CALCULATION OF THE UNPERTURBED DIMENSIONS FOR LINEAR ATACTIC POLYMERS ON A SQUARE LATTICE

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ABSTRACT

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Body of Abstract

A two-dimensional square lattice model for linear atactic polymers of type CH_2-CHR has been formalized. The three-dimensional equations developed by Yoo and Kinsinger were reduced to a regular planar square lattice and several computer programs were written to calculate the mean-square end-to-end-dimensions for several polymeric models.

The model allows the carbon atoms of the polymer chain to occupy adjacent corners of the square lattice. Each step in the polymer chain has a fixed length l and is not allowed to reverse its previous direction. Thus, the bonds are permitted to go forward 0°, left turn -90°, or right turn +90°. This model accounts for both first and second neighbor interactions and the chain configuration can be either atactic, isotactic, or syndiotactic.

The values of $\langle h^2 \rangle / nl^2$ for the seven polymer cases ranged from 1.14 to 2.01 while a value of 1.67 was obtained for a polymer with randon configuration and randon conformation. Some comparisons are made between the results obtained on the two dimensional lattice and what would be expected for the three dimensional case.

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I. INTRODUCTION

A. General

In 1958, interest in the theory of dilute polymer solutions was rekindled when Volkenstein's calculations[1] of the relationship of discrete rotational states to the average unperturbed end-to-end dimensions of polymer chains became known to western scientists. By this time, Volkenstein and coworkers had developed their theories to include polymer chains with both symmetric and asymmetric structures with statistically independent rotational states. In addition, they had closed form solutions for the newly discovered isotactic and syndiotactic stereoisomeric polymers which related the average end-to-end dimensions to chain geometry. Moreover, they developed equivalent equations for atactic polymers, the configurational (d,l) placements mathematically described by a single distribution parameter, and the chain with statistically independent rotations.

Shortly, however, it was evident that a statistically independent model could not adequately describe the unperturbed dimensions, and Lifson[2] and Nagai[3] introduced the statistically dependent rotational model which was treated through the formalism of the linear Ising problem and took into account cooperative effects between first and second neighbors in the chain.

This successful treatment, however, made the mathematical process somewhat more complex, and in the past several years,

many papers have appeared[4,5,6,7] for chains with symmetric structure and for the asymmetric stereoregular isotactic and syndiotactic forms. Yoo and Kinsinger[8] developed a comprehensive formalism which included a two parameter distribution for the stereosequences in the chain plus a second neighbor interaction distribution for chain conformations, all based on a statistically dependent model. This master equation for atactic chains can, with appropriate change, be converted to handle either the asymmetric syndiotactic or isotactic chains and symmetric chains as well. The states of the chain, however, are numerous since two parameters are needed to describe the d,l sequences which arise from the polymerization conditions and these, in turn, have several conformational states for each different triplet d,l sequence in the backbone. This results in a large number of joint configurational-conformational states for the system, and the formalism requires a generator matrix of rather large size with an excessive number of parameters. Since, at best, two parameters can be obtained from current experimental data, the formalism cannot be evaluated properly. Future work on configurational and conformational distributions by various spectroscopic techniques may yield sufficient evidence to utilize and verify the theory.

However, it is instructive to reduce the formalism to computations based upon our best current knowledge of the distribution of configurational and conformational states of polymer chains. In this way, the formalism can be checked

independently for completeness and the effect of the joint distribution can be revealed. Even a cursory glance at the computational problem will show that a three dimensional representation of the chain has prohibitive complexity and detail. Hence, it was decided to reduce the chain problem to a regular two dimensional square lattice. While this seemingly may restrict the computations to a very special case, the principles contained therein in the formalism and the inter-relationship of the joint states should be revealed by such a calculation.

In this model, therefore, the two dimensional square lattice will have two types of lattice sites, corresponding to the d or l configuration in the chain. While the model is not truly asymmetric, the different sites will reflect the influence of the corresponding d,l states in the three dimensional chain. Each step will have a fixed length l as in a real polymer chain, but the bond angles will vary depending upon the steps taken along the lattice, and they will be permitted to go forward 0°, left turn -90°, right turn $+90^{\circ}$. In this sense, the variable bond angles will correspond to the rotational states in the three dimensional chain. While this may seem superficial, the fixed bond angles in the three dimensional chain contributes only a multiplicative term to the mean square end-to-end dimension and, hence, enters as a constant.

B. Experimental Model

The square lattice model used for this study of polymer type chains $(-CH_2-CHR-)_n$* is described as follows:

1. Let it be possible for an A or B to be present at every other corner of the square lattice. (see Figure 1) A and B are equivalent to the asymmetric carbon atoms of the vinylic chain.

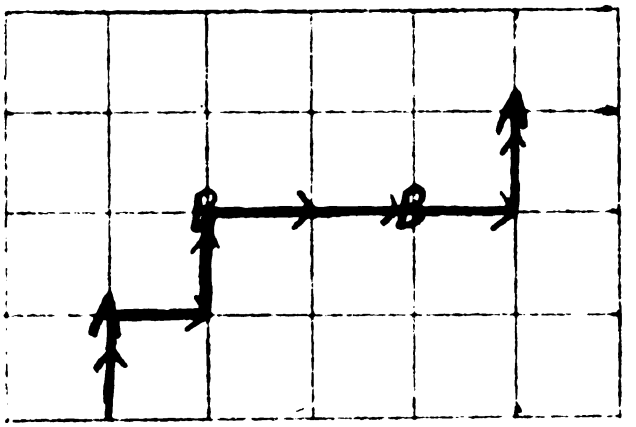


Figure 1. Polymer Chain on the Square Lattice.

2. Place the initial bond along the positive direction of the Y axis.

3. The conformational states are then defined as shown in Table 1.

---

* chains of this type have a periodicity of two

TABLE 1.

Conformational States for the Square Lattice Model

State	ν^{th} Bond Vector	$(\nu-1)+\nu^{th}$ Bonds	Bond Angle
1	↑	⇈	0
2	→	↑→	$3\pi/2$
3*	↓	↑↓	π
4	←	←↑	$\pi/2$

is measured in a counter-clockwise direction from the projection of the Y axis $(\nu-1)^{th}$ bond vector.

4. The configurational states are defined as shown in Table 2.

TABLE 2.

Configurational States for the Square Lattice Model

Configuration	Growing Chain Ends	Reaction Products		Free Energy of Activation
A A A→1	d d	d d d	I	ϵ_1
A A B→2	d d	d d l	H	ϵ_2
B B B→3	l l	l l l	I	ϵ_3
B B A→4	l l	l l d	H	ϵ_4
B A B→5	l d	l d l	S	ϵ_5
B A A→6	l d	l d d	H	ϵ_6
A B B→7	d l	d l l	H	ϵ_7
A B A→8	d l	d l d	S	ϵ_8

I = isotactic H = heterotactic S = syndiotactic

5. The numbering system used for the chain atoms and bonds is shown in Figure 2.

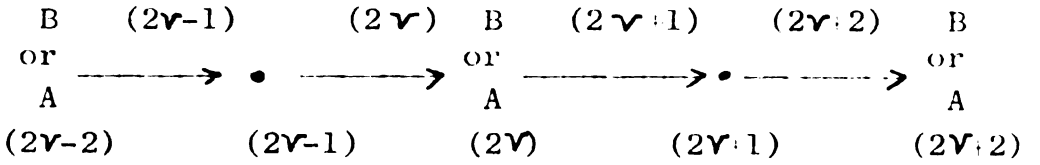


Figure 2. Numbering System Used for the Chain Atoms and Bonds.*

6. The coordinate system used is the same as that described by Yoo and Kinsinger. For a bond vector terminating at an asymmetric chain atom, a right-handed system is used for a bond terminating at a d configuration (A site) and a left-handed system is used for a bond terminating at an l configuration (B site). For a bond vector terminating at a methylenic type chain atom, a right-handed system is used if the CHR-CH_2 bond originates from a d configuration (A site) and a left-handed system is used if the CHR-CH_2 bond originates from an l configuration (B site).

7. The equations used are those described by Yoo and Kinsinger. We consider here only first and second neighbor interactions. The generator (or state) matrices are defined on the following pages.

*The numbers for the bonds appear at the top of the figure directly above the bond which is shown as an arrow. The numbers for the chain atoms appear at the bottom of the figure directly under the chain atom.

$$\left[U^{(W)}_{2\gamma-1}\right] \qquad \begin{bmatrix} U^{0(W)}_{11} & U^{0(W)}_{12} & U^{0(W)}_{13} & U^{0(W)}_{14} \\ U^{0(W)}_{21} & U^{0(W)}_{22} & U^{0(W)}_{23} & U^{0(W)}_{24} \\ U^{0(W)}_{31} & U^{0(W)}_{32} & U^{0(W)}_{33} & U^{0(W)}_{34} \\ U^{0(W)}_{41} & U^{0(W)}_{42} & U^{0(W)}_{43} & U^{0(W)}_{44} \end{bmatrix} \qquad (1)$$

where w = 1 when A ——•—— A

w = 2 when B ——•—— B

w = 3 when B ——•—— A

w = 4 when A ——•—— B

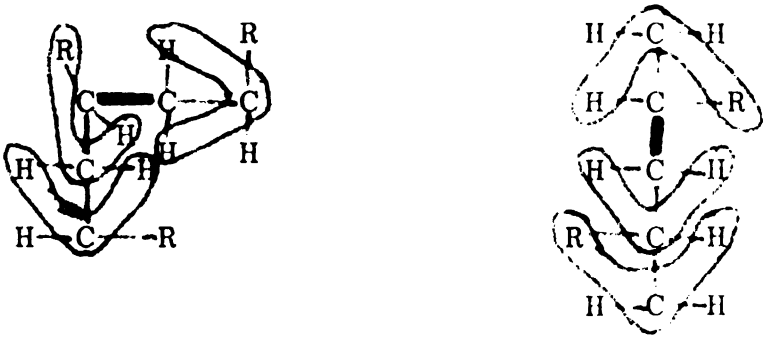
Matrix (1) is a generator matrix for one of the conformational matrices. The elements of matrix (1) are defined in equation (2).

$$U^{0(W)}_{rt} = \exp\left[-\left\{\epsilon^{(W)}(\theta^{(r)}_{2\gamma+1}) + \epsilon^{(W)}(\theta^{(t)}_{2\gamma}\,\theta^{(r)}_{2\gamma+1})\right\}\Big/_{RT}\right] \qquad (2)$$

first neighbor interaction term

second neighbor interaction term

In $U_{2\gamma+1}$ the $2\gamma+1$ signifies the rotation of the $2\gamma+2$ bond about $2\gamma+1$. $U^{(W)}_{rt}$ is a term proportional to the probability that the last bond will be in state r when the previous bond is in state t and the configuration state is (W). The first and second neighbor interactions are depicted schematically in Figure 3.



a $(2\ell+1)$ bond a (2ℓ) bond

Figure 3. Schematic diagram showing the first and second neighbor interactions for a $(2\ell+1)$ and a (2ℓ) bond.

$$\left[D^{(w)}_{2\ell+1}\right] = \begin{bmatrix} D^{1}_{2\ell+1} & 0 & 0 & 0 \\ 0 & D^{2}_{2\ell+1} & 0 & 0 \\ 0 & 0 & D^{3}_{2\ell+1} & 0 \\ 0 & 0 & 0 & D^{4}_{2\ell+1} \end{bmatrix} \qquad (3)$$

Matrix (3) is a transformation matrix which is part of the transformation matrix $[D_{2\ell+1}]$.

$$\left[\Phi_{2\nu+1}\right] = \begin{bmatrix} U^{(1)}_{2\nu+1} & 0 & 0 & 0 \\ 0 & U^{(2)}_{2\nu+1} & 0 & 0 \\ 0 & 0 & U^{(3)}_{2\nu+1} & 0 \\ 0 & 0 & 0 & U^{(4)}_{2\nu+1} \end{bmatrix} \quad (4)$$

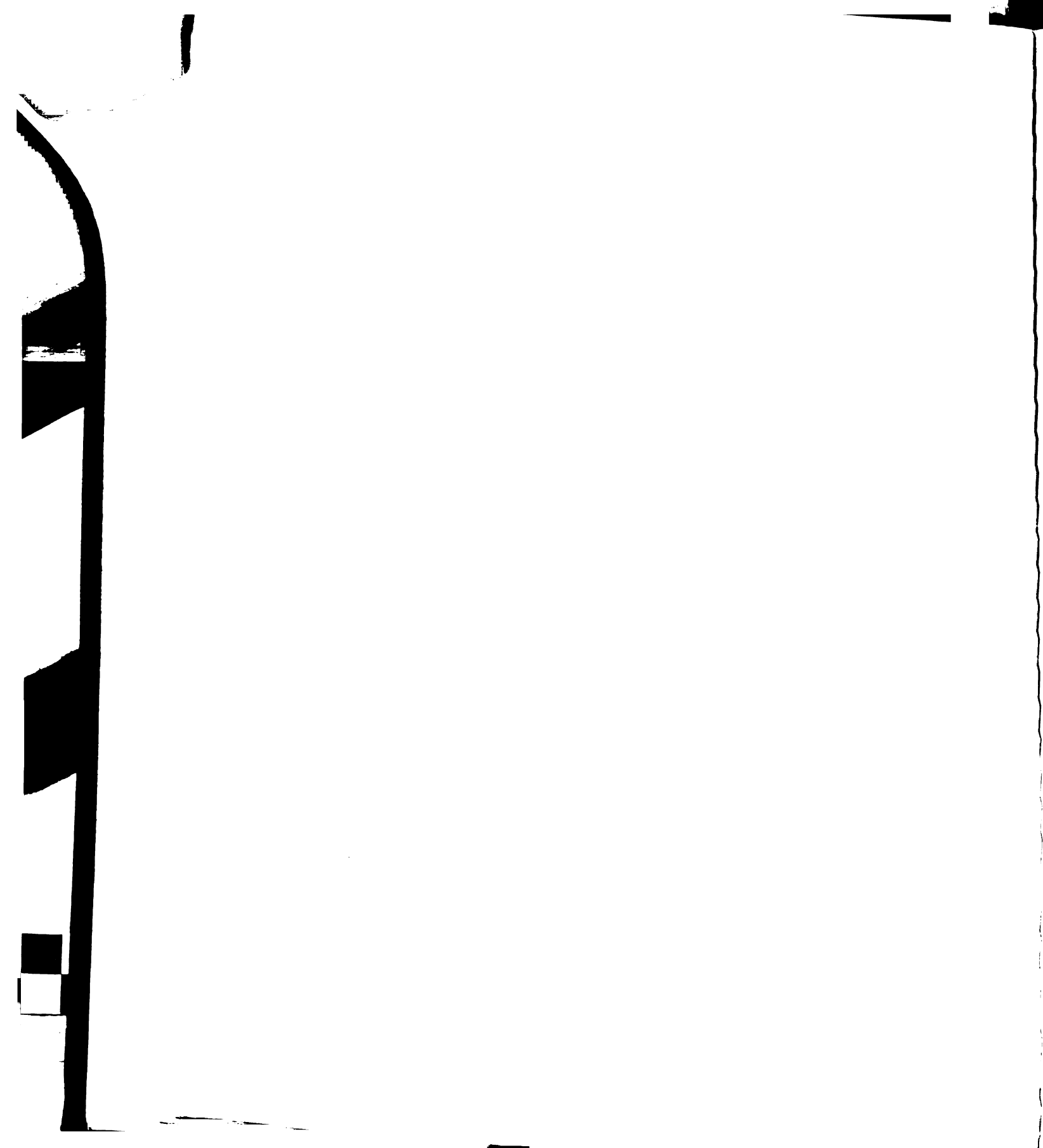
Matrix (4) is the conformational matrix for $2\nu+2$ bonds about $2\nu+1$ bonds.

$$\left[\Sigma_{2\nu+1}\right] = \begin{bmatrix} C_1 & 0 & C_6 & 0 \\ 0 & C_3 & 0 & C_7 \\ 0 & C_4 & 0 & C_8 \\ C_2 & 0 & C_5 & 0 \end{bmatrix} \quad (5)$$

Matrix (5) is the configuration generator matrix.

$$C_i \quad \exp \; -\epsilon_i/RT \quad (6)$$

where ϵ_i is the free energy of activation for a given configuration as defined in Table 2.



$$\left[D_{2\gamma+1}\right] = \begin{bmatrix} D^{(1)}_{2\gamma+1} & 0 & 0 & 0 \\ 0 & D^{(2)}_{2\gamma+1} & 0 & 0 \\ 0 & 0 & D^{(3)}_{2\gamma+1} & 0 \\ 0 & 0 & 0 & D^{(4)}_{2\gamma+1} \end{bmatrix} \qquad (7)$$

Matrix (7) is the transformation matrix for transforming the coordinates of a $2\gamma+2$ bond into the coordinate system for a $2\gamma+1$ bond and each element on the diagonal is a transformation matrix as given in (3).

