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A Theoretical Study of the Ionized State of Polymers with the Localized Molecular Orbital Method

Akira IMAMURA,* Kehong YE, and Masahiro TAKETOSHI
Department of Chemistry, Faculty of Science, Hiroshima University, Higashisenda-machi, Hiroshima 730
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A localized molecular orbital method for the investigation of the ionized state of polymers is presented. It is based on the Crystal Orbital Method(CO). By performing a super-cell method and Edmiston and Ruedenberg's LMO method, the Bloch function was transformed into a nearly completely localized Wannier function. Furthermore, the calculation of the configuration interaction was introduced to obtain more reasonable results. The present method was applied to polyacetylene (PA), polyethylene (PE), and polypropylene (PP). Ionization potentials of these polymers were calculated and compared with experimental and other theoretical results. All the calculations were performed using the CNDO/S approximation.

Interest in the theoretical studies of organic polymers has grown considerably in recent years. As the result of the remarkable development of computers, it has become possible to investigate the electronic structure of huge molecules or complicated systems which could not be treated before. Consequently, many theoretical methods have been proposed, and many calculated results have been reported. Most of these calculations, however, have been carried out on the ground state of polymers. Not many attempts have been done to investigate the ionized state of polymers. We carried out this study for the following two main reasons. One is that suitable theory has not yet been established. The second reason is the lack of precise experimental values, which makes the comparison between experimental and theoretical results defficult, sometimes even impossible.

It is known that, for the species in which the interaction between segments is very weak, the exciton model is useful, while for the species in which the interaction is very strong, the crystal orbital method provides a good description. However, for the species in which the interaction is between the above two, the theory seems not to be established. Therefore, the purpose of this study is to present a theoretical method for the investigation of the ionized state of polymers. In our method, by using a super-cell method[1] and Edmiston and Ruedenberg's LMO method[2,3] a nearly completely localized Wannier function can be obtained from Bloch's function. We can calculate the ionization potential from this Wannier function directly or after carrying out the configuration interaction procedure. We applied the method to polyacetylene, polyethylene, and polypropylene. The results seem to be in somewhat good agreement with the experimental values.

Method of Calculations

In the tight-binding approximation, one electron-crystal orbital for a linear-periodic polymer is given by Bloch's function as follows:[4]

$$\psi_{ks}(\boldsymbol{r}) = (1/N)^{1/2} \sum_{j=1}^{N} \sum_{t=1}^{n} C_{ks,jt} \chi_t \{\boldsymbol{T}^j(\boldsymbol{r} - \boldsymbol{r}_t - j\boldsymbol{a})\} \quad (1)$$

$$C_{ks,jt} = \exp(ikj) C_{ks,t} \quad (2)$$

$$k = 2\pi p/N \quad (p = 0, 1, 2 \cdots\cdots N-1) \quad (3)$$

where j denotes a cell in the polymer; t, an atomic orbital in the j-th cell; $\boldsymbol{r}_t$, its vector from the center of a segment; $\boldsymbol{T}$, the rotational operator around the helical axis, and $\boldsymbol{a}$, the unit vector of the translational symmetry which is paralled to the helical axis. N and n specify the total number of cells and the number of atomic orbitals in an unit cell, while the s value, ranging from 1 to n, indicates an energy band. $C_{ks,jt}$ can be rewritten as Eq. 2; here i denotes the imaginary number. The k value in Eq. 3 corresponds to the wavenumber vector defined by the solid state physics.

A localized molecular orbital (LMO) can be obtained in several ways. In the case of polymers, the Wannier transformation is well known. The Wannier function has a particular property: if the overlap integrals between neighbouring segments are very small, the MO coefficients, C_k's, do not depend on the wavenumber vector, k. That is, the MOs obtained are localized in a certain segment. However, in general, a nearly completely localized molecular orbital can not be expected by using the Wannier transformation only. Therefore, in order to get a well-localized molecular orbital for polymers, we considered two procedures before the Wannier transformation. One is called the super-cell method, and second, a modification of the Edmiston and Ruedenberg's LMO procedure which was performed for the wave function of super cells in each wavenumber vector. By performing these two procedures, the overlap integrals between corresponding localized orbitals in neighbouring segments become very small; that is, well-localized MOs can be expected with the two procedures, followed by the Wannier transformation.

