Academic Press, New York, 1968.
3. Eley, D. D., Parfitt, G. P., Perry, M. B. and Taytum, D. H., *Trans. Faraday Soc.*, 1953, **49**, 79.
4. Eley, D. D. and Spivey, D. J., *Trans. Faraday Soc.*, 1960, **56**, 1432; 1962, **58**, 411.
5. Pening, R. and Szent-Györgyi, A., *Proc. Natl. Acad. Sci. USA*, 1977, **74**, 226.
6. Bone, S., Levis, T. F., Pething, R. and Szent-Györgyi, A., *Proc. Natl. Acad. Sci. USA*, 1978, **75**, 315.

7. Gordy, W., Ard, W. B. and Shields, H., *Proc. Natl. Acad. Sci. USA*, 1955, **41**, 983.
8. Adam, G. E., Wilson, R. L., Aldrich, J. L. and Cundall, R. B., *Int. J. Radiat. Biol.*, 1969, **16**, 333.
9. Grossweiner, L. I. and Usui, Y., *Photochem. Photobiol.*, 1971, **13**, 195.
10. Bruke, S. D., *Nature* (*London*), 1973, **243**, 416.
11. Bruke, S. D., *Polymer*, 1975, **16**, 25.
12. Eden, J., Gascoyne, P. R. C. and Pething, R., *J. Chem. Soc. Faraday Trans.*, 1980, **176**, 426.
13. Bone, S., Eden, J. and Pething, R., *Int. J. Quantum Chem.*, 1981, **QBS8**, 307.
14. Behl, J., Bone, S., Morgan, H. and Pething, R., *Int. J. Quantum Chem.*, 1982, **QBS9**, 367.
15. Bone, S. and Pething, R., *Int. J. Quantum Chem.*, 1983, **QBS10**, 133.
16. Coulson, C., private communication.
17. Suard, M., Berthier, G. and Pullman, B., *Biochim, Biophys. Acta*, 1961, **52**, 254.
18. Suard, M., *Biochim. Biophys. Acta*, 1962, **64**, 400.
19. Itoh, R., *Ann. Rep. Res. Gp. Biophys. Jpn.*, 1961, **1**, 11.
20. Ladik, J., *Acta Phys. Acad. Sci. Hungary*, 1963, **15**, 287.
21. Ladik, J., *Nature* (*London*), 1964, **202**, 1208.
22. Yomosa, S., *J. Phys. Soc. Jpn.*, 1963, **18**, 1494.
23. Fujita, H. and Imamura, A., *J. Chem. Phys.*, 1970, **53**, 555.
24. Pullman, A., *C. R. Acad. Sci. Paris*, 1963, **256**, 5435.
25. Suard–Sender, M-, *J. Chim. Phys.*, 1965, **62**, 78.
26. Brillouin, L., In: *Horizons in biochemistry*, (eds.) M. Kasha and B. Pullman, Academic Press, New York, 1962, p. 295.
27. Fujita, H. and Imamura, A., *J. Chem. Phys.*, 1970, **53**, 4555.
28. Beveridge, D. L., Jano, I. and Ladik, J., *J. Chem. Phys.*, 1972, **56**, 4744.
29. Morokuma, K., *Chem. Phys. Lett.*, 1971, **9**, 129.
30. Suhai, S. and Ladik, J., *Int. J. Quantum Chem.*, 1973, **7**, 547.
31. Suhai, S., *Theor. Chim. Acta* (*Berlin*), 1974, **28**, 67.
32. Suhai, S. and Ladik, J., *Acta Chim. Acad. Sci. Hung.*, 1974, **82**, 67.
33. Duke, B. K., Eilers, J. E. and O'Leary, B., *Chem. Phys. Lett.*, 1973, **20**, 459.
34. Suhai, S., *Theor. Chim. Acta*, 1974, **34**, 157; *Biopolymers*, 1974, **13**, 1731.
35. Otto, P., Bakhshi, A. K., Ladik, J., Seel, M. and Chin, S., *Chem. Phys.*, 1986, **108**, 223.
36. Andre, J. M., Gouverneur, L. and Leroy, G., *Int. J. Quantum Chem.*, 1967, **1**, 427, 451.
37. Del Re, G., Ladik, J. and Biczo, G., *Phys. Rev.*, 1967, **155**, 997.
38. Gianolio, L., Pavani, R. and Clementi, E., *Gazz. Chim. Ital*, 1978, **108**, 18.
39. Paling, L., Gory, R. B. and Branson, H. R., *Proc. Natl. Acad. Sci. USA*, 1951, **37**, 205.
40. Sasisekharan, V., *Acta Crystallogr.*, 1959, **12**, 897.
41. Chen, R. S., Liegner, C. M., Otto, P. and Ladik, J., *Acta Biochim. Biophys. Hung.*, 1987, 22, 205.
42. Liegner, C. M., Otto, P., Chen, R. S. and Ladik, J., *Theor. Chim. Acta*, (submitted).
43. Bakhshi, A. K., Ladik, J., Seel, M. and Otto, P., *Chem. Phys.*, 1986, **108**, 233.
44. Bakhshi, A. K., Otto, P. and Ladik, *J. Molec. Struct.* (*Theochem.*), 1988, **180**, 113.
45. Dean, P., *Rev. Mod. Phys.*, 1972, **44**, 122.
46. Pumpernik, D., Borstnik, B., Kertz, M. and Azman, A., *Z. Naturforsch.*, 1977, **A32**, 295.
47. Seel, M., *Chem. Phys.*, 1979, **43**, 103.
48. Day, R. S., Suhai, S. and Ladik, J., *Chem. Phys.*, 1981, **62**, 165; Day, R. S. and Ladik, J., *Int. J. Quantum Chem.*, 1982, **21**, 917.
49. Bakhshi, A. K., Otto, P., Ladik, J. and Seel, M., *Chem. Phys.*, 1986, **108**, 215.
50. Bakhshi, A. K., Ladik, J. and Seel, M., *Phys. Rev.*, 1987, **B35**, 704.
51. Bakhshi, A. K. and Ladik, J., *Solid State Commun.*, 1986, **60**, 316.
52. Bakhshi, A. K., Ladik, J. and Liegner, C. M., *Synth. Metals*, 1987, **20**, 43.
53. Mott, N. F. and Twose, W. D., *Adv. Phys.*, 1961, **10**, 107.
54. Ishii, K., *Prog. Theor. Phys.* (*Suppl.*), 1973, **53**, 77.
55. Wilkinson, J. H., *The algebraic eigenvalue problem*, Clarendon Press, Oxford, 1965.
56. Ladik, J., Seel, M., Otto, P. and Bakhshi, A. K., *Chem. Phys.*, 1986, **108**, 203.
57. Szent-Györgyi, A., *The living state with observations on cancer*, Academic Press, New York, 1972, p. 88.
58. Mott, N. F. and Davis, E. A., In: *Electronic processes in non-gystalume materials*, Clarendon Press, Oxford, 1971.
59. Grunewald, M., Pohlmann, B., Movaghar, B. and Wurtz, D., *Philos. Mag.*, 1984, **B49**, 341.
60. Grunewald, M., Movaghar, B., Pohlmann, B. and Wurtz, D., *Phys. Rev.*, 1985, **32**, 8191.
61. Parak, F., In: *Structure and motion: membranes, nucleic acids and proteins*, (eds) E. Clementi, G. Corongiu, M. H. Sarma and R. H. Sarma, Adenine Press, New York, 1985, p. 243.