Up to this point we have been considering the bond type $\left[\bullet \text{---} \begin{matrix} A \\ \text{or} \\ B \end{matrix}\right]$

Now in a similar fashion we will consider the bond type $\left[\begin{matrix} A \\ \text{or} \\ B \end{matrix} \text{---} \bullet\right]$

Then:

$$\left[U^{(w)}_{2\gamma}\right] \qquad \begin{bmatrix} U^{E(w)}_{11} & U^{E(w)}_{12} & U^{E(w)}_{13} & U^{E(w)}_{14} \\ U^{E(w)}_{21} & U^{E(w)}_{22} & U^{E(w)}_{23} & U^{E(w)}_{24} \\ U^{E(w)}_{31} & U^{E(w)}_{32} & U^{E(w)}_{33} & U^{E(w)}_{34} \\ U^{E(w)}_{41} & U^{E(w)}_{42} & U^{E(w)}_{43} & U^{E(w)}_{44} \end{bmatrix} \qquad (8)$$

Matrix (8) is a generator matrix for one of the conformational matrices.

where $w = 1$ when $\bullet$ ——— A ——— $\bullet$

$w = 2$ when $\bullet$ ——— B ——— $\bullet$

$$U_{rt}^{E(w)} \qquad \exp\left[-\left\{ \epsilon^{(w)}(\theta_{2\nu}^{(r)}) + \epsilon^{(w)}(\theta_{2\nu-1}^{t}\ \theta_{2\nu}^{r}) \right\} / RT \right] \qquad (9)$$

first neighbor interaction term

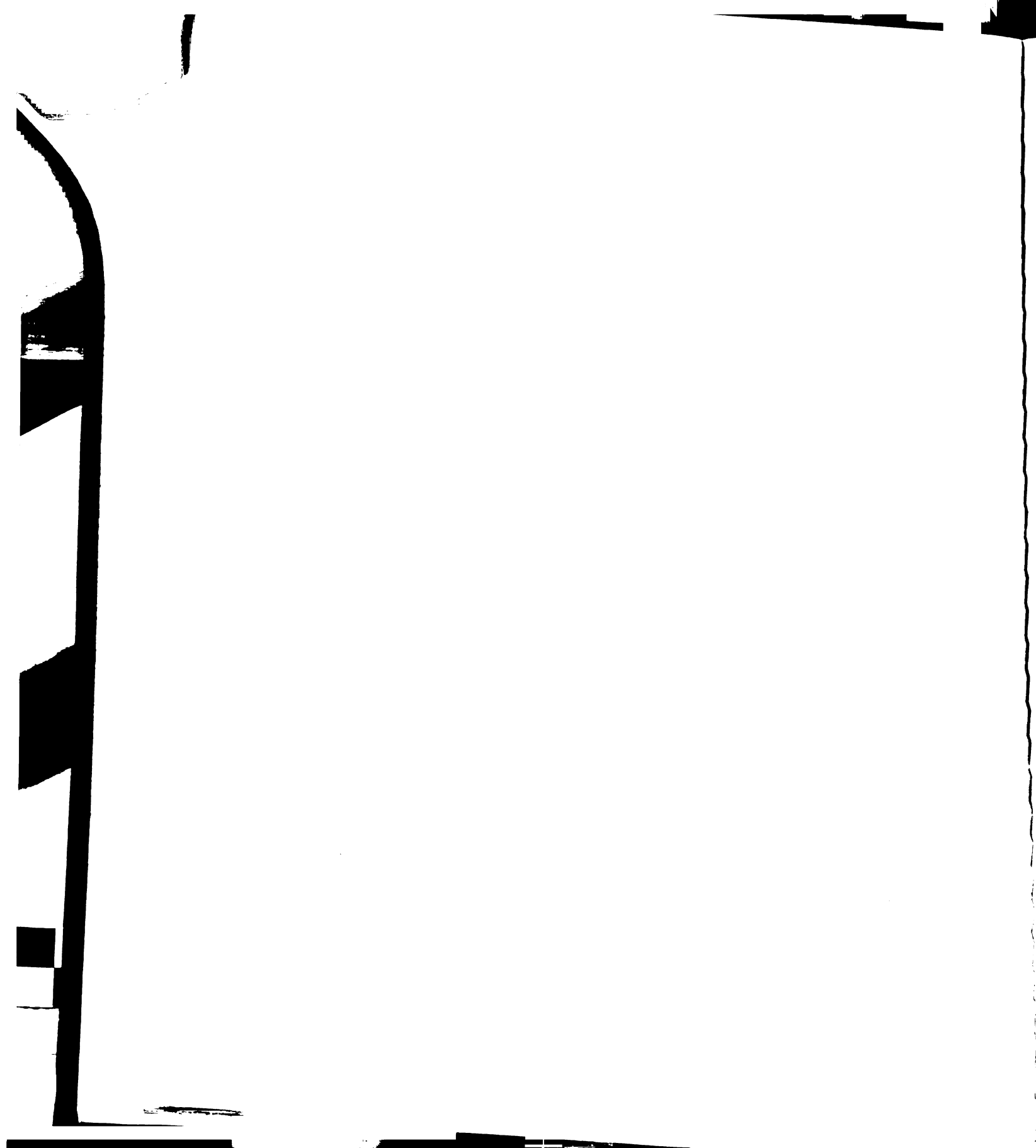
second neighbor interaction term

$$\left[D_{2\nu}^{(w)}\right] \qquad \begin{bmatrix} D_{2\nu}^{1} & 0 & 0 & 0 \\ 0 & D_{2\nu}^{2} & 0 & 0 \\ 0 & 0 & D_{2\nu}^{3} & 0 \\ 0 & 0 & 0 & D_{2\nu}^{4} \end{bmatrix} \qquad (10)$$

Matrix (10) is a transformation matrix which is part of the transformation $\left[D_{2\nu}\right]$.

$$\left[\Phi_{2\nu}\right] \qquad \begin{bmatrix} U_{2\nu}^{(1)} & 0 & 0 & 0 \\ 0 & U_{2\nu}^{(2)} & 0 & 0 \\ 0 & 0 & U_{2\nu}^{(1)} & 0 \\ 0 & 0 & 0 & U_{2\nu}^{(2)} \end{bmatrix} \qquad (11)$$

Matrix (11) is the conformational matrix for $2\nu-1$ bonds about 2ν bonds.



$$[D_{2\nu}] = \begin{bmatrix} D_{2\nu}^{(1)} & 0 & 0 & 0 \\ 0 & D_{2\nu}^{(2)} & & \\ 0 & & D_{2\nu}^{(3)} & \\ 0 & & & D_{2\nu}^{(4)} \end{bmatrix} \quad (12)$$

Matrix (12) is the transformation matrix for transforming the coordinates of a $2\nu+1$ bond into the coordinate system for a 2ν bond and each element on the diagonal is a transformation matrix as given in (10).

The final equation used to calculate the unperturbed dimensions of the various cases is shown in equation (13) as adopted from the three dimensional formalism of Yoo and Kinsinger.[8]

$$\langle r_n^2 \rangle_{n1}^2 = [0\ 1]\left[E_2 + \Delta^* N \Delta \cdot \Delta^* (E_{32}+N)(E_{32}-M)^{-1}(M+D_{2\nu})\Delta\right]\begin{bmatrix}0\\1\end{bmatrix} \quad (13)$$

where $M = \dfrac{[D_{2\nu}][\Phi_{2\nu}]_2 [D_{2\nu+1}][\Phi_{2\nu+1}]_2 [\Sigma_{2\nu+1}]_{4\times 2}}{\mathcal{J}}$

$$N = \frac{[\Phi_{2\nu}]_2 [D_{2\nu+1}][\Phi_{2\nu+1}]_2 [\Sigma_{2\nu+1}]_{4\times 2}}{\mathcal{J}}$$

$\Delta = [\mathcal{J}]_2$

$\Delta^* = [\mathcal{J}^*]_2$

$\mathcal{J}$ = the largest positive eigenvalue of $[\Phi_{2\nu}][\Phi_{2\nu+1}][\Sigma_{2\nu+1}]_4$

$\mathcal{J}$ = the eigenvector corresponding to the above eigenvalue

$\mathcal{J}^*$ = the eigenrow corresponding to the above eigenvalue

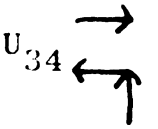
E_2 = a 2 x 2 identity matrix

E_{32} = a 32 x 32 identity matrix

The bonds considered in matrices $[\Phi_{2r}]$ and $[\Phi_{2r+1}]$ are shown in Tables 3 and 4. The matrices $[D_{2r}]$, $[D_{2r+1}]$, $[\Phi_{2r}]_2$, $[\Phi_{2r+1}]_2$, and $[\Sigma_{2r+1}]_{2 \times 4}$ are shown in Tables 5, 6, 7, 8, and 9. The derivations of the two transformation matrices are given in Appendix A.

8. In this square lattice we only allow the growing chain end to go in three directions. We disallow it to reverse its previous direction. This causes the following elements of the U matrices to be zero.

U_{13} U_{23}  U_{33}  U_{43} 

U_{31}  U_{32}  U_{34} 

Due to symmetry many of the elements within U are identical to other U elements. These identities are shown in Tables 10 and 11.

TABLE 3.

Bonds of Matrix $[\Phi_{2n}]_2$

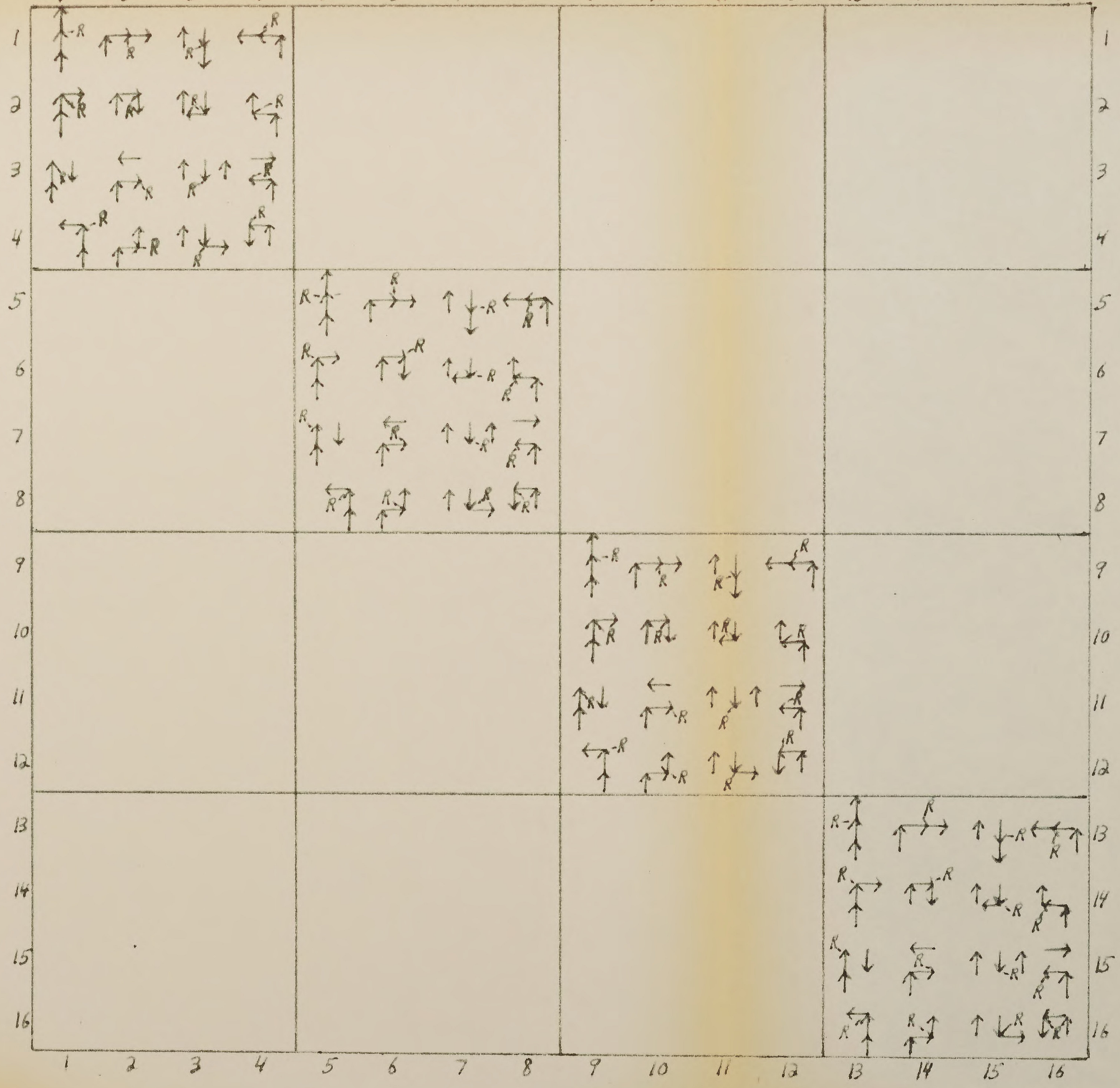


TABLE 4.

Bonds of

Matrix $\left[\Phi_{2V+1}\right]_2$

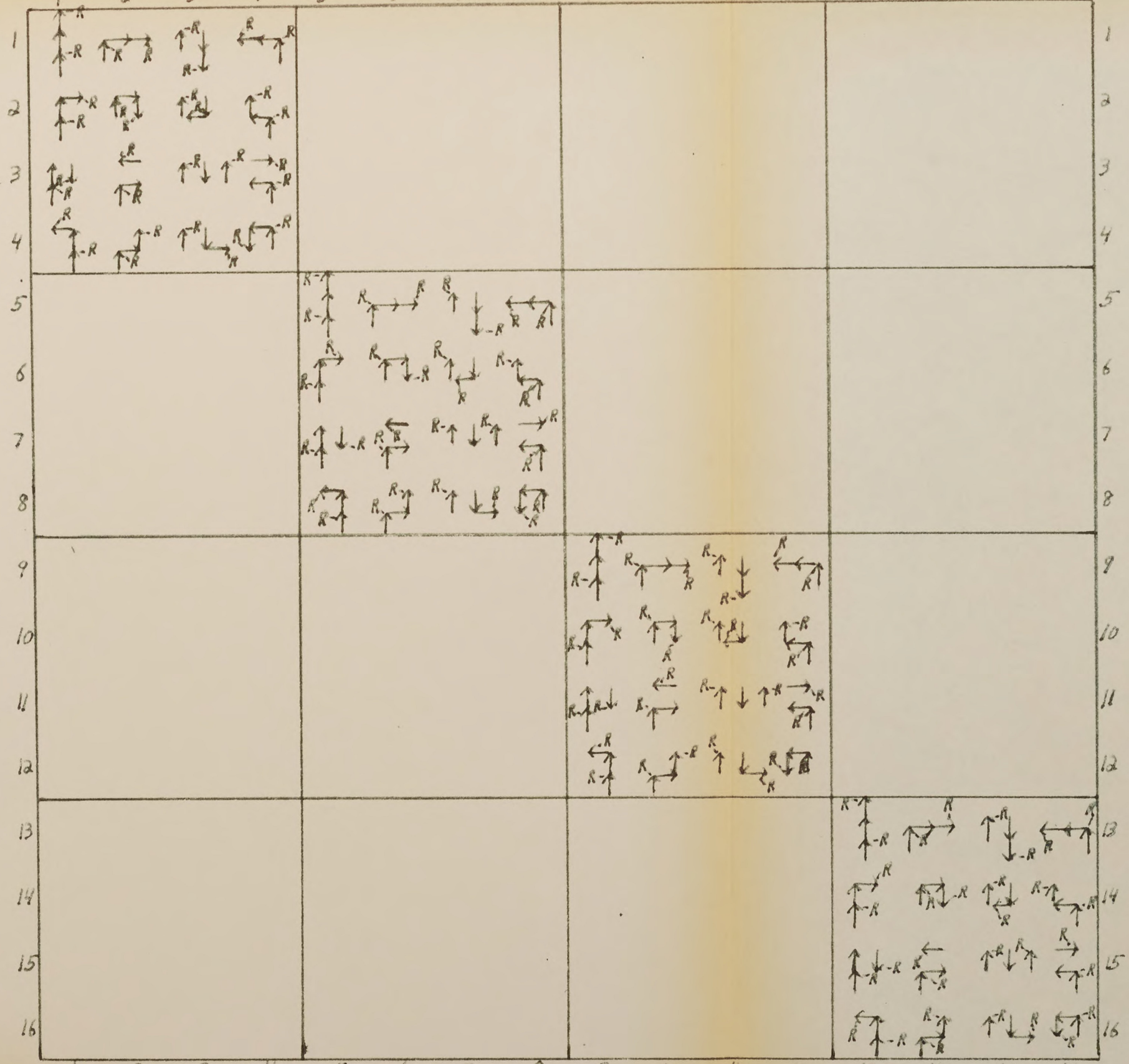


TABLE 5.