The details of the super-cell method can be found in Ref. 1. Here we will give just a simple outline. It assumed that, in a linea-periodic polymer system, several units can be considered as big units, named "super cells", if the relation between such a super cell and the

unit cells satisfies the following equations:

$$k' = mk - 2\pi j \quad (j: \text{integer}) \tag{4}$$

$$C_{k's,t}(l) = C_{ks,t} \exp\{i(l-1)k\} \tag{5}$$

where k' and $C_{k's,t}$ denote the wave vector and the MO coefficient of the super cell, while k and $C_{ks,t}$ are those of the unit cells. The integer j in Eq. 4 must be chosen so that the value of k is in the range of the first Brillouin zone (0—2 π); l indicates the l-th cell in the super cell.

After the super cells were created, as has been mentioned above, we treated the super cell thus obtained in each wavenumber vector with the modification of the Edmiston and Ruedenberg's energy-localized MO method. In general, however, the wave functions of polymers are complex; so in this procedure we completed the LMO by considering three kinds of transformations, which will be described in detail below.

1. Orthogonal transformation:

$$\begin{pmatrix} u_1 \\ u_2 \end{pmatrix} = \begin{pmatrix} \cos\gamma & \sin\gamma \\ -\sin\gamma & \cos\gamma \end{pmatrix} \begin{pmatrix} \psi_1 \\ \psi_2 \end{pmatrix} \tag{6}$$

where u_1, u_2, and ψ_1, ψ_2 are the complex functions. After the transformation, the sum of the diagonal elements is given by the following equations:

$$D(u) = D(\psi) + A_{12} + (A_{12}+B_{12})^{1/2} \cos 4(\gamma-\alpha) \tag{7}$$

$$2A_{12} = [\psi_1^*\psi_2 + \psi_1\psi_2^* | \psi_1^*\psi_2 + \psi_1\psi_2^*] - [\psi_1\psi_1^* - \psi_2\psi_2^* | \psi_1\psi_1^* - \psi_2\psi_2^*] \tag{8}$$

$$B_{12} = [\psi_1\psi_1^* - \psi_2\psi_2^* | \psi_1^*\psi_2 + \psi_1\psi_2^*] \tag{9}$$

$$\tan 4\alpha = -B_{12}/A_{12} \tag{10}$$

In Eq. 7, when the value of $\gamma=\alpha+(n\pi/2)$, $D(u)$ reaches a maximum. By placing the Bloch function, Eq. 1, into Eqs. 8 and 9 and by using the periodic boundary condition and the CNDO/S[5] approximation, Eqs. 8 and 9 can be rewritten as follows:

$$2A_{k,12} = 1/N \sum_{t=1}^{n}\sum_{u=1}^{n} \{(C_{k1,t}^* C_{k2,t} + C_{k1,t} C_{k2,t}^*)(C_{k1,u}^* C_{k2,u} + C_{k1,u} C_{k2,u}^*) - (C_{k1,t} C_{k1,t}^* - C_{k2,t} C_{k2,t}^*)(C_{k1,u} C_{k1,u}^* - C_{k2,u} C_{k2,u}^*)\} \sum_{j=1}^{N} \gamma_{tu}^{0j} \tag{11}$$

$$B_{k,12} = 1/N \sum_{t=1}^{n}\sum_{u=1}^{n} (C_{k1,t} C_{k1,t}^* - C_{k2,t} C_{k2,t}^*)(C_{k1,u}^* C_{k2,u} + C_{k1,u} C_{k2,u}^*) \sum_{j=1}^{N} \gamma_{tu}^{0j} \tag{12}$$

$$\gamma_{tu}^{0j} = [\chi_t\chi_t | \chi_u(\boldsymbol{T}^j\boldsymbol{r} - j\boldsymbol{a})\chi_u(\boldsymbol{T}^j\boldsymbol{r} - j\boldsymbol{a})] \tag{13}$$

2. Transformation between the real part of one MO and the imaginary part of the other MO:

$$\begin{pmatrix} u_1 \\ u_2 \end{pmatrix} = \begin{pmatrix} \cos\gamma & i\sin\gamma \\ i\sin\gamma & \cos\gamma \end{pmatrix} \begin{pmatrix} \psi_1 \\ \psi_2 \end{pmatrix} \tag{14}$$