62. Silver, M., Schoenherr, G. and Baessler, H., *Phys. Rev. Lett.*, 1982, **481**, 352.
63. Scher, H. and Lax, M., *Phys. Rev.*, 1973, **B7**, 4491, 4502.
64. Odagaki, T. and Lax, M., *Phys. Rev.*, 1981, **B24**, 5284.
65. Bernasconi, J., Schneider, W. R. and Wyss, W., *Z. Phys.*, 1980, **B37**, 175.
66. Bernasconi, J., Beyelder, H. U., Strassler, S. and Alexander, S., *Phys. Rev. Lett.*, 1979, **42**, 819.
67. Richards, P. M., *Phys. Rev.*, 1977, **B16**, 1393.
68. Richards, P. M. and Renken, R. L., *Phys. Rev.*, 1980, **B21**, 3740.
69. Alexander, S., Bernasconi, J., Schneider, W. R. and Orbach, R., *Rev. Mod. Phys.*, 1981, **53**, 175.
70. Odagaki, T. and Lax, M., *Phys. Rev.*, 1982, **B25**, 2301.
71. Odagaki, T. and Lax, M., *Phys. Rev.*, 1982, **B25**, 2307.
72. Odagaki, T. and Lax, M., *Phys. Rev. Lett.*, 1980, **45**, 847.

ANNOUNCEMENTS

SATELLITE SYMPOSIUM ON POLYUNSATURATED FATTY ACIDS AND EICOSANOIDS AND SECOND ANNUAL CONFERENCE OF THE SOCIETY FOR PUFA RESEARCH

The two meetings will be held at the Department of Zoology, Sri Venkateswara University, Tirupati, from **30 October to 1 November 1989**. The satellite symposium follows the International Symposium on Biological Oxidation Systems at the Indian Institute of Science, Bangalore, 23–26 October 1989 (announced in *Current Science* of 20 April 1989). The **programme** will include plenary lectures by some of the scientists who will attend the international symposium and scientific sessions on the following topics: (i) Marine fish fatty acids (W-3 PUFAs) in human health, (ii) PUFAs, free radicals and lipid peroxidation; role of vitamin E and selenium (iii) Eicosanoids of cyclo-oxygenase pathway—prostaglandins, thromboxanes and prostacyclin; (iv) Eicosanoids of lipoxygenase pathway—hydroperoxides (HPETES), leukotrienes and lipoxins, (v) Oxidation of PUFAs via the mono-oxygenase pathway. **Abstracts** (not more than 300 words) of presentations in any of these topics are invited and must be sent **before 20 July** with the registration fee of Rs. 200 in favour of Dr P. Reddanna. Preliminary **registration cards** are available from the Convener. Completed cards must be returned **before 15 June** to Dr P. Reddanna, Convener, Satellite Symposium on PUFAs and Eicosanoids, Department of Zoology, S.V. University, Tirupati 517 502.

THIRTEENTH SCIENTIFIC MEETING OF THE INTERNATIONAL SOCIETY OF HYPERTENSION

The thirteenth scientific meeting of the International Society of Hypertension will be held at Montreal, Canada, from 24 to 29 June 1990. For details write to Dr Shailendra Vajpayee, Indian Society of Hypertension, M. P. Shah Medical College, Jamnagar 361 008.