TRANSFORMATION MATRIX $D_{2\gamma}$

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32
1	1	0																														
2	0	1																														
3			0	-1																												
4			1	0																												
5					-1	0																										
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29																													-1	0		
30																													0	-1		
31																															0	-1
32																															1	0

TABLE 6.

TRANSFORMATION MATRIX $D_{2^{\gamma}+1}$

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32
1	1	0																														
2	0	1																														
3			0	-1																												
4			1	0																												
5					-1	0																										
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31																															-1	0
32																															0	1

TABLE 7. Matrix $[\bar{\Phi}_{2v}]_2$

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32
1	U^{E1}_{11}		U^{E1}_{12}				U^{E1}_{14}																									
2		U^{E1}_{11}		U^{E1}_{12}				U^{E1}_{14}																								
3	U^{E1}_{21}		U^{E1}_{22}				U^{E1}_{24}																									
4		U^{E1}_{21}		U^{E1}_{22}				U^{E1}_{24}																								
5 and 6																																
7	U^{E1}_{41}		U^{E1}_{42}				U^{E1}_{44}																									
8		U^{E1}_{41}		U^{E1}_{42}				U^{E1}_{44}																								
9									U^{E2}_{11}		U^{E2}_{12}				U^{E2}_{14}																
10										U^{E2}_{11}		U^{E2}_{12}				U^{E2}_{14}																
11									U^{E2}_{21}		U^{E2}_{22}				U^{E2}_{24}																
12										U^{E2}_{21}		U^{E2}_{22}				U^{E2}_{24}																
13 and 14																																
15									U^{E2}_{41}		U^{E2}_{42}				U^{E2}_{44}																
16										U^{E2}_{41}		U^{E2}_{42}				U^{E2}_{44}																
17																	U^{E3}_{11}		U^{E3}_{12}			U^{E3}_{14}										
18																		U^{E3}_{11}		U^{E3}_{12}			U^{E3}_{14}									
19																	U^{E3}_{21}		U^{E3}_{22}			U^{E3}_{24}										
20																		U^{E3}_{21}		U^{E3}_{22}			U^{E3}_{24}									
21 and 22																																
23																	U^{E3}_{41}		U^{E3}_{42}			U^{E3}_{44}										
24																		U^{E3}_{41}		U^{E3}_{42}			U^{E3}_{44}									
25																					U^{E4}_{11}		U^{E4}_{12}			U^{E4}_{14}						
26																						U^{E4}_{11}		U^{E4}_{12}			U^{E4}_{14}					
27																					U^{E4}_{21}		U^{E4}_{22}			U^{E4}_{24}						
28																						U^{E4}_{21}		U^{E4}_{22}			U^{E4}_{24}					
29 and 30																																
31																					U^{E4}_{41}		U^{E4}_{42}			U^{E4}_{44}						
32																						U^{E4}_{41}		U^{E4}_{42}			U^{E4}_{44}					

TABLE 8. Matrix $[\Phi_{2v+1}]_2$

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32
1	U^{01}_{11}		U^{01}_{12}				U^{01}_{14}																									
2		U^{01}_{11}		U^{01}_{12}				U^{01}_{14}																								
3	U^{01}_{21}		U^{01}_{22}				U^{01}_{24}																									
4		U^{01}_{21}		U^{01}_{22}				U^{01}_{24}																								
5 and 6																																
7	U^{01}_{41}		U^{01}_{42}				U^{01}_{44}																									
8		U^{01}_{41}		U^{01}_{42}				U^{01}_{44}																								
9									U^{02}_{11}		U^{02}_{12}				U^{02}_{14}															
10										U^{02}_{11}		U^{02}_{12}				U^{02}_{14}															
11									U^{02}_{21}		U^{02}_{22}				U^{02}_{24}															
12										U^{02}_{21}		U^{02}_{22}				U^{02}_{24}															
13 and 14																																
15									U^{02}_{41}		U^{02}_{42}				U^{02}_{44}															
16										U^{02}_{41}		U^{02}_{42}				U^{02}_{44}															
17																	U^{03}_{11}		U^{03}_{12}				U^{03}_{14}									
18																		U^{03}_{11}		U^{03}_{12}				U^{03}_{14}								
19																	U^{03}_{21}		U^{03}_{22}				U^{03}_{24}									
20																		U^{03}_{21}		U^{03}_{22}				U^{03}_{24}								
21 and 22																																
23																	U^{03}_{41}		U^{03}_{42}				U^{03}_{44}									
24																		U^{03}_{41}		U^{03}_{42}				U^{03}_{44}								
25																									U^{04}_{11}		U^{04}_{12}				U^{04}_{14}	
26																										U^{04}_{11}		U^{04}_{12}				U^{04}_{14}
27																									U^{04}_{21}		U^{04}_{22}				U^{04}_{24}	
28																										U^{04}_{21}		U^{04}_{22}				U^{04}_{24}
29 and 30																																
31																									U^{04}_{41}		U^{04}_{42}				U^{04}_{44}	
32																										U^{04}_{41}		U^{04}_{42}				U^{04}_{44}

TABLE 9. $\left[\sum_2 \nu^{-1}\right]_{2\times 4}$

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32
1	C_1																C_6															
2		C_1																C_6														
3			C_1																C_6													
4				C_1																C_6												
5					C_1																C_6											
6						C_1																C_6										
7							C_1																C_6									
8								C_1																C_6								
9									C_3																C_7							
10										C_3																C_7						
11											C_3																C_7					
12												C_3																C_7				
13													C_3																C_7			
14														C_3																C_7		
15															C_3																C_7	
16																C_3																C_7
17									C_4																C_8							
18										C_4																C_8						
19											C_4																C_8					
20												C_4																C_8				
21													C_4																C_8			
22														C_4																C_8		
23															C_4																C_8	
24																C_4																C_8
25	C_2																C_5															
26		C_2																C_5														
27			C_2																C_5													
28				C_2																C_5												
29					C_2																C_5											
30						C_2																C_5										
31							C_2																C_5									
32								C_2																C_5								

TABLE 10.

Equalities in the U_{ij} elements.

$$U_{11}^{E1} = U_{11}^{E2} = U_{11}^{E3} = U_{11}^{E4}$$

$$U_{12}^{E1} = U_{14}^{E2} = U_{12}^{E3} = U_{14}^{E4}$$

$$U_{14}^{E1} = U_{12}^{E2} = U_{14}^{E3} = U_{12}^{E4}$$

$$U_{21}^{E1} = U_{41}^{E2} = U_{21}^{E3} = U_{41}^{E4}$$

$$U_{22}^{E1} = U_{44}^{E2} = U_{22}^{E3} = U_{44}^{E4}$$

$$U_{24}^{E1} = U_{42}^{E2} = U_{24}^{E3} = U_{42}^{E4}$$

$$U_{41}^{E1} = U_{21}^{E2} = U_{41}^{E3} = U_{21}^{E4}$$

$$U_{42}^{E1} = U_{24}^{E2} = U_{42}^{E3} = U_{24}^{E4}$$

$$U_{44}^{E1} = U_{22}^{E2} = U_{44}^{E3} = U_{22}^{E4}$$

$$U_{11}^{01} = U_{11}^{02}$$

$$U_{11}^{03} = U_{11}^{04}$$

$$U_{12}^{01} = U_{14}^{02}$$

$$U_{12}^{03} = U_{14}^{04}$$

$$U_{14}^{01} = U_{12}^{02}$$

$$U_{14}^{03} = U_{12}^{04}$$

$$U_{21}^{01} = U_{41}^{02}$$

$$U_{21}^{03} = U_{41}^{04}$$

$$U_{22}^{01} = U_{44}^{02}$$

$$U_{22}^{03} = U_{44}^{04}$$

$$U_{24}^{01} = U_{42}^{02}$$

$$U_{24}^{03} = U_{42}^{04}$$

$$U_{41}^{01} = U_{21}^{02}$$

$$U_{41}^{03} = U_{21}^{04}$$

$$U_{42}^{01} = U_{24}^{02}$$

$$U_{42}^{03} = U_{24}^{04}$$

$$U_{44}^{01} = U_{22}^{02}$$

$$U_{44}^{03} = U_{22}^{04}$$

Table 11

Equalities in the first and second neighbor parts of the U_{ij} elements.

α - first neighbor $\quad U = e^{-\epsilon/RT}\, U_{11}^{E1} \cdot (U_{11}^{\alpha E1})(U_{11}^{\beta E1})$

β - second neighbor

$U_{11}^{\alpha E1} = U_{11}^{\alpha E2} = U_{11}^{\alpha E3} = U_{11}^{\alpha E4} = U_{12}^{\alpha E1} = U_{12}^{\alpha E2} = U_{12}^{\alpha E3} = U_{12}^{\alpha E4} = U_{14}^{\alpha E1} = U_{14}^{\alpha E2} = U_{14}^{\alpha E3} = U_{14}^{\alpha E4}$

$U_{21}^{\alpha E1} = U_{41}^{\alpha E2} = U_{21}^{\alpha E3} = U_{41}^{\alpha E4} = U_{22}^{\alpha E1} = U_{44}^{\alpha E2} = U_{22}^{\alpha E3} = U_{44}^{\alpha E1} = U_{24}^{\alpha E1} = U_{42}^{\alpha E2} = U_{24}^{\alpha E3} = U_{42}^{\alpha E4}$

$U_{41}^{\alpha E1} = U_{21}^{\alpha E2} = U_{41}^{\alpha E3} = U_{21}^{\alpha E4} = U_{44}^{\alpha E1} = U_{22}^{\alpha E2} = U_{44}^{\alpha E3} = U_{22}^{\alpha E4} = U_{42}^{\alpha E1} = U_{24}^{\alpha E2} = U_{42}^{\alpha E3} = U_{24}^{\alpha E4}$

$U_{11}^{\alpha 01} = U_{11}^{\alpha 02} = U_{11}^{\alpha 03} = U_{11}^{\alpha 04} = U_{12}^{\alpha 01} = U_{12}^{\alpha 02} = U_{12}^{\alpha 03} = U_{12}^{\alpha 04} = U_{14}^{\alpha 01} = U_{14}^{\alpha 02} = U_{14}^{\alpha 03} = U_{14}^{\alpha 04}$

$U_{21}^{\alpha 01} = U_{41}^{\alpha 02} = U_{21}^{\alpha 03} = U_{41}^{\alpha 04} = U_{22}^{\alpha 01} = U_{44}^{\alpha 02} = U_{22}^{\alpha 03} = U_{44}^{\alpha 04} = U_{24}^{\alpha 01} = U_{42}^{\alpha 02} = U_{24}^{\alpha 03} = U_{42}^{\alpha 04}$

$U_{41}^{\alpha 01} = U_{21}^{\alpha 02} = U_{41}^{\alpha 03} = U_{21}^{\alpha 04} = U_{44}^{\alpha 01} = U_{22}^{\alpha 02} = U_{44}^{\alpha 03} = U_{22}^{\alpha 04} = U_{42}^{\alpha 01} = U_{24}^{\alpha 02} = U_{42}^{\alpha 03} = U_{24}^{\alpha 04}$

$U_{11}^{\beta E1} = U_{11}^{\beta E2} = U_{11}^{\beta E3} = U_{11}^{\beta E4} \qquad U_{11}^{\beta 03} = U_{11}^{\beta 04} = U_{11}^{\beta 01} = U_{11}^{\beta 02}$

$U_{12}^{\beta E1} = U_{14}^{\beta E2} = U_{12}^{\beta E3} = U_{14}^{\beta E4} \qquad U_{14}^{\beta E1} = U_{12}^{\beta E2} = U_{14}^{\beta E3} = U_{12}^{\beta E4}$

$U_{21}^{\beta E1} = U_{41}^{\beta E2} = U_{21}^{\beta E3} = U_{41}^{\beta E4} \qquad U_{41}^{\beta E1} = U_{21}^{\beta E2} = U_{41}^{\beta E3} = U_{21}^{\beta E4}$

$U_{22}^{\beta E1} = U_{44}^{\beta E2} = U_{22}^{\beta E3} = U_{44}^{\beta E4} \qquad U_{44}^{\beta E1} = U_{22}^{\beta E2} = U_{44}^{\beta E3} = U_{22}^{\beta E4}$

$U_{24}^{\beta E1} = U_{42}^{\beta E2} = U_{24}^{\beta E3} = U_{42}^{\beta E4} \qquad U_{42}^{\beta E1} = U_{24}^{\beta E2} = U_{42}^{\beta E3} = U_{24}^{\beta E4}$

$U_{14}^{\beta 01} = U_{12}^{\beta 02} = U_{14}^{\beta 03} = U_{12}^{\beta 04} \qquad U_{12}^{\beta 03} = U_{14}^{\beta 04} = U_{12}^{\beta 01} = U_{14}^{\beta 02}$

$U_{42}^{\beta 01} = U_{24}^{\beta 02} = U_{42}^{\beta 03} = U_{24}^{\beta 04} \qquad U_{24}^{\beta 03} = U_{42}^{\beta 04} = U_{24}^{\beta 01} = U_{42}^{\beta 02}$

$U_{41}^{\beta 01} = U_{21}^{\beta 02} = U_{41}^{\beta 03} = U_{21}^{\beta 04} \qquad U_{21}^{\beta 03} = U_{41}^{\beta 04} = U_{21}^{\beta 01} = U_{41}^{\beta 02}$

$U_{44}^{\beta 01} = U_{22}^{\beta 02} = U_{44}^{\beta 03} = U_{22}^{\beta 04} \qquad U_{22}^{\beta 03} = U_{44}^{\beta 04} = U_{22}^{\beta 01} = U_{44}^{\beta 02}$

II. CASES STUDIED AND COMPUTATIONAL PROCEDURE

A. Cases Studied

A description of the seven cases studied is shown on the following pages.

Case 1

$C_i = e^{-\epsilon_i/RT}$; $\epsilon_1 = \epsilon_2 = \epsilon_3 = \epsilon_4 = \epsilon_5 = \epsilon_6 = \epsilon_7 = \epsilon_8 = 7{,}000$ Cal/mole

$U = e^{-\epsilon/RT}$ where ϵ is the sum of the first and second neighbor interaction energies.

In case one the polymer has a random configuration.

U Conformation Element	Rotational Energy Assumed*
αO's = αE's	1000 Cal/mole
βO's = βE's	1000 Cal/mole

where αO is the 2+1 first neighbor interaction energy

αE is the 2+ first neighbor interaction energy

βO is the 2+1 second neighbor interaction energy

βE is the 2+ second neighbor interaction energy

This specifies that the polymer in case one has a random conformation in addition to a random configuration.

* The rotational energy values correspond to the energy differences between an arbitrary energy level and the lowest point in the rotational potential well.