In this case, the sum of the diagonal elements has the following forms:

$$D(u) = D(\psi) + A_{12} + (A_{12}+B_{12})^{1/2} \cos 4(\gamma-\alpha) \tag{15}$$

$$2A_{12} = [\psi_1^*\psi_2 - \psi_1\psi_2^* | \psi_1^*\psi_2 - \psi_1\psi_2^*] - [\psi_1\psi_1^* - \psi_2\psi_2^* | \psi_1\psi_1^* - \psi_2\psi_2^*] \tag{16}$$

$$B_{12} = [\psi_1\psi_1^* - \psi_2\psi_2^* | \psi_1^*\psi_2 - \psi_1\psi_2^*]i \tag{17}$$

$$\tan 4\alpha = -B_{12}/A_{12} \tag{18}$$

By using the same procedures as in Transformation 1, Eqs. 16 and 17 become:

$$2A_{k,12} = -1/N \sum_{t=1}^{n}\sum_{u=1}^{n} \{(C_{k1,t}^* C_{k2,t} - C_{k1,t} C_{k2,t}^*)(C_{k1,u}^* C_{k2,u} - C_{k1,u} C_{k2,u}^*) + (C_{k1,t} C_{k1,t}^* - C_{k2,t} C_{k2,t}^*)(C_{k1,u} C_{k1,u}^* - C_{k2,u} C_{k2,u}^*)\} \sum_{j=1}^{N} \gamma_{tu}^{0j} \tag{19}$$

$$B_{k,12} = i/N \sum_{t=1}^{n}\sum_{u=1}^{n} (C_{k1,t} C_{k1,t}^* - C_{k2,t} C_{k2,t}^*)(C_{k1,u}^* C_{k2,u} - C_{k1,u} C_{k2,u}^*) \sum_{j=1}^{N} \gamma_{tu}^{0j} \tag{20}$$

Well-localized MOs can be obtained by carrying out the above two transformations iteratively for every wavenumber vector. Finally, to rearrange the MO coefficients to similar types for all k values, a third transformation will be performed.

3. Transformation between real part and imaginary part in the same MO:

$$u_1 = \{a(a^2+b^2)^{1/2} - ib(a^2+b^2)^{1/2}\}\psi_1 \tag{21}$$

The LMO of the super cell completely obtained can be expressed in the following form:

$$\psi_{ks}(\boldsymbol{r}) = (1/N)^{1/2} \sum_{j=1}^{N}\sum_{t=1}^{n} \exp(ikj) C_{ks,t}(\text{LMO}) \chi_t(\boldsymbol{T}^j\boldsymbol{r} - j\boldsymbol{a}) \tag{22}$$

Using the above formula, we can derive the Wannier function easily. It is well-known that the Wannier function[6] is described as follows:

$$a_s(\boldsymbol{r} - l) = (1/N)^{1/2} \sum_{k} \exp(-ikl)\psi_{ks}(\boldsymbol{r}) \tag{23}$$

where l is the l-th segment of the Wannier function. By inserting Eq. 22 into Eq. 23, we obtain:

$$a_s(\boldsymbol{r} - l) = \sum_{j=1}^{N}\sum_{t=1}^{n} A_{ls,jt} \chi_t(\boldsymbol{T}^j\boldsymbol{r} - j\boldsymbol{a}) \tag{24}$$

$$A_{ls,jt} = (1/N) \sum_{k} \exp\{ik(j-l)\} C_{ks,t}\,(\text{LMO}) \tag{25}$$

In order to calculate the ionization potential from the Wannier function, four kinds of calculation models were considered; the ionization was assumed to arise from the central cell of the Wannier function. Next, we will give an outline for each model.

Model 1. The ionization energy is calculated from the above-obtained Wannier function directly:

$$I.P = E(M) - E(M^+) = H_{m0} + \sum_{l=1}^{N}\sum_{s=1}^{n} (2J_{ls,m0} - K_{ls,m0}) \tag{26}$$

where M corresponds to the ground state, and M^+ to the ionized state.

$$H_{m0} = [a_m(\boldsymbol{r}_1) | \hat{h} | a_m(\boldsymbol{r}_1)] \tag{27}$$

$$J_{ls,m0} = [a_s(\boldsymbol{r}_1 - l) a_m(\boldsymbol{r}_2) | 1/r_{12} | a_s(\boldsymbol{r}_1 - l) a_m(\boldsymbol{r}_2)] \tag{28}$$

$$K_{ls,m0} = [a_s(\boldsymbol{r}_1 - l) a_m(\boldsymbol{r}_2) | 1/r_{12} | a_m(\boldsymbol{r}_1) a_s(\boldsymbol{r}_2 - l)] \tag{29}$$

