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The Electronic Structure of Periodic Protein Models

II. Energy Band Structure and Anisotropy of Electrical Conduction in the Parallel-Chain β Conformation of Polyglycine

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The all-valence electron energy band structure has been calculated for β polyglycine in the parallel-chain pleated sheet conformation. The anisotropy of the charge carrier effective masses and mobilities have been investigated. The direction of the polypeptide backbone is found theoretically to be more favourable for electrical conduction than that of the hydrogen bonds.

Key words: Periodic protein models, electronic structure – Polyglycine, parallel-chain β-conformation

Introduction

More than thirty years elapsed since Szent-Györgyi and Laki directed attention to the possibility and significance of semiconductive-type charge and excitation energy transfer in biological macromolecules [1]. Experimental investigations of a considerable number confirmed since then the existence of electronic delocalization in polynucleotides and polypeptides, but the nature of the mechanism of conduction in these systems still constitutes a question to be solved from the theoretical point of view. This is understandable, since in consequence of the extremely complicated geometrical structure of these macromolecules and due to the presence of numerous different interactions, the quantum mechanical calculation of the physical properties (carrier mobility, activation energy of conductivity, etc.), which could help in answering the above question, can be carried out only gradually by using more and more refined models and calculation methods.

In a preceding paper [2] (referred to as Part I of this series) we gave a short review of the calculations performed up till now on the electronic structure of periodic protein models. The basic idea of these theoretical investigations was to build up the polypeptide chain by the regular translation of the peptide unit either along the hydrogen bridges or perpendicular to them and to treat the resulting one-dimensional crystal by solid state physical methods. In Part I we showed that the array of molecules obtained by simultaneous translation of the peptide unit along the above mentioned two directions (called polyformamide network) can be more adequately treated if we take into account interactions along the hydrogen bonds and the main polypeptide chain at the same time. Another model calculation showed [3] that in polypeptides of β conformation

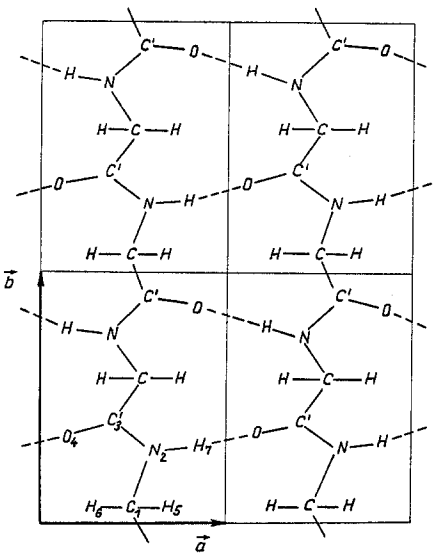

Fig. 1. The structure of β polyglycine in the parallel-chain pleated sheet configuration. The elementary translation vectors are indicated by $\boldsymbol{a}$ and $\boldsymbol{b}$ along the direction of the hydrogen bonds and along the polypeptide backbone, respectively. The atoms of the asymmetric unit are numbered

one has to consider also the second neighbours' interactions which may have a very strong influence on the positions of the bands as well as on their widths.

In polypeptides of β structure, from which polyglycine is the simplest one (Fig. 1), there is no planar symmetry which would allow the separation of the σ and π electron systems. Therefore the correct description of their electronic properties requires at least an all-valence electron treatment. Previous investigations showed that among the SCF LCAO all-valence electron crystal orbital schemes the MINDO/2 parametrization yields the most realistic band structures [2–4], so this method is applied in this work for polyglycine.

The computation of the energy bands forms only the first step in determining the characteristic quantities of the electrical conduction. The second and, if possible, even more intricated task is to calculate the interactions between the excess electrons or holes and the lattice vibrations. The direct evaluation of the electron-phonon scattering matrix elements is out of the scope of this paper. Instead we attempt to get an overall picture of the charge carrier motion in these systems by estimating some dynamical properties like the effective mass of the charge carriers at the corresponding band edges, the anisotropy and the order of magnitude of the mobility along the different crystal axes using the constant relaxation time approximation.