Case 2

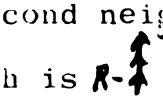
$$\epsilon_1 = \epsilon_2 = \epsilon_3 = \epsilon_4 = \epsilon_5 = \epsilon_6 = \epsilon_7 = \epsilon_8 = 7{,}000 \text{ cal/mole}$$

This polymer has a random configuration.

U Conformation Element	Rotational Energy assumed
$\alpha O^{'s} = \alpha E^{'s}$	1000 cal/mole
βEl_{11}	100 cal/mole
all other $\beta E^{'s}$ except βEl_{11}	200 cal/mole
$\beta 03_{11}$	100 cal/mole
all $\beta 03^{'s}$ that have a bent conformation	750 cal/mole
all $\beta 01^{'s}$ that have a bent conformation that permits the R groups to be further apart	1250 cal/mole
all $\beta 01^{'s}$ that have a bent conformation that permits the R groups to be closer together	2000 cal/mole

The preferred conformations have the lowest rotational energies.

βEl_{11} is the $2r$ second neighbor interaction energy of element $U_{11}^{(1)}$ which is 

$\beta 03_{11}$ is the $2r+1$ second neighbor interaction energy of element $U_{11}^{(3)}$ which is 

Case 3

$$\epsilon_1 = \epsilon_2 = \epsilon_3 = \epsilon_4 = \epsilon_5 = \epsilon_6 = \epsilon_7 = \epsilon_8 = 7{,}000 \text{ cal/mole}$$

This polymer has a random configuration.

U Conformation Element	Rotational energy assumed
$\alpha O^{'s} = \alpha E^{'s}$	500 cal/mole
$\beta O^{'s} = \beta E^{'s}$	500 cal/mole

This polymer has a random conformation.

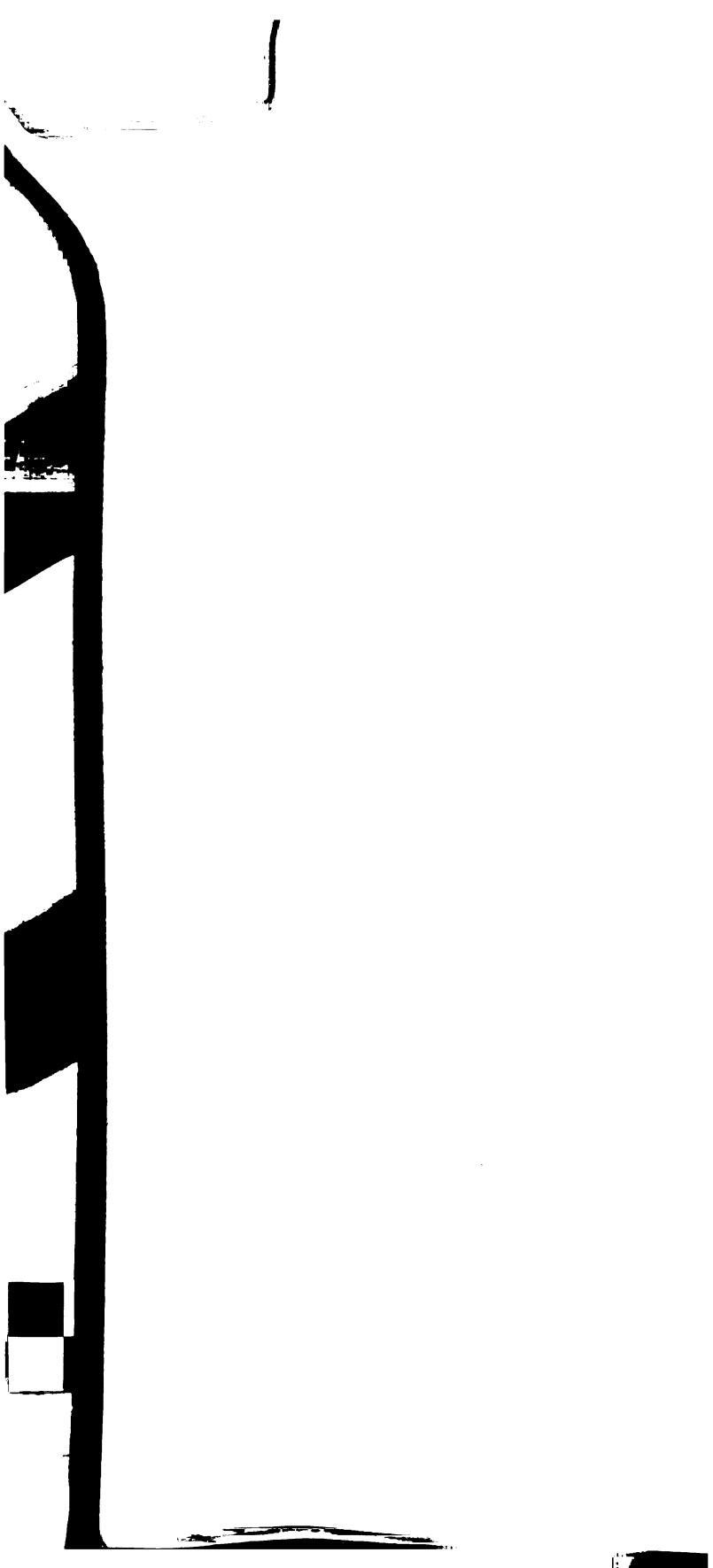
Case 4

$$\epsilon_1 = \epsilon_2 = \epsilon_3 = \epsilon_4 = \epsilon_5 = \epsilon_6 = \epsilon_7 = \epsilon_8 = 7{,}000 \text{ cal/mole}$$

This polymer has a random configuration.

U Conformation Element	Rotational Energy assumed
first neighbor H . . . H	50 cal/mole
first neighbor H . . . R	250-1000 cal/mole
second neighbor H . . . H	50-600 cal/mole
second neighbor H . . . R	200-2000 cal/mole
second neighbor R . . . R	800-2500 cal/mole

The rotational energies assumed were assigned after comparing the first and second neighbor interactions which can be seen in Tables 3 and 4. A "most probable" energy was assigned to each conformation based on our best interpretation of a real chain.



Case 5

$$\epsilon_1 = \epsilon_2 = \epsilon_3 = \epsilon_4 = \epsilon_5 = \epsilon_6 = \epsilon_7 = \epsilon_8 = 7{,}000 \text{ cal mole}$$

This polymer has a random configuration.

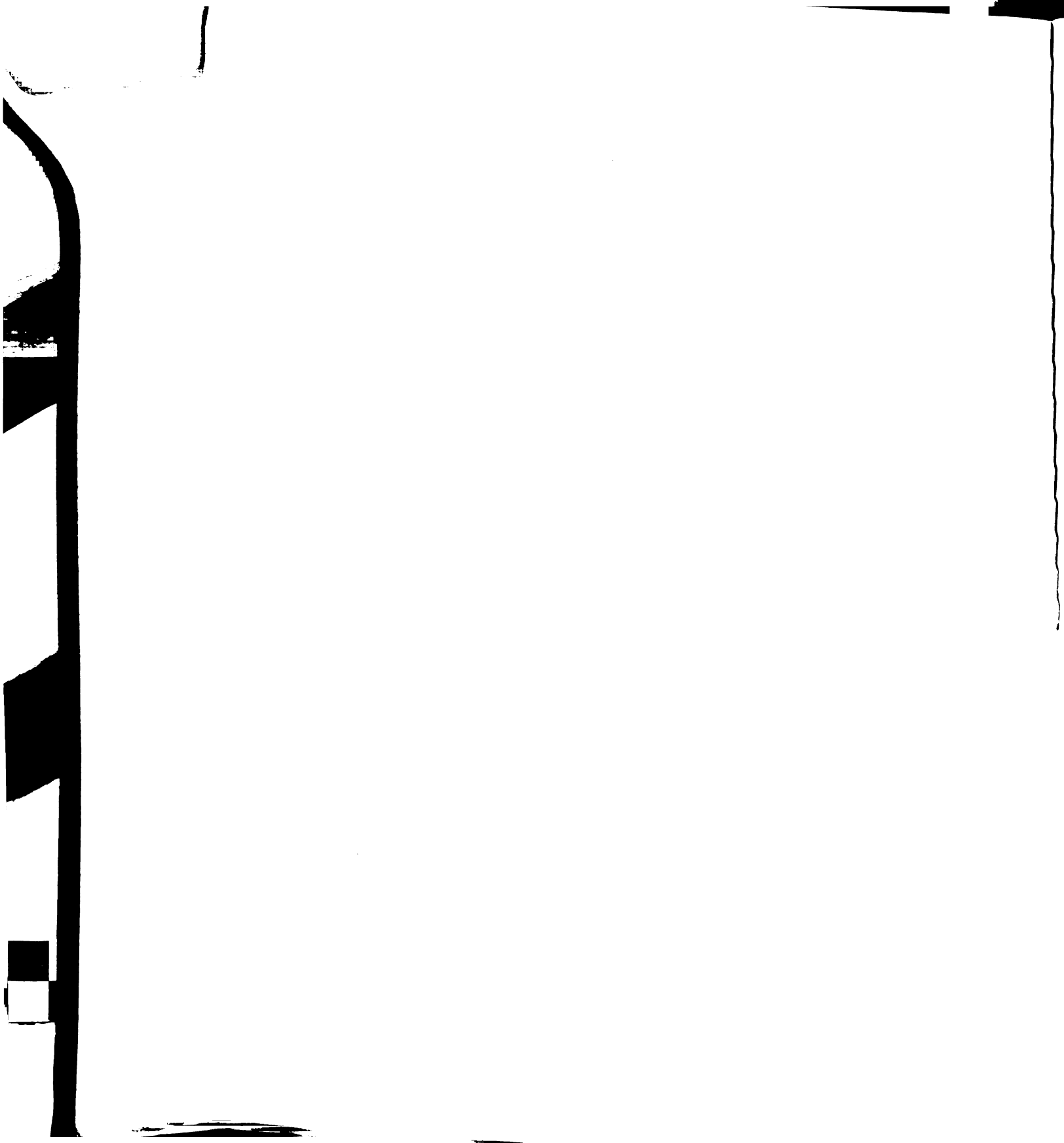
U Conformation Element	Rotational Energy assumed
α 0's = E's	500 cal/mole
β 03_{11} R -R	50 cal/mole
β 01_{44} R R	50 cal/mole
all other β 0's	1000 cal/mole
all β E's	1000 cal/mole

Case 6

$$\epsilon_1 = \epsilon_2 = \epsilon_3 = \epsilon_4 = \epsilon_6 = \epsilon_7 = 7{,}000 \text{ cal/mole}$$

$$\epsilon_5 = \epsilon_8 = 2{,}000 \text{ cal/mole}$$

This polymer has a predominantly syndiotactic configuration.



U Conformation Element	Rotational Energy Assumed
α O's = α E's	500 Cal/mole
$\beta 03_{11}$ R- ↑ -R	50 Cal/mole
$\beta 01_{44}$ R- ↓ ↑ -R	50 Cal/mole
all other β O's	1000 Cal/mole
all β E's	1000 Cal/mole

Case 7

$$\epsilon_2 = \epsilon_4 = \epsilon_5 = \epsilon_6 = \epsilon_7 = \epsilon_8 = 7{,}000 \text{ Cal/mole}$$

$$\epsilon_1 = \epsilon_3 = 2{,}000 \text{ Cal/mole}$$

This polymer has a predominately isotactic configuration preferred.

U Conformation Element	Rotational Energy Assumed
α O's = α E's	500 Cal/mole
$\beta 03_{11}$ R- ↑ -R	50 Cal/mole
$\beta 01_{44}$ R- ↓ ↑ -R	50 Cal/mole
All other β O's	1000 Cal/mole
All β E's	1000 Cal/mole

Tables 12, 13, and 14 show the reduced 12 x 12 matrix of $\left[\Phi_{2\nu}\right]\left[\Phi_{2\nu+1}\right]\left[\sum_{2\nu+1}\right]_4$.

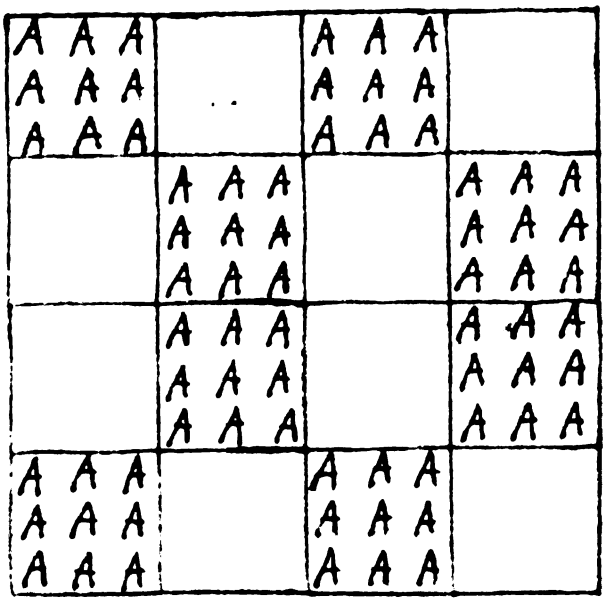
B. Computational Procedure

Case 1 will now be used as an example and the methods of computation will be described. The first step after assigning energies and calculating the various $U_{i,j}$ elements was to calculate the 16 x 16 matrix $\left[\Phi_{2\nu}\right]\left[\Phi_{2\nu+1}\right]\left[\sum_{2\nu+1}\right]_4$

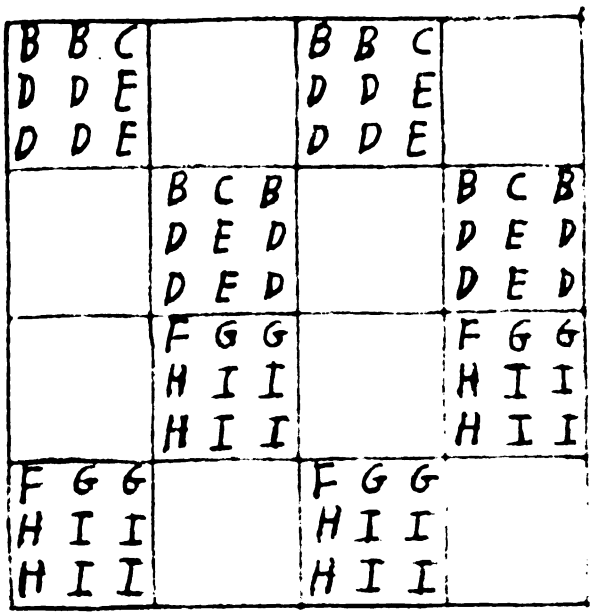
Table 12

Matrix $[\Phi_{av}][\Phi_{avt}][\Sigma_{avt}]_q$ cases 1-4

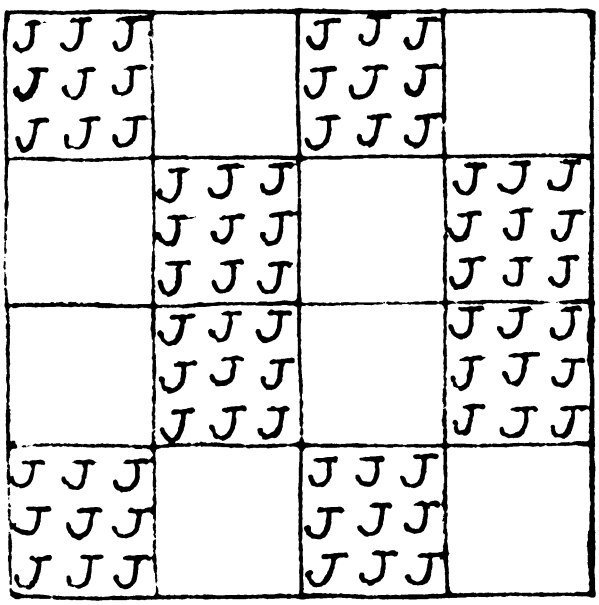
case 1



case 2



case 3



case 4

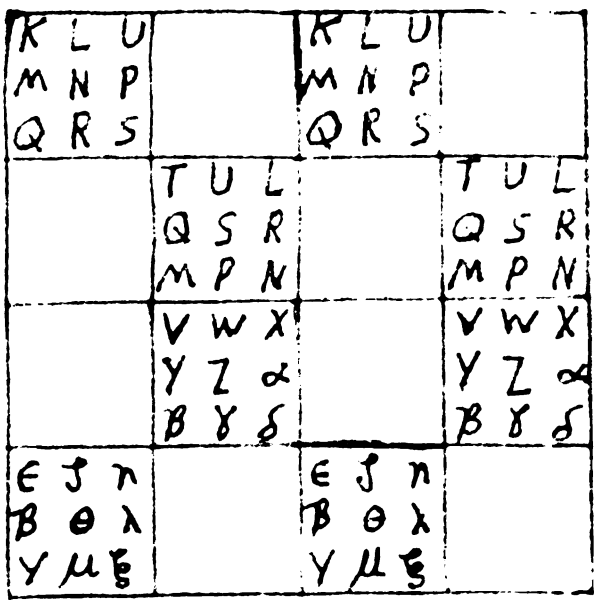
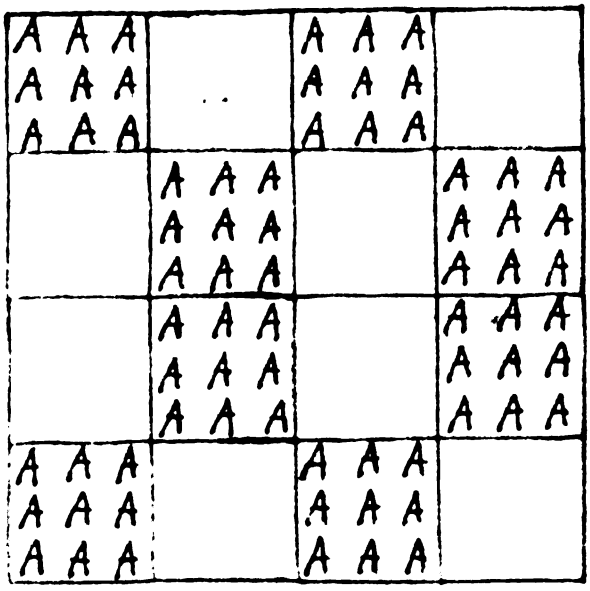