Using the Wannier function, the one electron term in Eq. 26 becomes:

$$H_{m0} = \sum_{tt'}\sum_{jj'} A_{m0,jt}^* A_{m0,j't'} [\chi_t(\boldsymbol{T}^j\boldsymbol{r} - j\boldsymbol{a}) | \hat{h} | \chi_{t'}(\boldsymbol{T}^{j'}\boldsymbol{r} - j'\boldsymbol{a})] \tag{30}$$

while the two electron term is:

$$\sum_l \sum_s (2J_{ls,m0}-K_{ls,m0})$$
$$=2\sum_{tt'}\sum_{jj'} A^*_{m0,j't}A_{m0,j't'}\gamma^{jj'}_{tt'} \sum_l \sum_s A^*_{js,jt}A_{ls,jt}$$
$$-\sum_{tt'}\sum_{jj'} A^*_{m0,j't}A_{m0,jt}\gamma^{jj'}_{tt'} \sum_l \sum_s A^*_{js,jt}A_{ls,j't'} \quad (31)$$

Model 2. In order to get even more reliable results, that is, results more comparable with the experimental values, in this model we introduced a configuration interaction treatment and carried it out in a unit cell of the polymer.

In the present work, a complete singly excited configuration interation (SECI) was considered. The elements of matrix for SECI can be simply expressed in the following way:

Diagonal elements:

$$H_{kk}=-\{h_{kk}+\sum_i (2J_{ik}-K_{ik})\} \quad (32)$$

Non-diagonal elements:

$$H_{kl}=-h_{kl}-\sum_i \{2(kl|ii)-(ki|ii)\}-(kl|kk)-(kl|ll) \quad (33)$$

Using the Wannier function and the parameters of the CNDO/S approximation, the ionization potential can be obtained by diagonalizing the above matrix.

Model 3. It is known that, in the CI calculation, the more configurations interact, the better results can be obtained. In this case, therefore, we extended the above CI calculation to a super cell. The CI matrix in this model is similar to that in Model 2.

Model 4. Generally speaking, ionization can be considered as arising from a rather localized state. However, due to some disagreements between the theoretical and experimental results, a question arises: is the excitation of a polymer limited in a particular space or does it arise from a more extended space? In other words, can the ionized state move along the polymer chain or not? In an attemp to answer this question, in this model, based on the concept of exciton, we change the above CI matrix into a new hermit matrix by using the following equation, which satisfies the periodic boundary condition.

$$H^{(0,0)}_{tu}=H^{(0,0)}_{tu}+\sum_{m=1} \cos mk(H^{(0,m)}_{tu}+H^{(0,-m)}_{tu})$$
$$+i\sum_{m=1} \sin mk(H^{(0,m)}_{tu}-H^{(0,-m)}_{tu}) \quad (34)$$

Also, the ionization potential of a polymer can be obtained by diagonalizing the new matrix.

Results and Discussion

We applied the present method to polyacetylene, polyethylene, and polypropylene. The structures of these polymers are shown in Fig. 1. The ionization potentials were calculated by using the four models of calculation described in the previous section.

In order to compare the polymers, first we calculate the ionization energies of some small molecules. These molecules can be considered as oligomers of the corresponding polymers. The results are shown in Table 1. The values obtained seem to be in good agreement with the experimental results. This means that the present method is suitable for investigating the ionized state of oligomers; consequently, it may also be suitable for polymers. From ethane to isobutane, as the number of carbons in the molecule increases, the corresponding values decrease. Table 1 shows that the ionization energies of alkenes are lower than those of corresponding alkanes because of the existence of a double bond in the molecules. This