Method of Calculation

It is *a priori* postulated in this crystal orbital study that the electronic structure of the macromolecule can be best described in terms of Bloch-type delocalized orbitals extending over the whole molecular aggregate. The use of Bloch's

theorem and the LCAO approximation permits one to write down the one-electron crystal orbitals of a two-dimensional system in the form

$$\Psi_n(\boldsymbol{k}, \boldsymbol{r}) = (N_a N_b)^{-1/2} \sum_{h=1}^{N_a} \sum_{j=1}^{N_b} \sum_{\alpha=1}^{A} \exp(i\boldsymbol{k}\boldsymbol{R}_{hj})\, C_{\alpha n}(\boldsymbol{k})\, \phi_\alpha(\boldsymbol{r} - \boldsymbol{R}_{hj}), \tag{1}$$

where n is the band index, $\boldsymbol{k} = (k_a, k_b)$ stands for the crystal momentum vector, N_a and N_b give the number of elementary cells along the crystal axes with basis vectors $\boldsymbol{a}$ and $\boldsymbol{b}$, respetively, $\phi_\alpha(\boldsymbol{r} - \boldsymbol{R}_{hj})$ is the αth atomic orbital centered at cell with position vector $\boldsymbol{R}_{hj} = h\boldsymbol{a} + j\boldsymbol{b}$, and finally A gives the total number of atomic orbitals in the elementary cell. The expansion coefficients of the linear combination $C_{\alpha n}(\boldsymbol{k})$ and the corresponding one-electron energy levels $\varepsilon_n(\boldsymbol{k})$ can be determined within the framework of the zero differential overlap approximation by solving the complex matrix eigenvalue equation

$$\boldsymbol{F}(\boldsymbol{k})\, \boldsymbol{C}_n(\boldsymbol{k}) = \varepsilon_n(\boldsymbol{k})\, \boldsymbol{C}_n(\boldsymbol{k}) \tag{2}$$

for the energetically inequivalent, representative points of the first Brillouin zone [5]. The Fock matrix $\boldsymbol{F}(\boldsymbol{k})$ in Eq. (2) has the structure

$$\boldsymbol{F}(\boldsymbol{k}) = \sum_{\boldsymbol{q}} \exp(i\boldsymbol{k}\boldsymbol{R}_{\boldsymbol{q}})\, \boldsymbol{F}(\boldsymbol{q}), \tag{3}$$

where $\boldsymbol{q}$ stands for the cell at position $\boldsymbol{R}_{\boldsymbol{q}} = q_a\boldsymbol{a} + q_b\boldsymbol{b}$, and $\boldsymbol{F}(\boldsymbol{q})$ contains the interactions between the reference cell (0, 0) and cell $\boldsymbol{q}$.

The actual form of the matrix elements $F_{\mu\nu}(\boldsymbol{q})$ depends on the integral approximations used in the calculations. For the MINDO/2 crystal orbital method they are explicitly given in Ref. [2]. The atomic coordinates used in the computation of the interatomic integrals were taken from Ref. [6] and are listed for the asymmetric unit of the crystal in Table 1. The second part of the elementary cell can be obtained by the transformation $(x, y, z) \rightarrow (-x, y + 1/2b, z)$. The translational units along the hydrogen bonds and the backbone are $a = 4.85$ Å and $b = 6.50$ Å, respectively. The number of the different interacting cells in Eq. (3) is obviously limited for practical reasons. It is very important, however, to consider all those neighbours for which the various two-center integrals are comparable in magnitude with those for the immediately neighbouring cells. Having in sight the results of model calculations [3] we allowed in this study for the following values of $\boldsymbol{q}$: (1, 0), (−1, 0), (0, 1), 0, −1), (1, 1), (−1, −1), (1, −1), (−1, 1). Looking at Fig. 1 it can be seen that authors considering delocalization along the hydrogen bonds or along the main peptide chain paid attention to cells (1, 0), (−1, 0), or cells (0, 1), (0, −1), respectively. The interactions with the last four cells are, however, of equal importance and this is why systems of this type can be suitably treated only by two-dimensional models.

Possessing the energy band structure we can immediately calculate two characteristic quantities of the charge carrier dynamics. The effective mass tensor is defined by

$$m_{ij}^{-1}(\boldsymbol{k}_0) = \hbar^{-2} \left(\frac{\partial^2 \varepsilon(\boldsymbol{k})}{\partial k_i\, \partial k_j} \right)_{\boldsymbol{k} = \boldsymbol{k}_0}, \tag{4}$$

where the derivative has to be taken at the corresponding band edge, i.e. at the bottom of the conduction band for the electron, and at the top of the valence band for the hole [7]. The elements of the mobility tensor have the following form in the constant relaxation time approximation [7]:

$$\mu_{ij} = \frac{e\tau}{k_0 T} \langle v_i(\boldsymbol{k})\, v_j(\boldsymbol{k}) \rangle \,, \tag{5}$$

where e denotes the charge of the electron, τ is the relaxation time, k_0 and T are the Boltzmann constant and the absolute temperature, respectively. The Bloch velocity of the particles can be calculated from the expression

$$\boldsymbol{v}(\boldsymbol{k}) = \hbar^{-1} \nabla_{\boldsymbol{k}} \varepsilon(\boldsymbol{k}) \,. \tag{6}$$