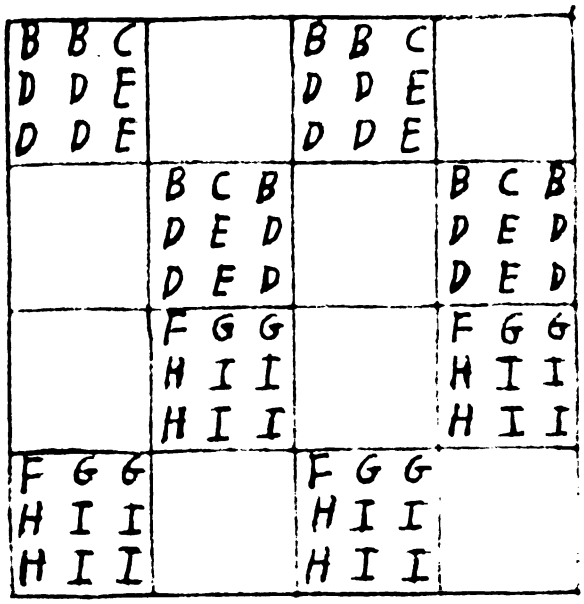
Table 12

Matrix $[\Phi_{av}][\Phi_{av+}][\Sigma_{av}]_{ij}$ cases 1-4

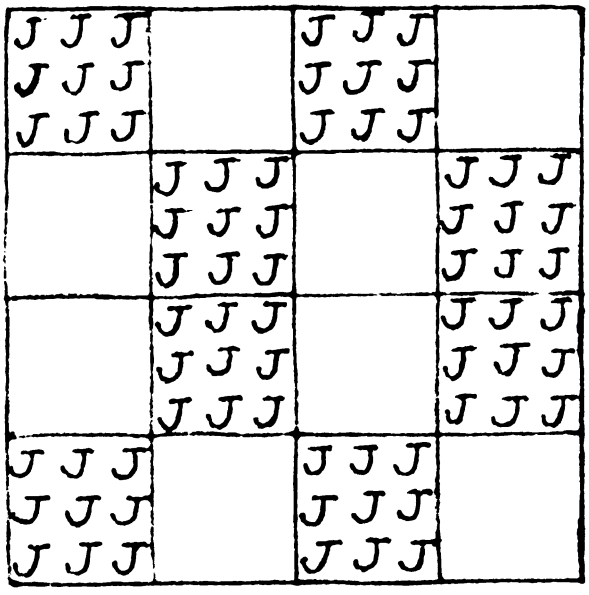
case 1



case 2



case 3



case 4

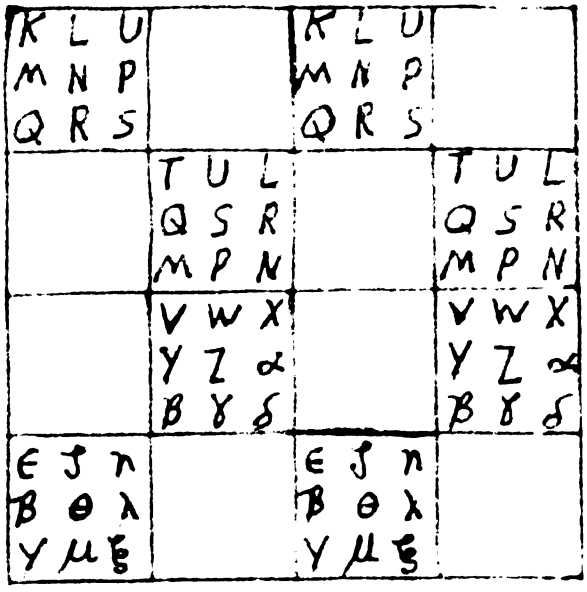
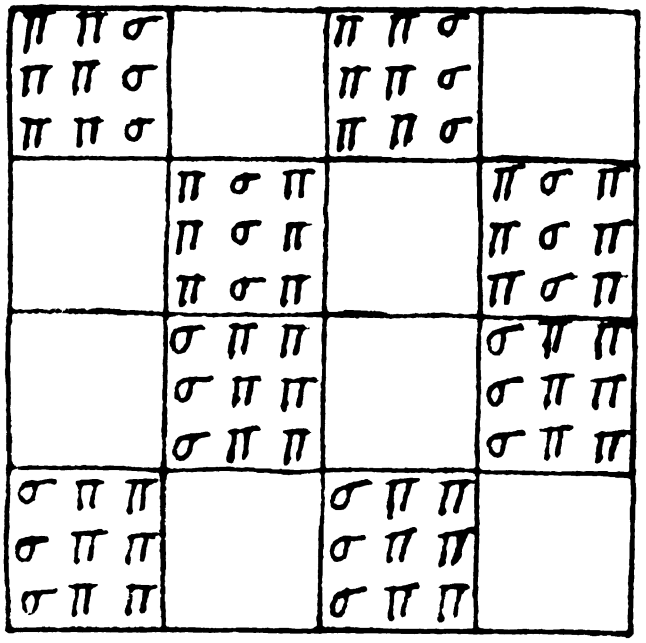


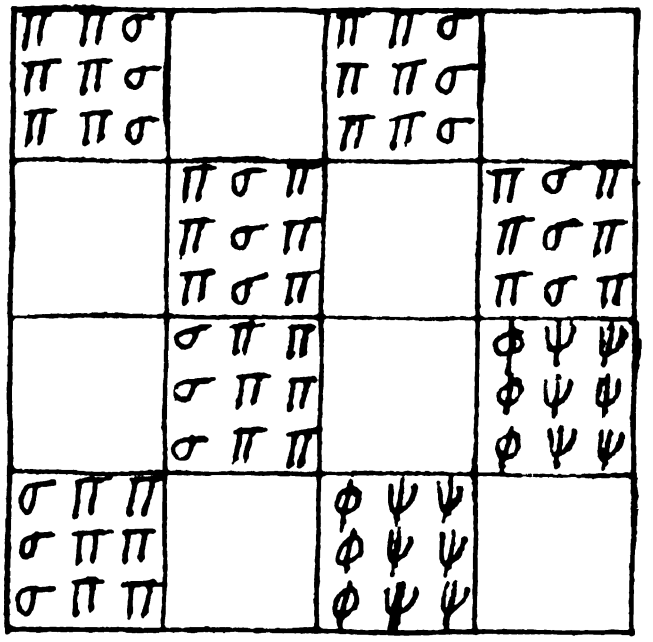
Table 13

Matrix $[\Phi_{2r}][\Phi_{2r+1}][\Sigma_{2r+1}]_\psi$ cases 5-7

case 5



case 6



case 7

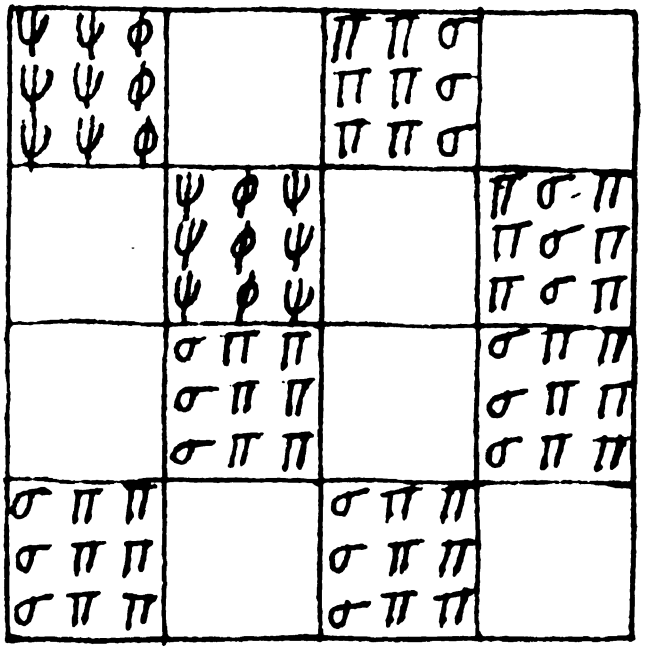


Table 14

Key to the symbols in Tables 13 and 14

A = 2.57×10^{-8}	B = 3.51×10^{-8}	C = 5.35×10^{-8}
D = 3.39×10^{-8}	E = 4.32×10^{-8}	F = 2.80×10^{-7}
G = 1.61×10^{-7}	H = 2.52×10^{-7}	I = 1.51×10^{-7}
J = 7.53×10^{-7}	K = 3.96×10^{-6}	L = 3.37×10^{-6}
M = 6.19×10^{-7}	N = 5.88×10^{-7}	P = 8.20×10^{-7}
Q = 1.67×10^{-6}	R = 1.24×10^{-6}	S = 3.52×10^{-6}
T = 3.96×10^{-6}	U = 6.66×10^{-6}	V = 4.87×10^{-6}
W = 4.52×10^{-6}	X = 2.02×10^{-6}	Y = 5.76×10^{-7}
Z = 5.61×10^{-7}	α = 1.42×10^{-7}	β = 2.66×10^{-6}
γ = 2.42×10^{-6}	δ = 1.81×10^{-6}	ϵ = 4.87×10^{-6}
ζ = 2.84×10^{-6}	η = 5.85×10^{-6}	θ = 1.72×10^{-6}
λ = 2.87×10^{-6}	μ = 3.03×10^{-7}	ξ = 7.78×10^{-7}
π = 1.39×10^{-7}	σ = 3.24×10^{-7}	ϕ = 9.24×10^{-8}
ψ = 3.98×10^{-8}		

Matrix $[\Sigma_{2v+1}]_4$ is an expanded form of matrix $[\Sigma_{2v+1}]$ in which each element of the 4 x 4 matrix is multiplied by E_4, a 4 x 4 identity matrix. Because we do not allow the bond to reverse its direction, rows 3, 7, 11, 15 and columns 3, 7, 11, 15 are all zero. This then allows the matrix to be reduced to a 12 x 12 for the purpose of calculating the largest positive eigenvalue and the corresponding eigenvector and eigenrow. A machine language program to do these calculations was written for Michigan States' digital computor which was called MISTIC. This program calculated the 16 x 16 matrix $[\Phi_{2v}][\Phi_{2v+1}][\Sigma_{2v+1}]_4$ from the 28 distinct U_{ij} elements and the 8 C_i elements. Michigan State University computor program MA5M was then used to determine the characteristic polynomial of the 12 x 12 reduced matrix. Michigan State University computor program J2 was then used to determine the roots of this polynomial which would be the eigenvalues of the matrix. This approach gave erroneous answers because of its method of calculating the characteristic polynomial. Program MA5M uses the N + 1 points method which will give erroneous results when the eigenvalues lie close together. Case 1 has only two different rows in its reduced 12 x 12 matrix which indicates that it has not more than two non-zero eigenvalues.

Various other methods were investigated until a program was written to use the iterated vector method.[9,10] The remaining programs were run on a Burroughs 220 digital

computer at Dow Chemical Company's Computations Research Laboratory at Midland, Michigan. These programs were written in Burroughs Algol 58. Some hand calculations using the iterated vector method gave the largest positive eigenvalue for Cases 1, 2, 3, and 5 before the computer program was written.

A method of blocking the matrix was used to solve for all of the eigenvalues of the matrix for Cases 1 and 3. The procedure is described in Appendix B.

The eigenvector and eigenrow output from the first program in Appendix A had to be normalized so that $\sum_{i=1}^{16} X_i = 1$. Then the next step was to calculate matrices $[N]$, $[M + D_{2v}]$ and $[E_{32} - M]^{-1}$. This data was output on cards because of a limit of 8000 words of core memory available on the computer. This data could have been put on magnetic tape and used later but since the time required to punch out the matrices was reasonably short, it was decided to take the easiest approach. The final program in Appendix A calculates $\langle h^2 \rangle$ nl^2. The new Burroughs B 5000 which is at the Computations Research Laboratory now could very easily handle all of the total calculations in one step. This would require only the 28 U_{ij} variables and the 8 C_i variables to be input.

III. CONCLUSIONS

A. Results

The eigenvalues, eigenvectors, eigenrows and $\langle n^2 \rangle / n1^2$ are shown in Tables 15, 16, 17, 18, and 19. Table 19 also includes the values of two 2 x 2 matrices which are called MAT2 and MAT3. MAT2 is the product of multiplying Δ^* N Δ while MAT3 is the product of $\Delta^* [E_{32} + N] [E_{32} - M]^{-1} [M \cdot D_2 v] \Delta$ (see equation 13). One can see upon analysis of equation (13) that $\langle r^2 \rangle$ $n1^2$ is equal to 1 + MAT2(2,2) + MAT3(2,2).

TABLE 15. Non-normalized eigenvectors.

NON-NORMALIZED EIGENVECTOR

	CASE 1	CASE 2	CASE 3	CASE 4	CASE 5	CASE 6	CASE 7
X_1	.1000,+01	.4093,-01	.1000,+01	.9318,+00	.1000,+01	.1000,+01	.1000,+01
X_2	.1000,+01	.3316,-01	.1000,+01	.1893,-01	.1000,+01	.1000,+01	.1000,+01
X_3	.0000,+00	.0000,+00	.0000,+00	.0000,+00	.0000,+00	.0000,+00	.0000,+00
X_4	.1000,+01	.3327,-01	.1000,+01	.2010,+00	.1000,+01	.1000,+01	.1000,+01
X_5	.1000,+01	.4093,-01	.1000,+01	.9944,+00	.1000,+01	.7840,-07	.7840,-07
X_6	.1000,+01	.3316,-01	.1000,+01	.2147,+00	.1000,+01	.7840,-07	.7840,-07
X_7	.0000,+00	.0000,+00	.0000,+00	.0000,+00	.0000,+00	.0000,+00	.0000,+00
X_8	.1000,+01	.3316,-01	.1000,+01	.2033,-01	.1000,+01	.7840,-07	.7840,-07
X_9	.1000,+01	.9998,+00	.1000,+01	.9080,+00	.1000,+01	.1574,-07	.1574,-07
X_{10}	.1000,+01	.8499,+00	.1000,+01	.1270,-01	.1000,+01	.1574,-07	.1574,-07
X_{11}	.0000,+00	.0000,+00	.0000,+00	.0000,+00	.0000,+00	.0000,+00	.0000,+00
X_{12}	.1000,+01	.8499,+00	.1000,+01	.2809,+00	.1000,+01	.1574,-07	.1574,-07
X_{13}	.1000,+01	.1000,+01	.1000,+01	.1000,+01	.1000,+01	.1254,-03	.1254,-03
X_{14}	.1000,+01	.8499,+00	.1000,+01	.2892,+00	.1000,+01	.1254,-03	.1254,-03
X_{15}	.0000,+00	.0000,+00	.0000,+00	.0000,+00	.0000,+00	.0000,+00	.0000,+00
X_{16}	.1000,+01	.8499,+00	.1000,+01	.1563,-01	.1000,+01	.1254,-03	.1254,-03

TABLE 15. Non-normalized eigenvectors.