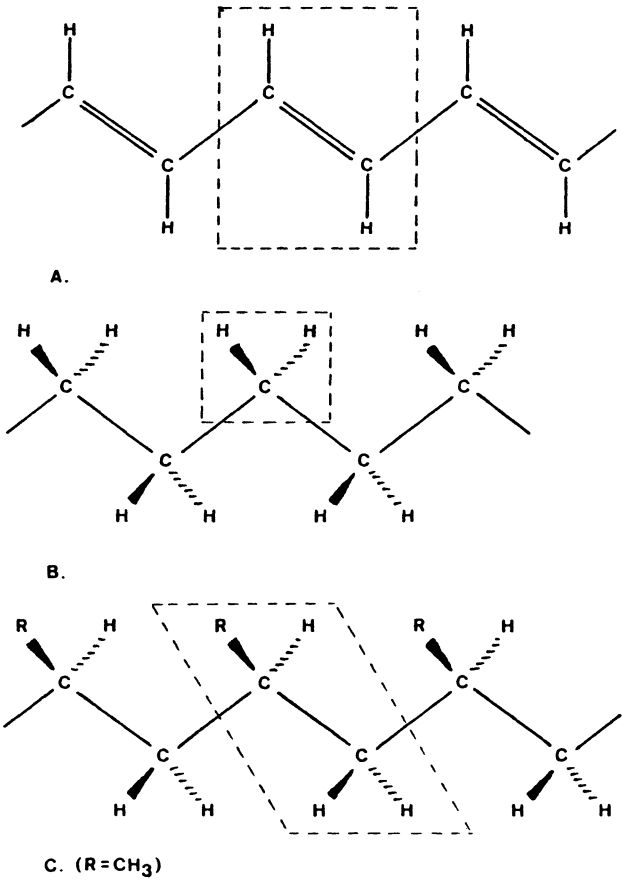

Fig. 1. Structures of *all-trans*-polyacetylene (A), polyethylene (B), and polypropylene (C). Unit cells are surrounded by broken lines.

Table 1. Ionization Energies of Some Small Molecules (eV)

Molecule	Symmetry	This work	Experiment
Ethane	Ag	14.898	12.1
	Eg	14.196	13.6
	Eu	19.167	15.4
Propane	A1	13.778	12.1
	B2	13.579	12.7
	A2	15.914	13.5
Isobutane	E	12.923	11.4
	A1	12.923	12.1
	A2	13.243	12.8
Ethylene	B3u	10.796	10.5
Butadiene	Bg	9.369	9.03
	Au	12.696	11.46

suggests that the ionization energy of polyacetylene is smaller than that of polyethylene. In fact, this is true, as can be seen from Tables 4 and 7. Consequently, the CNDO/S parameters are adequately reliable for the calculation of the ionization energies of the polymers under consideration.

Polyacetylene (PA). First, the MO's coefficient will be considered. The results are listed in Tables 2 and 3. These tables show that the molecular orbitals obtained are quite localized on the central cell. With the number of unit cells contained in a super cell increased from 3 to 4, the MO's coefficients undergo a little change, but not a very large one. For example, in the case of C-C (π), the difference is about 0.0003. We can expect that such a small difference would not affect the values of the ionization potential. Also, this means that, in our calculation for PA, taking the number of unit cells in a super cell as 3 or 4 is sufficient.

Next, let us compare our results with those obtained by experiments and other theoretical calculations.[7-10] The results are shown in Table 4. Peak 1 corresponds to the C-C π bonding orbital; the value given by Model 1 is larger than the others. The reason for this disagreement can be understood as follows. π-electrons, generally, are considered as moving in a broad space. However, in this method they are described as localized upon a particular bond. This may produce the disagreement. Peaks 2 and 3 in Model 1 also give very large values; these ionization arise from C-H bonds. The most probable explanation may be that these ionization arise from a more delocalized space instead of a localized one; that is, ionization occurs not just in a limited bond, but in a broader space extending to the neighboring bonds. The results would be improved if the CI procedure is introduced. In fact, this can be seen by comparing Model 1 with Models 2—4. For Peak 2, the result obtained from Model 4 is rather good, while the value given by Model 2 is desirable for Peak 3. This also means that the delocalized space in Peak 2 is broader than that in Peak 3. Finally, Peaks 4 and 5 are related to the C-C σ orbitals; the results of Model 1 are in good agreement with the experimental values and some other theoretical ones.