The brackets in Eq. (5) denote averaging with Boltzmann statistics over the band states since the organic semiconductors may be assumed to be non-degenerate. Equation (5) makes it possible to estimate the relative mobility of the charge carriers along the different directions in the crystal. To obtain the absolute value of the mobility we would need to know explicitely τ which could be calculated only from the electron-phonon interaction. To turn this difficulty we will assume for the moment $\tau = 10^{-14}$ s, a fairly common value in organic semiconductors, and by using this we can get some information from Eq. (5) about the order of magnitude of the mobilities in these systems.

Results

From the matrices $\boldsymbol{C}_n(\boldsymbol{k})$ one can determine the charge distribution in the crystal by numerical integration over the values of $\boldsymbol{k}$ in the first Brillouin zone [5].

The resulting atomic valence charges are given in the last column of Table 1.

Table 2 contains the energy band structure of β polyglycine. The second and third column indicate the lower and upper limits of the energetically allowed zones, respectively (in parentheses we give the positions of the minima and maxima). In the last column the bandwidths are shown.

In Table 3 we summarize the most important dynamical properties of the charge carriers. The diagonal elements of the effective mass and mobility tensors, and the mobility ratios are given for electrons and holes, respectively. The band

Table 1. The atomic Descartes coordinates (in Å) and the distribution of the valence electrons in the asymmetric unit of the parallel-chain β polyglycine (the numbering of the atoms is the same as in Fig. 1)

Atom	x	y	z	Valence charge
C_1	−0.058	0.000	−0.980	3.827
N_2	0.320	1.209	−0.260	5.594
C_3	−0.572	2.048	0.280	3.173
O_4	−1.799	1.918	0.250	6.730
H_5	0.301	0.061	−2.007	0.985
H_6	−1.144	−0.099	−0.981	1.000
H_7	1.286	1.399	−0.184	0.691

Table 2. The energy band structure of the parallel-chain β polyglycine (energy values in eV)

No. of band	$\varepsilon_{min}(k_a \cdot a, k_b \cdot b)$	$\varepsilon_{max}(k_a \cdot a, k_b \cdot b)$	$\delta\varepsilon$
1	5.921 (0, 0)	5.926 (π, 0)	0.005
2	5.707 (π, π)	5.730 (0, π)	0.023
3	4.998 (π, π)	5.093 (0, π)	0.095
4	4.888 ($\pi/4$, π)	5.039 (0, π)	0.095
5	3.663 (π, π)	3.682 (π, 0)	0.019
6	3.279 (π, 0)	3.408 (0, 0)	0.129
7	3.129 ($\pi/8$, π)	3.293 (0, π)	0.164
8	3.070 (π, 0)	3.194 (0, π)	0.124
9	2.959 (π, π)	2.993 ($3\pi/4$, 0)	0.034
10	2.748 ($\pi/4$, π)	2.940 (0, π)	0.192
11	2.191 (π, π)	2.326 (π, 0)	0.135
12	1.671 ($\pi/2$, 0)	1.908 (0, π)	0.237
13	1.285 (0, π)	1.352 (π, 0)	0.067
14	0.950 ($7\pi/8$, 0)	1.040 (0, $\pi/2$)	0.090
15	0.786 (0, π)	0.891 (π, 0)	0.105
16	− 2.328 (0, 0)	− 0.649 (0, π)	1.679
17[a]	*− 8.324 (0, π)*	*− 7.090 (0, 0)*	*1.234*
18	− 9.331 (0, 0)	− 9.171 (π, π)	0.160
19	−10.196 (π, 0)	− 9.958 ($\pi/4$, 0)	0.238
20	−10.276 (0, $\pi/8$)	−10.206 (π, π)	0.070
21	−11.413 (π, π)	−10.326 (π, π)	1.087
22	−11.951 (π, 0)	−10.435 (0, π)	1.516
23	−12.139 ($\pi/4$, 0)	−11.637 (π, $7\pi/8$)	0.502
24	−12.513 (π, $\pi/8$)	−11.812 (π, π)	0.701
25	−13.402 (0, π)	−12.458 (π, π)	0.944
26	−13.618 (0, π)	−12.835 (0, 0)	0.783
27	−14.100 (π, π)	−13.062 ($3\pi/4$, 0)	1.038
28	−15.478 (0, 0)	−13.322 (π, 0)	2.156
29	−16.113 (π, 0)	−15.482 (0, π)	0.631
30	−16.433 (π, $\pi/4$)	−15.756 (0, π)	0.677
31	−18.652 (0, π)	−16.775 (π, $7\pi/8$)	1.877
32	−18.876 (0, 0)	−17.112 (π, π)	1.764
33	−25.676 (π, $3\pi/8$)	−22.646 (π, 0)	3.030
34	−29.775 (π, 0)	−25.622 (0, π)	4.153
35	−34.958 (π, $\pi/8$)	−31.623 (0, 0)	3.335
36	−35.486 (π, π)	−32.639 (0, π)	2.847
37	−42.960 (0, π)	−37.458 (π, 0)	5.502
38	−46.002 (0, 0)	−40.563 (π, π)	5.439