NON-NORMALIZED EIGENVECTOR	CASE 1	CASE 2	CASE 3	CASE 4	CASE 5	CASE 6	CASE 7
X_1	.1000,+01	.4093,-01	.1000,+01	.9318,+00	.1000,+01	.1000,+01	.1000,+01
X_2	.1000,+01	.3316,-01	.1000,+01	.1893,-01	.1000,+01	.1000,+01	.1000,+01
X_3	.0000,+00	.0000,+00	.0000,+00	.0000,+00	.0000,+00	.0000,+00	.0000,+00
X_4	.1000,+01	.3327,-01	.1000,+01	.2010,+00	.1000,+01	.1000,+01	.1000,+01
X_5	.1000,+01	.4093,-01	.1000,+01	.9944,+00	.1000,+01	.7840,-07	.7840,-07
X_6	.1000,+01	.3316,-01	.1000,+01	.2147,+00	.1000,+01	.7840,-07	.7840,-07
X_7	.0000,+00	.0000,+00	.0000,+00	.0000,+00	.0000,+00	.0000,+00	.0000,+00
X_8	.1000,+01	.3316,-01	.1000,+01	.2033,-01	.1000,+01	.7840,-07	.7840,-07
X_9	.1000,+01	.9998,+00	.1000,+01	.9080,+00	.1000,+01	.1574,-07	.1574,-07
X_{10}	.1000,+01	.8499,+00	.1000,+01	.1270,-01	.1000,+01	.1574,-07	.1574,-07
X_{11}	.0000,+00	.0000,+00	.0000,+00	.0000,+00	.0000,+00	.0000,+00	.0000,+00
X_{12}	.1000,+01	.8499,+00	.1000,+01	.2809,+00	.1000,+01	.1574,-07	.1574,-07
X_{13}	.1000,+01	.1000,+01	.1000,+01	.1000,+01	.1000,+01	.1254,-03	.1254,-03
X_{14}	.1000,+01	.8499,+00	.1000,+01	.2892,+00	.1000,+01	.1254,-03	.1254,-03
X_{15}	.0000,+00	.0000,+00	.0000,+00	.0000,+00	.0000,+00	.0000,+00	.0000,+00
X_{16}	.1000,+01	.8499,+00	.1000,+01	.1563,-01	.1000,+01	.1254,-03	.1254,-03

TABLE 16. Non-normalized eigenrows.

NON-NORMALIZED EIGENROW	CASE 1	CASE 2	CASE 3	CASE 4	CASE 5	CASE 6	CASE 7
Y_1	.1000,+01	.1000,+01	.1000,+01	.4771,+00	.1000,+01	.4301,+00	.4301,+00
Y_2	.1000,+01	.4034,+00	.1000,+01	.1900,+00	.3619,+00	.4301,+00	.4301,+00
Y_3	.0000,+00	.0000,+00	.0000,+00	.0000,+00	.0000,+00	.0000,+00	.0000,+00
Y_4	.1000,+01	.4616,+00	.1000,+01	.1000,+01	.1000,+01	.1000,+01	.1000,+01
Y_5	.1000,+01	.9978,+00	.1000,+01	.4850,+00	.1000,+01	.6068,-07	.6068,-07
Y_6	.1000,+01	.4615,+00	.1000,+01	.8071,+00	.1000,+01	.7956,-07	.7956,-07
Y_7	.0000,+00	.0000,+00	.0000,+00	.0000,+00	.0000,+00	.0000,+00	.0000,+00
Y_8	.1000,+01	.4032,+00	.1000,+01	.2025,+00	.3619,+00	.3488,-07	.3488,-07
Y_9	.1000,+01	.9978,+00	.1000,+01	.4771,+00	.1000,+01	.9243,-05	.9243,-05
Y_{10}	.1000,+01	.4034,+00	.1000,+01	.1898,+00	.3619,+00	.9243,-05	.9243,-05
Y_{11}	.0000,+00	.0000,+00	.0000,+00	.0000,+00	.0000,+00	.0000,+00	.0000,+00
Y_{12}	.1000,+01	.4616,+00	.1000,+01	.9942,+00	.1000,+01	.2149,-03	.2149,-03
Y_{13}	.1000,+01	.9978,+00	.1000,+01	.4850,+00	.1000,+01	.2696,-07	.2696,-07
Y_{14}	.1000,+01	.4615,+00	.1000,+01	.8071,+00	.1000,+01	.1176,-08	.1176,-08
Y_{15}	.0000,+00	.0000,+00	.0000,+00	.0000,+00	.0000,+00	.0000,+00	.0000,+00
Y_{16}	.1000,+01	.4032,+00	.1000,+01	.2025,+00	.3619,+00	.1160,-08	.1160,-08

TABLE 17. Normalized eigenvectors.

NORMALIZED EIGENVECTOR	CASE 1	CASE 2	CASE 3	CASE 4	CASE 5	CASE 6	CASE 7
ϕ_1	.2887,+00	.8538,-01	.2887,+00	.4366,+00	.2887,+00	.5774,+00	.5774,+00
ϕ_2	.2887,+00	.7686,-01	.2887,+00	.6224,-01	.2887,+00	.5774,+00	.5774,+00
ϕ_3	.0000,+00	.0000,+00	.0000,+00	.0000,+00	.0000,+00	.0000,+00	.0000,+00
ϕ_4	.2887,+00	.7698,-01	.2887,+00	.2028,+00	.2887,+00	.5774,+00	.5774,+00
ϕ_5	.2887,+00	.8538,-01	.2887,+00	.4311,+00	.2887,+00	.4527,-07	.4527,-07
ϕ_6	.2887,+00	.7686,-01	.2887,+00	.2096,+00	.2887,+00	.4527,-07	.4527,-07
ϕ_7	.0000,+00	.0000,+00	.0000,+00	.0000,+00	.0000,+00	.0000,+00	.0000,+00
ϕ_8	.2887,+00	.7686,-01	.2887,+00	.6450,-01	.2887,+00	.4527,-07	.4527,-07
ϕ_9	.2887,+00	.4220,+00	.2887,+00	.4310,+00	.2887,+00	.9089,-08	.9089,-08
ϕ_{10}	.2887,+00	.3891,+00	.2887,+00	.5098,-01	.2887,+00	.9089,-08	.9089,-08
ϕ_{11}	.0000,+00	.0000,+00	.0000,+00	.0000,+00	.0000,+00	.0000,+00	.0000,+00
ϕ_{12}	.2887,+00	.3891,+00	.2887,+00	.2397,+00	.2887,+00	.9089,-08	.9089,-08
ϕ_{13}	.2887,+00	.4221,+00	.2887,+00	.4523,+00	.2887,+00	.7242,-04	.7242,-04
ϕ_{14}	.2887,+00	.3891,+00	.2887,+00	.2433,+00	.2887,+00	.7242,-04	.7242,-04
ϕ_{15}	.0000,+00	.0000,+00	.0000,+00	.0000,+00	.0000,+00	.0000,+00	.0000,+00
ϕ_{16}	.2887,+00	.3891,+00	.2887,+00	.5654,-01	.2887,+00	.7242,-04	.7242,-04

TABLE 18. Normalized eigenrows.

NORMALIZED EIGENROW	CASE 1	CASE 2	CASE 3	CASE 4	CASE 5	CASE 6	CASE 7
ζ_1^*	.2887,+00	.3663,+00	.2887,+00	.2748,+00	.3254,+00	.3675,+00	.3675,+00
ζ_2^*	.2887,+00	.2326,+00	.2887,+00	.1734,+00	.1957,+00	.3675,+00	.3675,+00
ζ_3^*	.0000,+00	.0000,+00	.0000,+00	.0000,+00	.0000,+00	.0000,+00	.0000,+00
ζ_4^*	.2887,+00	.2489,+00	.2887,+00	.3979,+00	.3254,+00	.8543,+00	.8543,+00
ζ_5^*	.2887,+00	.3659,+00	.2887,+00	.2771,+00	.3254,+00	.5184,-07	.5184,-07
ζ_6^*	.2887,+00	.2488,+00	.2887,+00	.3574,+00	.3254,+00	.6797,-07	.6797,-07
ζ_7^*	.0000,+00	.0000,+00	.0000,+00	.0000,+00	.0000,+00	.0000,+00	.0000,+00
ζ_8^*	.2887,+00	.2326,+00	.2887,+00	.1790,+00	.1957,+00	.2980,-07	.2980,-07
ζ_9^*	.2887,+00	.3659,+00	.2887,+00	.2748,+00	.3254,+00	.7896,-05	.7896,-05
ζ_{10}^*	.2887,+00	.2326,+00	.2887,+00	.1733,+00	.1957,+00	.7896,-05	.7896,-05
ζ_{11}^*	.0000,+00	.0000,+00	.0000,+00	.0000,+00	.0000,+00	.0000,+00	.0000,+00
ζ_{12}^*	.2887,+00	.2489,+00	.2887,+00	.3967,+00	.3254,+00	.1836,-03	.1806,-03
ζ_{13}^*	.2887,+00	.3659,+00	.2887,+00	.2771,+00	.3254,+00	.2303,-07	.2303,-07
ζ_{14}^*	.2887,+00	.2488,+00	.2887,+00	.3574,+00	.3254,+00	.1005,-08	.1005,-08
ζ_{15}^*	.0000,+00	.0000,+00	.0000,+00	.0000,+00	.0000,+00	.0000,+00	.0000,+00
ζ_{16}^*	.2887,+00	.2326,+00	.2887,+00	.1790,+00	.1957,+00	.9913,-09	.9913,-09

TABLE 19. Final results.

	CASE 1	CASE 2	CASE 3	CASE 4	CASE 5	CASE 6	CASE 7
	.154,-06	.628,-06	.452,-05	.153,-04	.120,-05	.280,-02	.230,-02
MAT2(1,1)	+.167,+00	+.425,-01	+.167,+00	+.500,+00	+.471,+00	+.456,-04	+.212,+00
MAT2(1,2)	+.167,+00	+.382,+00	+.167,+00	+.534,+00	+.412,+00	+.603,-04	+.281,+00
MAT2(2,1)	+.167,+00	+.272,+00	+.167,+00	+.209,+00	+.113,+00	-.603,-04	-.281,+00
MAT2(2,2)	+.167,+00	+.425,-01	+.167,+00	+.183,+00	+.113,+00	+.456,-04	+.212,+00
MAT3(1,1)	+.500,+00	+.615,+00	+.500,+00	+.653,+00	+.847,+00	+.212,+00	-.675,-01
MAT3(1,2)	+.167,+00	+.612,+00	+.167,+00	+.169,+01	+.668,+00	+.281,+00	+.282,+00
MAT3(2,1)	+.167,+00	+.467,+00	+.167,+00	-.889,-01	+.298,+00	-.281,+00	-.282,+00
MAT3(2,2)	+.500,+00	+.633,+00	+.500,+00	+.830,+00	+.509,+00	+.212,+00	-.675,-01
h^2/nl^2	1.67	1.68	1.67	2.01	1.62	1.21	1.14

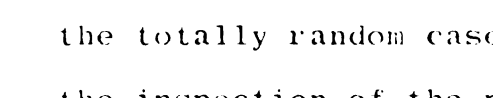
B. Discussion of Results

The final results for the unperturbed dimensions of the seven cases are shown in Table 16. Case one is an example of both totally random configuration and random conformation. The value of $\langle h^2 \rangle / nl^2$ is entirely independent of the energies assumed for the totally random case. This results from the fact that matrices M and N (see equations 14 and 15) are divided by , the largest positive eigenvalue of $[\Phi_{2\nu}][\Phi_{2\nu-1}][\Sigma_{2\nu-1}]_4$ and that the normalized eigenvector and eigenrow are used. Case three is simply a check on case one.

Case two has totally random configuration, totally random first neighbor interactions, all second neighbor 2ν interactions except one are random, and a distinction is made between only the second neighbor $2\nu-1$ interactions (see part A section two). This does not noticeably change the quantity $\langle h^2 \rangle / nl^2$ from that obtained for the totally random case. This implies that for this model the second neighbor interactions must be quite far apart to noticeably effect the end-to-end dimension of the polymer.

In case four a distinction is made in both first and second neighbor interaction energies while the configuration is still kept random (see part A section two). This has a significant effect on the result. The rotational energies assumed were "most probable" values assigned after

comparison of the first and second neighbor interactions which are depicted schematically in Tables 3 and 4. The value of $\langle h^2 \rangle / nl^2$ obtained in case four (2.01) is essentially that obtained by considering a freely rotating polymethylene chain consisting of n bonds of identical length l joined at fixed valence angles θ. For large n and a tetrahedrally bonded chain ($\theta = 109.5°$) a value of $\bar{r}^2 / nl^2 = 2$ is obtained. Hence on a two dimensional lattice a value of 2 represents a reasonably expanded chain.

Cases 5, 6, and 7 are identical with respect to conformation but case 5 has a random configuration, while case 6 has a preferred syndiotactic configuration, and case 7 has a preferred isotactic configuration. The result for case 5 is very close to the result obtained for the totally random case. One would probably predict from the inspection of the preferred configurations for cases 5, 6, and 7  . that case 6 with a preferred syndiotactic configuration would have a higher value of $\langle h^2 \rangle / nl^2$ than a random case while case 7 with a preferred isotactic configuration would have a lower value than a random case.

The result for case 7 is in agreement with this reasoning while that for case 6 is not in agreement. Because of the disagreement of case 6 with this theory, case 6 was run thru the various computer programs a second time. The same result was obtained in both determinations.

Further study on the model in case 6 led to the idea that the polymer was actually running in a straight line for a while and then turning around and going back in the direction in which it previously came. A schematic diagram depicting this is shown in Figure 4.

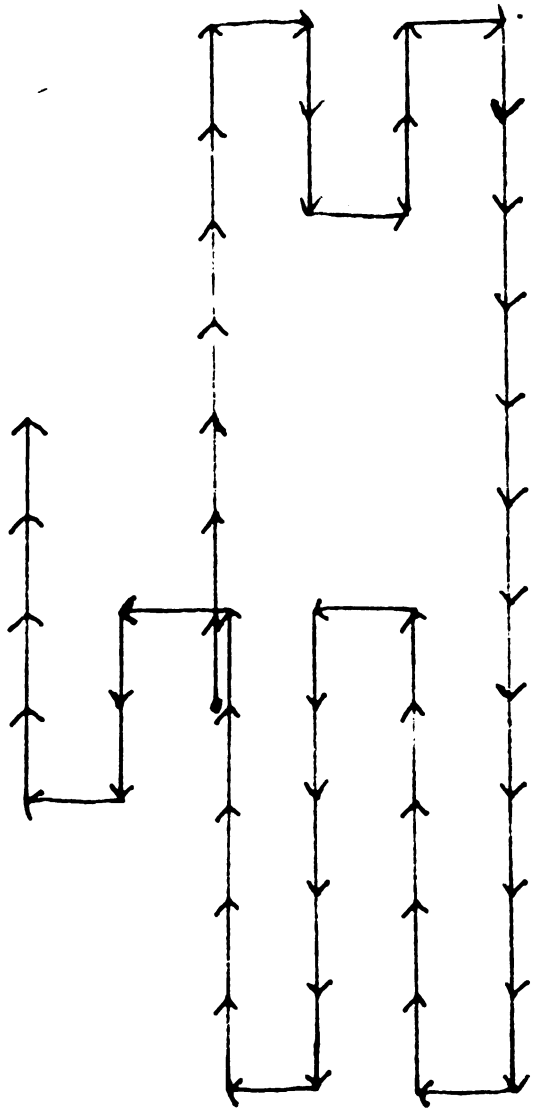


Figure 4

Schematic diagram depicting the polymer chain in case 6

A three dimensional model would allow the polymer to make many more moves than the square lattice and hence the results would be different in many cases. If the isotactic polymer in case 7 were allowed to proceed in three dimensions it would undoubtedly coil up and form a helix with a longer end-to-end dimension.