Polyethylene (PE). The MO's coefficients of PE

Table 2. Square of MO Coefficients
C-H Bonding Orbital (PA)

		4 Units[a]	3 Units[a]
Central cell-1	C S	0.16279	0.16380
	C Py	0.34784	0.34692
	C Pz	0.00000	0.00001
	H S	0.48558	0.48553
Central cell-2	C S	0.00030	0.00029
	C Py	0.00060	0.00061
	C Pz	0.00003	0.00003
	H S	0.00092	0.00092
1st cell-1	C S	0.00015	0.00013
	C Py	0.00000	0.00000
	C Pz	0.00002	0.00002
	H S	0.00003	0.00003
1st cell-2	C S	0.00003	0.00003
	C Py	0.00001	0.00001
	C Pz	0.00004	0.00004
	H S	0.00000	0.00000

a) Number of unit cells in a super cell.

Table 3. Square of MO Coefficients
C-C(π) Bonding Orbital (PA)

		4 Units[a]	3 Units[a]
Central cell	C Px	0.47406	0.47433
	C Px	0.47386	0.47331
1st cell	C Px	0.01299	0.01285
	C Px	0.01068	0.01059
2nd cell	C Px	0.00054	0.00047
	C Px	0.00132	0.00119

a) Number of unit cells in a super cell.

Table 4. Ionization Energies of Polyacetylene (eV)

	Peak 1	Peak 2	Peak 3	Peak 4	Peak 5
Model 1	12.26	22.30	22.30	24.54	26.08
Model 2	12.27	16.17	19.73	24.10	30.58
Model 3	10.03	14.07	16.73	20.37	26.82
Model 4	11.18	13.32	16.04	24.73	30.08
Band Model	8.02	14.66	15.00	22.05	29.58
XPS[a]	4.84	12.25	19.96	25.40	27.82
VEH[b]	7.26	13.30	20.68	26.03	31.65
MNDO[c]	4.7				
ab initio[d]	6.19				

a) From the X-ray-photoelectron spectroscopy (XPS) data of M. Kitani. b) From the XPS theoretical spectrum obtained by using the valence effective hamiltonian (VEH) calculation by Bredas et al. c) By Tripathy et al. d) Calculation for the model molecule C_8H_{10} reported by Kirtman.

Table 5. Square of MO Coefficients
C-H Bonding Orbital (PE)

		4 Units[a]	3 Units[a]
Central cell	C S	0.12337	0.12157
	C Px	0.12953	0.13159
	C Py	0.25152	0.25152
	C Pz	0.00000	0.00000
	H S	0.49278	0.49269
	H S	0.00000	0.00000
1st cell	C S	0.00011	0.00007
	C Px	0.00007	0.00011
	C Py	0.00036	0.00036
	C Pz	0.00006	0.00000
	H S	0.00053	0.00053
	H S	0.00001	0.00001
2nd cell	C S	0.00013	0.00002
	C Px	0.00004	0.00000
	C Py	0.00002	0.00002
	C Pz	0.00000	0.00000
	H S	0.00002	0.00002
	H S	0.00000	0.00000

a) Number of unit cells in a super cell.

Table 6. Square of MO Coefficients C-C Bonding Orbital (PE)

		4 Units[a)]	3 Units[a)]
	C S	0.12425	0.12646
	C Px	0.12302	0.12097
	C Py	0.00000	0.00000
	C Pz	0.25147	0.25145
	H S	0.00000	0.00000
	H S	0.00000	0.00000
Central cell			
	C S	0.12429	0.12649
	C Px	0.12306	0.12101
	C Py	0.00000	0.00000
	C Pz	0.25143	0.25145
	H S	0.00000	0.00000
	H S	0.00000	0.00000
	C S	0.00002	0.00001
	C Px	0.00041	0.00018
	C Py	0.00000	0.00000
	C Pz	0.00024	0.00024
	H S	0.00001	0.00002
	H S	0.00001	0.00002
1st cell			
	C S	0.00025	0.00011
	C Px	0.00015	0.00034
	C Py	0.00000	0.00000
	C Pz	0.00005	0.00004
	H S	0.00000	0.00003
	H S	0.00000	0.00003

a) Number of unit cells in a super cell.

Table 7. Ionization Energies of Polyethylene (eV)

	Peak 1	Peak 2	Peak 3
Model 1	21.74	21.74	22.85
Model 2	17.91	18.44	26.03
Model 3	14.15	17.34	26.29
Model 4	10.62	20.54	25.94
Band Model	11.37	14.39	23.72
ESCA[a)]	8.3	18.7	23.5
CNDO/2[b)]	13	20	30
Extended Huckel[c)]	11.9		
ab initio[d)]	13.2		

a) By Delhalle et al. b) By Wood et al.; results for the model molecule $C_{36}H_{74}$. c) By Delhalle et al. d) By Teramae et al.; the STO-3G basis set was used.