[a] Highest filled band.

Table 3. Effective masses (in free electron mass), mobilities (in $cm^2\ V^{-1}\ s^{-1}$, assuming $\tau = 10^{-14}$ s), and mobility ratios in the conduction and valence band of the parallel-chain β polyglycine

	Conduction band	Valence band
m_{aa}	1.295	1.870
m_{bb}	0.216	0.252
μ_{aa}	8.33	5.64
μ_{bb}	59.24	44.77
μ_{bb}/μ_{aa}	7.11	7.94

structure derivatives needed for the calculation of these quantities [Eqs. (4)–(6)] were computed analytically by interpolating the numerically given band structures with cosine polynomials.

Discussion

It is very extensively documented from the experimental side [8] that the electronic mechanism must play an essential role in the conductivity of proteins. Theoretically there are two possible pathways for electronic decolization in these systems: along the hydrogen bonds and along the polypeptide backbone, respectively. On the basis of early π-electron calculations it is widely accepted that the former mechanism is actually realized in polypeptides, though there are some experimental facts which seem to contradict this picture. ESR measurements have shown, for instance, that there is no evidence for an electron migration along the hydrogen bonds [9]. Study of the radiation effects in proteins on the other hand has shown that the mechanisms for the formation of secondary protein radicals can be understood if one assumes migration of electrons or holes along the backbone to the specific trapping sites [10].

In the present calculations we have taken into account simultaneously both possibilities for delocalization. From Table 3 it can be seen that the diagonal elements of the effective mass tensor are definitely larger both for electrons and holes in the direction of the hydrogen bonds (m_{aa}) than along the polypeptide backbone (m_{bb}). In accordance with this anisotropy the charge carrier mobilities are about 7–8 times larger along the backbone. It is evident that one should expect the same anisotropy of conductivity independently of the origin of carriers.

It is interesting to note that the obtained mobility values of $\sim 50\,\mathrm{cm^2\,V^{-1}\,s^{-1}}$ (which are very probably strongly underestimated by using the value of 10^{-14} s for the relaxation time) are considerably larger than $1\,\mathrm{cm^2\,V^{-1}\,s^{-1}}$. This fact indicates [11] that in calculating the electrical properties the conventional methods worked out for broad band semiconductors will be applicable also in the case of these systems.

For the forbidden energy gap between the highest filled and lowest unfilled band we obtain from Table 2 the value of $\Delta E = 4.762$ eV. If we assume an intrinsic mechanism of semiconduction this gap should be related to the thermal activation energy of conductivity. The experimental value of ΔE is in β alanine for instance 4.07 eV [12] so the discrepancy between experiment and theory is not too large. It can be probably further reduced if also the perturbing side-chain effects will be taken into account in future calculations. It is remarkable in this respect that a one-dimensional calculation performed with the same method for a single polyglycine backbone resulted $\Delta E = 7.015$ eV [13]. This is a further support for the two-dimensional treatment of these systems.

We are planning similar calculations in the near future for polypeptides of α-helical geometry. Since the properties of the protein molecule are determined both by the configuration of the backbone and by the character of the side chains, the effect of these latter groups will be also investigated. It would be desirable of course to perform an *ab initio* calculation for these systems without empirical

parameters. Because of the enormous number of intra- and intercell integrals, however, such a calculation would be feasible for polypeptides only by using some simplifications in the many-center electron-electron repulsion integrals. Work along these lines is in progress in our laboratory.

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