These preliminary analyses have aroused more problems and questions than they have answered. It would be extremely interesting to determine the effect of temperature on the end-to-end dimension. There are many more different cases which would provide more information about the polymer model. It would be quite beneficial to have the matrices M and N (equations 14 and 15) multiplied out in symbolic form so that one could see the positions of the favored conformations in the two matrices.

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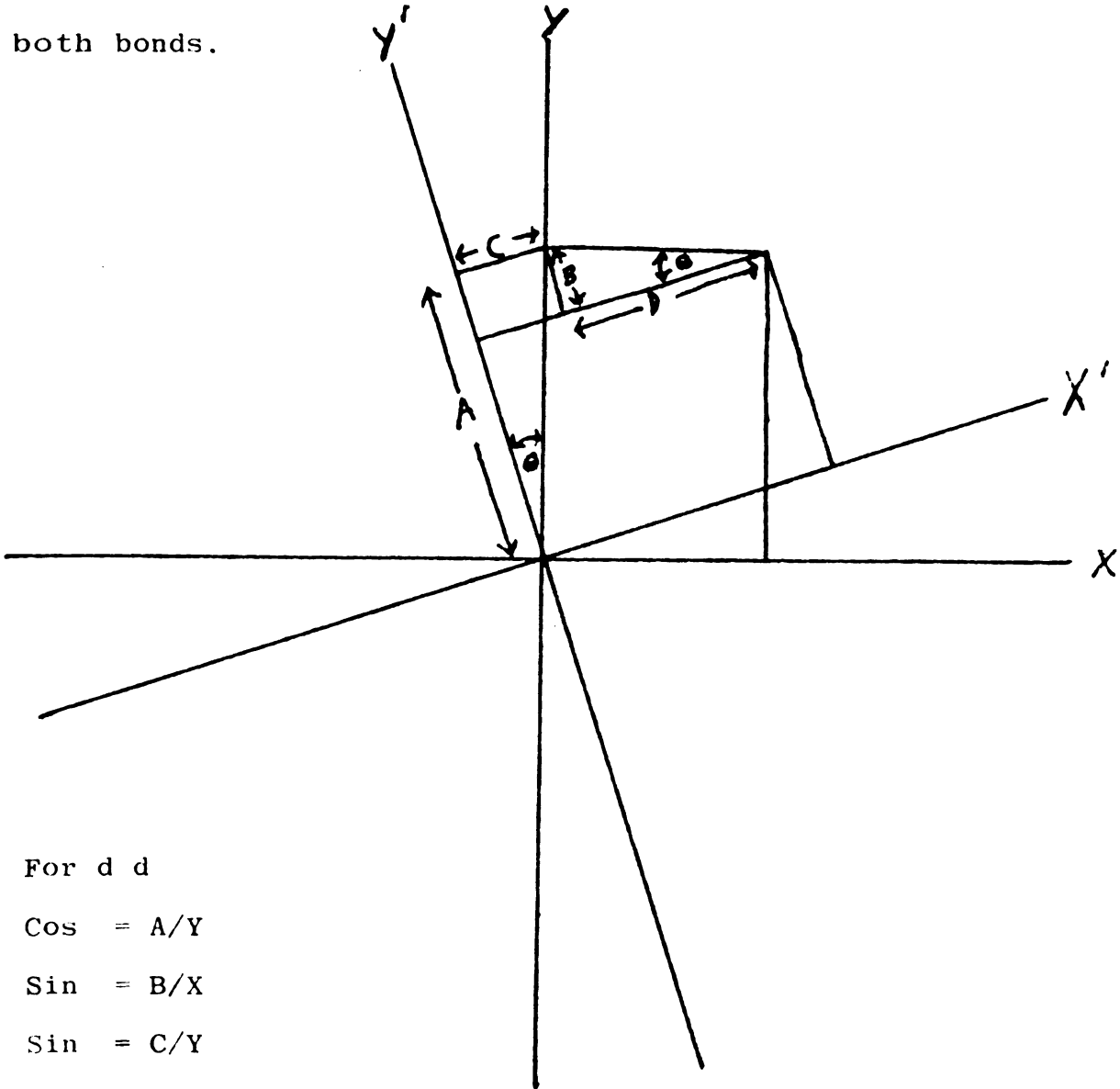
APPENDIX A

FIGURE 5

Diagram used to determine the sin-cosine transformation matrices when the same coordinate system is used for both bonds.



For d d

Cos = A/Y

Sin = B/X

Sin = C/Y

Cos = D/X

X'=C+D = XCos + YSin

Y'=A-B = -XSin + YCos

$$\begin{bmatrix} \text{Cos} & \text{Sin} \\ -\text{Sin} & \text{Cos} \end{bmatrix}$$

For l l exchange X's and Y's

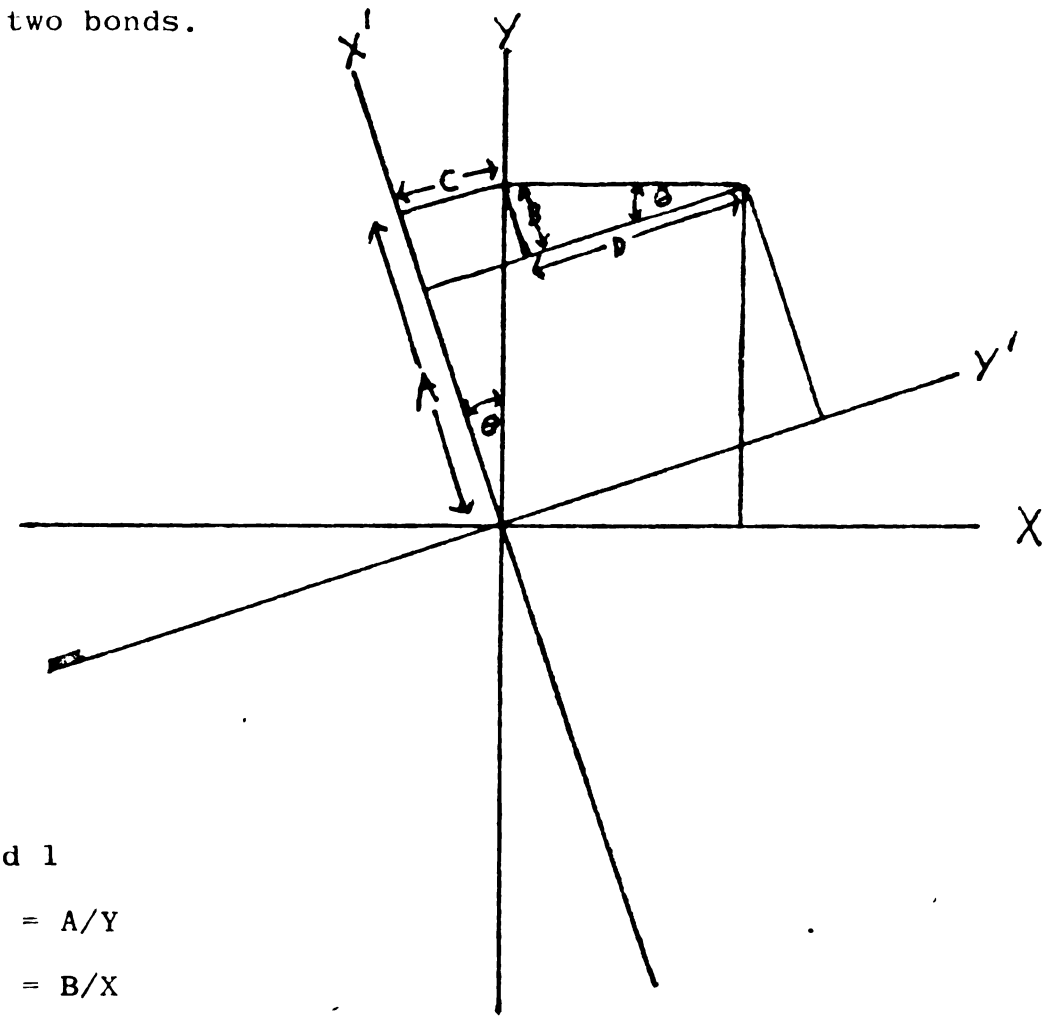
X'= XCos - YSin

Y'= XSin + YCos

$$\begin{bmatrix} \text{Cos} & -\text{Sin} \\ \text{Sin} & \text{Cos} \end{bmatrix}$$

FIGURE 6

Diagram used to determine the sin-cosine transformation matrices when different coordinate systems are used for the two bonds.



For d l

Cos = A/Y

Sin = B/X

Sin = C/Y

Cos = D/X

X'=A-B = -XSin + YCos

Y'=C+D = XCos + YSin

$$\begin{bmatrix} -\text{Sin} & \text{Cos} \\ \text{Cos} & \text{Sin} \end{bmatrix}$$

For l d exchange X'^{s} and Y'^{s}

X'= XSin + YCos

Y'= XCos - YSin

$$\begin{bmatrix} \text{Sin} & \text{Cos} \\ \text{Cos} & -\text{Sin} \end{bmatrix}$$

The values of the sin and cosine of the four bond angles are shown below.

angle	0	$\pi/2$	π	$3\pi/2$
sin	0	1	0	-1
cos	1	0	-1	0

Matrix $\left[D^{(1)}_{2J+1}\right]$ is d d therefore the sin-cosine matrix used is $\begin{bmatrix} \cos & \sin \\ -\sin & \cos \end{bmatrix}$

state	bond angle	matrix
1	0	1 0 0 1
2	$3\pi/2$	0 -1 1 0
3	π	-1 0 0 -1
4	$\pi/2$	0 1 -1 0

Matrix $\left[D^{(2)}_{2J+1}\right]$ is 1 1 therefore the sin-cosine matrix used is $\begin{bmatrix} \cos & -\sin \\ \sin & \cos \end{bmatrix}$

state	bond angle	matrix
1	0	1 0 0 1
2	$3\pi/2$	0 1 -1 0
3	π	-1 0 0 -1
4	$\pi/2$	0 -1 1 0

Matrix $\left[D^{(1)}_{2r+1}\right]$ is l d therefore the sin-cosine matrix used is $\begin{bmatrix}\sin & \cos \\ \cos & -\sin\end{bmatrix}$

state	bond angle	matrix
1	0	$\begin{matrix}0 & 1\\ 1 & 0\end{matrix}$
2	$3\pi/2$	$\begin{matrix}-1 & 0\\ 0 & 1\end{matrix}$
3	π	$\begin{matrix}0 & -1\\ -1 & 0\end{matrix}$.
4	$\pi/2$	$\begin{matrix}1 & 0\\ 0 & -1\end{matrix}$

Matrix $\left[D^{(4)}_{2r+1}\right]$ is d l therefore the sin-cosine matrix used is $\begin{bmatrix}-\sin & \cos \\ \cos & \sin\end{bmatrix}$

state	bond angle	matrix
1	0	$\begin{matrix}0 & 1\\ 1 & 0\end{matrix}$
2	$3\pi/2$	$\begin{matrix}1 & 0\\ 0 & -1\end{matrix}$
3	π	$\begin{matrix}0 & -1\\ -1 & 0\end{matrix}$
4	$\pi/2$	$\begin{matrix}-1 & 0\\ 0 & 1\end{matrix}$

But for matrix $[D_{2r}]$

$$\left[D^{(1)}_{2r}\right] = \left[D^{(1)}_{2r+1}\right]$$

$$\left[D^{(2)}_{2r}\right] = \left[D^{(2)}_{2r+1}\right]$$

APPENDIX B

BLOCK METHOD FOR DETERMINING THE EIGENVALUES OF A MATRIX

Let $\beta = \begin{bmatrix} A & A & A \\ A & A & A \\ A & A & A \end{bmatrix}$ and $O = \begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}$ as shown for case one in Table 10. The 12x12 matrix then becomes

$$\begin{bmatrix} \beta & O & \beta & O \\ O & \beta & O & \beta \\ O & \beta & O & \beta \\ \beta & O & \beta & O \end{bmatrix}$$

Upon solving for the eigenvalues(Y), the matrix becomes

$$\begin{bmatrix} \beta-Y & O & \beta & O \\ O & \beta-Y & O & \beta \\ O & \beta & -Y & \beta \\ \beta & O & \beta & -Y \end{bmatrix}$$

Which upon multiplication yields

$$\beta-Y \begin{bmatrix} \beta-Y & O & \beta \\ \beta & -Y & \beta \\ O & \beta & -Y \end{bmatrix} + \beta \begin{bmatrix} O & \beta-Y & \beta \\ O & \beta & \beta \\ \beta & O & -Y \end{bmatrix} = 0$$

Upon multiplying out further

$$(\beta-Y)^2(Y^2-\beta^2) + (\beta-Y)\,\beta\,\beta^2 + \beta\,(\beta-Y)(+\beta^2) + \beta^2(-\beta^2) = 0$$

$$\beta^2Y^2 - 2\beta Y^3 + Y^4 - \beta^4 + 2\beta^3Y - \beta^2Y^2 + \beta^4 - \beta^2Y + \beta^4 - \beta^3Y - \beta^4 = 0$$

$$-2\beta Y^3 + Y^4 = 0 \qquad Y^3(Y-2\beta) = 0. \quad Y = 0,0,0,+2\beta$$

But $\beta = \begin{bmatrix} A & A & A \\ A & A & A \\ A & A & A \end{bmatrix}$, so $2\beta = 2A \begin{bmatrix} 1 & 1 & 1 \\ 1 & 1 & 1 \\ 1 & 1 & 1 \end{bmatrix}$

The next step is to solve for the eigenvalues(x) of the 3by3 matrix.

Upon solving for the eigenvalues(x) the matrix becomes

$$\begin{bmatrix} 1-x & 1 & 1 \\ 1 & 1-x & 1 \\ 1 & 1 & 1-x \end{bmatrix}$$

Which upon multiplication becomes

$$(1-x)\left[(1-x^2)-1\right] - 1\left[(1-x)-1\right] + 1\left[1-(1-x)\right] = 0$$

$$(1-x)(1-2x+x^2-1)+x+x=0 \qquad -2x+x^2+2x^2-x^3+2x=0$$

$$3x^2-x^3=0 \qquad -x^2(x-3)=0 \qquad x=0,0,+3$$

Therefore the twelve eigenvalues of the original 12 by 12 matrix are eleven zeros and 6A. Thus the largest positive eigenvalue of $[\Phi_{2r}][\Phi_{2r+1}][\Sigma_{2r+1}]$ for case 1 is 6A or $6(2.57\times10^{-8})$ which is 1.54×10^{-7}.