Table 8. Square of MO Coefficients C-H Bonding Orbtal (PP)

		3 Units[a)]
	C S	0.11815
	C Px	0.25203
Central cell	C Py	0.13442
	C Pz	0.00000
	H S	0.49273
	H S	0.00000
	C S	0.00001
	C Px	0.00000
1st cell	C Py	0.00004
	C Pz	0.00003
	H S	0.00000
	H S	0.00005

a) Number of unit cells in a super cell.

Table 9. Square of MO Coefficients C-C Bonding Orbital (PP)

		3 Units[a)]
	C S	0.12811
	C Px	0.00002
	C Py	0.12192
	C Pz	0.24871
	H S	0.00000
Central cell		
	C S	0.12975
	C Px	0.00001
	C Py	0.11935
	C Pz	0.24875
	H S	0.00001
	H S	0.00000
	C S	0.00025
	C Px	0.00000
	C Py	0.00015
	C Pz	0.00007
	H S	0.00001
1st cell		
	C S	0.00003
	C Px	0.00000
	C Py	0.00021
	C Pz	0.00021
	H S	0.00002
	H S	0.00002

a) Number of unit cells in a super cell.

are shown in Tables 5 and 6. Table 5 shows the MO's of the C-H bonding orbital, and Table 6, those of the C-C bond. We can see that the MO coefficients are localized completely on the central cell and are almost independent of the numbers of unit cell, contained in a super cell. Therefore, taking 3 or 4 unit cells for a super cell is enough for our treatment.

Next, it is interesting to compare our results with other theoretical and experimental ones.[11-13] The results are shown in Table 7. First, let us examine Peak 1, which is obtained from the ionization that arise from one C-H bond. The value given by Model 1 is very large, even greater than the result of CNDO/2. This may suggest that the ionization arises from a more delocalized space, similar to Peaks 2 and 3 in PA discussed above. On the other hand, Model 4 gives a reasonable result. This may be due to the fact that CI was taken into account. From Model 2 to Model 4, as the space of configuration interaction is extended, the results seem to be improved greatly. Next, as for Peak 2, the value from Model 1 seems greater than the others, but not very large, and it is degenerate when compared with Peak 1. The results given by Models 2 and 3 show a very good agreement with the ESCA's, while Model 4 gives an overestimated value. Finally, in the case of Peak 3, Model 1 gives a very good result. This may imply that, for the high-energy region, an ionized state can be well described by a localized model.

Table 10. Ionization Energies of Polypropylene (eV)

	Peak 1	Peak 2	Peak 3	Peak 4	Peak 5
Model 1	21.49	21.51	21.59	21.60	22.20
Model 2	15.07	16.33	17.63	18.11	18.97
Model 3	9.80	13.41	13.85	14.45	16.68
Model 4	7.69	9.89	12.83	15.95	19.01
Band model	7.51	11.80	13.17	13.69	17.78

Polypropylene (PP). Some of the Mo's coefficients of PP are given in Tables 8 and 9. In this case, we just consider the super cell that contains only 3 unit cells. From these tables, we can see that, as with PA and PE, the molecular orbitals are well localized. For PP, unfortunately, we can not find any related experimental results at present. Therefore, our results are shown in Table 10 just with those obtained by the use of the Band model. The values given by Model 1 also seem to be too large, especially in Peak 1 to Peak 3, they were improved by introducing the CI calculation from Model 2 to Model 4. Therefore, it seems that the general tendency of the ionization of PP is the same as those of PA and PE.

Conclusion

The present method seems to be applicable to the investigation of the ionized state of one-dimensional periodic polymers such as PE and PA. The localized model (Model 1) described ionizations from the high-energy region quite well, but failed to explain those from the low-energy region. By introducing the models including configuration interaction (Model 2 to Model 4), the results of ionization from the low-energy region were improved and became comparable with the experimental values. Therefore, we concluded that, in the high-energy region, ionizations arise from a rather localized space, so Model 1 is suitable. In the low-energy region, especially in the first ionization potential, ionization occurs from a more delocalized space; here, Model 4 is excellent, In the middle region, ionized states can be well described by Models 2 and 3.

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