APPENDIX C

ALGOL 58 COMPUTER PROCEDURES

```
COMMENT ITERATED VECTOR METHOD FOR CALCULATING THE
LARGEST POSITIVE EIGENVALUE OF A TWELVE BY TWELVE
MATRIX.  THIS PROGRAM ALSO PRINTS OUT THE CORRESPONDING
EIGENVECTOR AND EIGENROW.
R. C. THOMAS:
INTEGER I,J,K,L;
ARRAY TMATRIX(12,12),MATRIX(12,12),PRESVECTOR(12),
PREVVECTOR(12),Y(12);
L0.. K L=0;
     FOR I (1,1,12) PREVVECTOR(I)=0.0;
     PRESVECTOR(1)=1.0;
     FOR J=(2,1,12): PRESVECTOR(J)=0.0;
     INPUT MAT (FOR I=(1,1,12): FOR J (1,1,12):
     MATRIX(I,J)):
     READ (;;MAT);
L1.. K=K+1; IF K EQL 100; GO TO L0;
     FOR I=(1,1,12):
     BEGIN Y(I)=0.0;
     FOR J=(1,1,12):
     Y(I) = Y(I) + MATRIX (I,J).PRESVECTOR(J) END;
L2.. LRG=0.0;
     FOR I=(1,1,12); BEGIN
     IF Y(I) GTR LRG; BEGIN
     LRG = Y(I) END END;
```

```
L3 . . WRITE( : ;LARGE,FORM1) ;
       OUTPUT LARGE (LRG) ;
       FORMAT FORM1(B7,F11.5,W) ;
L4 . . FOR I=(1,1,12); PREVVECTOR(I) = PRESVECTOR(I) :
       FOR I=(1,1,12); PRESVECTOR(I) = Y(I) 'LRG;
L5 . . FOR I=(1,1,12); BEGIN
       IF (ABS(PRESVECTOR(I) - PREVVECTOR(I))GTR 0.00001) :
       GO L1 END;
L6 . . FOR I=(1,1,12): BEGIN
       WRITE( : ;VECROW,FORM1) ;
       OUTPUT VECROW (PRESVECTOR(I)) END;
       L=L+1 ; IF (L EQL 2); GO TO L0:
L7 . . FOR I=(1,1,12). FOR J=(1,1,12);
       TMATRIX(J,I) = MATRIX(I,J) :
       FOR I=(1,1,12); FOR J=(1,1,12):
       MATRIX(I,J) = TMATRIX(I,J) :
L0 . . GO TO L1;
       FINISH;
```

```
COMMENT THIS PROGRAM CALCULATES MATRICES M AND N.  IT
ALSO PUNCHES OUT ON CARDS IN THE FOLLOWING ORDER MATRICES
N, (M+D2V), AND (E32-M)-1.  (PHI2V)2.(D2V+1) AND
(PHI2V+1)2.(SIGMA2V+1)2x4 AND LEIG ARE READ IN ON CARDS
IN THAT ORDER. R. C. THOMAS;
ARRAY MATA(32,32),MATB(32,32),MATC(32,32),MATD(32,32),
MATE(32,32);
INTEGER I,J,K,N;
PROCEDURE INVERT1 (N,A(,)::ERR1): BEGIN
COMMENT  INVERT A SQUARE MATRIX, IN PLACE, BY THE NBS
      PIVOTAL ROW METHOD.  INPUT CONSISTS OF THE ORDER
      AND NAME OF THE MATRIX.  OUTPUT IS THE INVERSE,
      WITH THE SAME NAME.  REFERENCE MUST INCLUDE A
      STATEMENT LABEL TO WHICH A TRANSFER MAY BE MADE IF
      THE MATRIX IS SINGULAR, A PRINT OUT STATING INVERSION
      FAILURE WILL BE MADE.
      NOTE THAT ARRAY DECLARATION ALLOWS FOR A MAXIMUM
      MATRIX OF ORDER 30.  IF LARGER ORDER IS NEEDED,
      CHANGE ARRAY DECLARATIONS ACCORDINGLY.
      AUTHOR - C.D. ALSTAD;
 INTEGER I,J,K,L,SJ,N;
 ARRAY ORDER(32),SAVE(32),SHIFT(32);
 FORMAT FINV1(B10,*MATRIX SINGULAR, INVERSION FAILED*,W0):
      FOR I=(1,1,N); BEGIN ORDER(I) = 0; SHIFT(I) = 0 END;
```

```
M1.   FOR L = (1,1,N); BEGIN  CHAMP = 0;
M2..  FOR I = (1,1,N): BEGIN Z = A(I,1):
M3..  IF ABS(Z) GEQ ABS(CHAMP); BEGIN K = I;
      FOR J =(1,1,L); IF ORDER(J) EQL K; GO ONSEEK;
      CHAMP = Z; ORDER(L) = K;
ONSEEK.. END M3 END M2;  Z = CHAMP;  K = ORDER(L):
      IF CHAMP EQL 0; BEGIN WRITE (::FINV1); GO ERR1 END:
      FOR J =(1,1,N-1):A(K,J,) = A(K,J+1)/Z;  A(K,N) = 1/Z;
M4..  FOR I =(1,1,N); BEGIN IF I EQL K: GO M5: MULT A(I,1):
      FOR J =(1,1,N-1); A(I,J) = A(I,J+1) - MULT.A(K,J):
      A(I,N) = -MULT.A(K,N);
M5..  END M4 END M1;
COMMENT MATRIX NOW INVERTED BUT SCRAMBLED, SO UNSCRAMBLE:
COMMENT UNSCRAMBLE ROWS; K=0;
MR1.. FOR L = (1,1,N); IF SHIFT(L) EQL 0; GO MR2;
MR2.. IF ORDER(L) EQL L; BEGIN SHIFT(L)=L;K = K+1;
      IF K EQL N; GO MC4: GO MR1 END;
      FOR J=(1,1,N); SAVE(J) = A(L,J): SJ = L;
MR3.. I = ORDER(L); FOR J=(1,1,N);  A(L,J) = A(I,J);
      SHIFT(L) = I; L=I; K=K+1; IF K EQL N; GO MC4;
      IF ORDER(L) NEQ SJ; GO MR3;
      FOR J=(1,1,N);  A(L,J) = SAVE(J):
      SHIFT(L) = SJ; K = K+1;
      IF K NEQ N; GO MR1;
```

```
COMMENT NOW UNSCRAMBLE COLUMNS;
MC4.. FOR I=(1,1,N); SHIFT(I) = 0; K = 0;
MC5.. FOR L=(1,1,N); IF SHIFT(L) EQL 0; GO MC6;
MC6.. IF ORDER(L) EQL L; BEGIN SHIFT(L) = L; K=K+1.
      IF K EQL N; GO MC9;  GO MC5 END MC6;
      FOR J=(1,1,N);  SAVE(J) = A(J,L);  SJ = L;
      FOR I=(1,1,N);  IF ORDER(K) EQL L; GO MC7;
MC7.. FOR J=(1,1,N);  A(J,L) = A(J,I);
      SHIFT(L) = I; L = I; K = K+1; IF K EQL N; GO MC9;
      FOR I =(1,1,N); IF ORDER(I) EQL L; GO MC8;
MC8.. IF I NEQ SJ; GO MC7;
      FOR J=(1,1,N); A(J,L) = SAVE(J);
      SHIFT(L) = SJ; K = K+1;  IF K NEQ N; GO MC5;
MC9.. RETURN END INVERT1();
L01.. FOR I=(1,1,32); FOR J=(1,1,32); BEGIN MATA(I,J)=0.0;
      MATB(I,J)=0.0; MATC(I,J)=0.0; MATD(I,J) 0.0;
      MATE(I,J)=0.0  END L01;
L02.. FOR I=(1,8,25); MATA(I,I)=1.0; FOR I=(2.8,26)
      MATA(I,I)=1.0; FOR I=(5,8,29); MATA(I,I)=-1.0;
      FOR I=(6,8,30); MATA(I,I)=-1.0;
      MATA(4,3)=1.0; MATA(3,4)=-1.0; MATA(7,8)=1.0;
      MATA(8,7)=-1.0; MATA(11,12)=1.0; MATA(12,11) -1.0;
      MATA(16,15)=1.0; MATA(15,16)=-1.0;
      FOR I=(1,1,32); MATB(I,I)=1.0;
L03.. INPUT MAT1(FOR I=(1,1,8); FOR J=(1,1,8); MATC(I,J));
      READ(;:MAT1);
```

```
      INPUT MAT2(FOR I=(9,1,16); FOR J=(9,1,16);
      MATC(I,J)); READ(;;MAT2);
      INPUT MAT3(FOR I=(17,1,24); FOR J=(17,1,24);
      MATC(I,J)); READ(;;MAT3);
      INPUT MAT4(FOR I=(25,1,32); FOR J=(25,1,32);
      MATC(I,J)); READ(;;MAT4);
L04.. INPUT MAT5(FOR I=(1,1,8); FOR J=(1,1,8);
      MATD(I,J)); READ(;;MAT5);
      INPUT MAT6(FOR I=(1,1,8); FOR J=(17,1,24);
      MATD(I,J)); READ(;;MAT6);
      INPUT MAT7(FOR I=(9,1,16); FOR J=(9,1,16);
      MATD(I,J)); READ(;;MAT7);
      INPUT MAT8(FOR I=(9,1,16); FOR J=(25,1,32);
      MATD(I,J)); READ(;;MAT8);
      INPUT MAT9(FOR I=(17,1,24); FOR J=(9,1,16);
      MATD(I,J)); READ(;;MAT9);
      INPUT MAT10(FOR I=(17,1,24); FOR J=(25,1,32);
      MATD(I,J)); READ(;;MAT10);
      INPUT MAT11(FOR I=(25,1,32); FOR J=(1,1,8);
      MATD(I,J)); READ(;;MAT11);
      INPUT MAT12(FOR I=(25,1,32); FOR J=(17,1,24);
      MATD(I,J)); READ(;;MAT12);
L05.. INPUT LEIGV(LEIG); READ(;;LEIGV);
      FORMAT FORM6(W5);
```

```
COMMENT INITIALLY AFTER INPUT MATA=D2V, MATB=L32,
      MATC=(PHI2V)2(D2V+1), MATD=(PHI2V+1)2(SIGMA2V+1)2x1;
L06..FOR I=(1,1,32); FOR J=(1,1,32); BEGIN S=0.0;
      FOR K=(1,1,32); S=S+MATC(I,K).MATD(K,J);
      MATE(I,J)=S END;
L07.. FOR I=(1,1,32); FOR J=(1,1,32); BEGIN S=0.0;
      FOR K=(1,1,32); S=S+MATA(I,K).MATE(K,J);
      MATC(I,J)=S/LEIG END;
COMMENT MATC NOW IS MATRIX(M);
      FOR I=(1,1,32); FOR J=(1,1,32); MATD(I,J)=MATE(I,J)
      /LEIG;
      COMMENT MATD NOW IS MATRIX(N);
      WRITE(;;FORM6);
      WRITE(;;N,FORM2); OUTPUT N(FOR I=(1,1,32);
      FOR J=(1,1,32); MATD(I,J));
      FORMAT FORM2 (*5*,6F12.5,W5);
      FOR I=(1,1,32); FOR J=(1,1,32);
      MATD(I,J)=MATA(I,J) + MATC(I,J);
COMMENT MATD NOW IS D2V+M;
      WRITE(;;FORM6);
      WRITE(;;D2VPM,FORM2);
      OUTPUT D2VPM (FOR I=(1,1,32); FOR J=(1,1,32);
      MATD(I,J));
L08.. FOR I=(1,1,32); FOR J=(1,1,32);
      MATD(I,J)=MATB(I,J)-MATC(I,J);
```

```
      FOR I=(1,1,32); FOR J=(1,1,32): MATB(I,J)=MATD(I,J):
      INVERT1 (32,MATD (,);; L01);
      FOR I=(1,1,32); FOR J=(1,1,32); BEGIN S=0.0;
      FOR K=(1,1,32); S=S+MATB(I,K).MATD(K,J):
      MATC(I,J)=S END;
      WRITE(;;FORM6);
      WRITE(;;E32MMM1,FORM2);
      OUTPUT E32MMM1 (FOR I=(1,1,32); FOR J=(1,1,32):
      MATD(I,J)); WRITE(;;UNITIFINV,FORM3);
      OUTPUT UNITIFINV (FOR I=(1,1,32); FOR J=(1,1,32):
      MATC(I,J)): FORMAT FORM3 (8(X9.5),W);
L09.. GO TO L01;
L10.. FINISH;
```

```
COMMENT THIS PROGRAM CALCULATES H2/NL2.  MATRICES M+D2V,
(E32-M)-1,N, DELV, AND DELR ARE INPUT IN THAT ORDER.
R. C. THOMAS;
ARRAY MATA(32,32), MATB(32,32), MATC(32,32), MATD(32,32),
DELV(32,2),DELR(2,32), SUM1(2,32), MAT1(2,2), MAT2(2,2),
MAT3(2,2), MAT4(2,2), MT1(1,2), MT2(2,1), MT3(1,2);
INTEGER I,J,K,L;
L01.. FOR I=(1,1,32); FOR J=(1,1,32); BEGIN MATA(I,J)=0.0;
      MATB(I,J)=0.0; MATC(I,J)=0.0; MATD(I,J)=0.0 END;
      FOR I=(1,1,32); FOR J=(1,1,2); DELV(I,J)=0.0;
      FOR J=(1,1,32); FOR I=(1,1,2); BEGIN DELR(I,J)=0.0;
      SUM1(I,J)=0.0 END;
L02.. FOR I=(1,1,2); FOR J=(1,1,2); BEGIN MAT1(I,J)=0.0;
      MAT2(I,J)=0.0; MAT3(I,J)=0.0; MAT4(I,J)=0.0 END'
      MT1(1,1)=0.0; MT1(1,2)=1.0; MT2(1,1)=0.0;
      MT2(2,1)=1.0; MT3(1,1)=0.0; MT3(1,2)=0.0;
      MAT1(1,1)=1.0; MAT1(1,2)=0.0; MAT1(2,1)=0.0;
      MAT1(2,2)=1.0;
L03.. INPUT MPD2V (FOR I=(1,1,32); FOR J=(1,1,32);
      MATA(I,J)); READ(''MPD2V);
L04.. INPUT E32MMM1 (FOR I=(1,1,32); FOR J=(1,1,32);
      MATB(I,J)); READ(;;E32MMM1);
L05.. INPUT N (FOR I=(1,1,32); FOR J=(1,1,32);
      MATC(I,J)); READ(;;N);
L06.. INPUT VECTOR (FOR I=(1,1,32); FOR J=(1,1,2);
```

```
      DELV(I,J); READ(:VECTOR);
L07.. INPUT ROW (FOR I=(1,1,2); FOR J=(1,1,32);
      DELR(I,J); READ(;;ROW);
L08.. FOR I=(1,1,32); FOR J=(1,1,32); BEGIN S=0.0;
      FOR K=(1,1,32); S=S+MATB(I,K).MATA(K,J);
      MATD(I,J)=S END;
L09.. FOR I=(1,1,32); FOR J=(1,1,32); MATA(I,J)=0.0;
      FOR I (1,1,32); MATA(I,J)=1.0; FOR I=(1,1,32);
      FOR J=(1,1,32); MATB(I,J)=MATA(I,J)+MATC(I,J);
L10.. FOR I=(1,1,32); FOR J=(1,1,32); BEGIN S=0.0;
      FOR K=(1,1,32); S=S+MATB(I,K).MATD(K,J);
      MATA(I,J)=S END;
COMMENT MATA NOW IS (E32+N).(E32-M)-1.(M+D2V);
L11.. FOR I=(1,1,2); FOR J=(1,1,32); BEGIN S+0.0;
      FOR K=(1,1,32); S=S+DELR(I,K).MATA(K,J);
     SUM1(I,J)=S END;
L12.. FOR I=(1,1,2); FOR J=(1,1,2); BEGIN S=0.0;
      FOR K=(1,1,32); S=S+SUM1(I,K).DELV(K,J);
      MAT3(I,J)=S END;
L13.. FOR I=(1,1,2); FOR J=(1,1,32); BEGIN S=0.0;
      FOR K=(1,1,32); S=S+DELR(I,K).MATC(K,J);
      SUM1(I,J)=S END;
L14.. FOR I=(1,1,2); FOR J=(1,1,2); BEGIN S=0.0;
      FOR K=(1,1,32); S=S+SUM1(I,K).DELV(K,J);
      MAT2(I,J)=S END;
```

```
      WRITE(;;SUM2,FORM5); OUTPUT SUM2 (FOR I=(1,1,2);
      FOR J=(1,1,2); MAT2(I,J));
      FORMAT FORM5(4(F13.6,B2,W0));
      WRITE(;;SUM3, FORM5); OUTPUT SUM3 (FOR I=(1,1,2);
      FOR J=(1,1,2); MAT3(I,J));
L15.. FOR I=(1,1,2): FOR J=(1,1,2); MAT4(I,J)=MAT1(I,J)+
      MAT2(I,J)+MAT3(I,J);
L16.. I=1; FOR J=(1,1,2); BEGIN S=0.0; FOR K=(1,1,2);
      S=S+MT1(I,K).MAT4(K,J); MT3(I,J)=S END;
L17.. S=0.0; S=MT3(1,1).MT2(1,1) + MT3(1,2).MT2(2,1);
L18.. WRITE(;;FINAL, FORM 4); OUTPUT FINAL (S);
      FORMAT FORM4(B7,F10.4,W);
L19.. GO TO L01;
L20.. FINISH;
```