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Cylindrical Coordinates of Each Atom in a Helical Polymer for a Given Set of Molecular Parameters

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A method is given for calculating cylindrical-polar coordinates of each atom in a helical polymer from a given set of bond lengths, bond angles, and angles of internal rotation. This should be useful for an analysis of an X-ray fiber diagram of the helical polymer.

The construction of a model for linear macromolecular chains at the atomic scale, considering their internal freedom and the forces between their structural units, is a subject of prime importance especially for the study of biological macromolecules having a regular chain conformation. In such a study, we usually assume a proper set of bond lengths, bond angles and dihedral angles at first, and then we often need to find the consequent set of cylindrical-polar coordinates of atoms, so that we can calculate, for example, the Fourier transform of the atoms on the helix by the use of the theory of Cochran, Crick, and Vand.[1] Thus, the problem here is to express explicitly the structural parameters of a helical conformations, *i. e.*, translation angle θ_i, radius ρ_i, and translation distance d_i, in terms of a set of internal coordinates: bond lengths r, bond angles ϕ, and angles of internal rotation τ. This problem has been solved in some special cases of a limited number of atoms in a repeating unit, by Shimanouchi and Mizushima,[2] and Miyazawa.[3] We are going to deal with the general case where a number of atoms are involved in a repeating unit.

1. Transformation Matrices between two Internal Coordinates

Let us consider rectangular coordinate systems $[\boldsymbol{X}_i]=(x_i, y_i, z_i)$ and $[\boldsymbol{X}_{i+1}]$ taking ith and $(i+1)$th atoms as their origins, respectively. The systems are shown in Fig. 1. In the $[\boldsymbol{X}_i]$-system, the x_i-axis penetrates the $(i+1)$th atom along the bond $(i, i+1)$, and the y_i-axis lies in the plane produced by the bonds $(i, i-1)$ and $(i, i+1)$ having its positive direction in the smaller-angle side of $\angle i-1, i, i+1$. The direction of the z_i-axis is chosen in such a way as to make the coordinate system right handed. The azimuthal angle about the bond $(i, i+1)$ is taken as zero at the *trans* position of the atoms $(i-1)$ and $(i+2)$, that is corresponding to a fully stretched zig-zag conformation. The positive direction of the rotation is taken as that of the clockwise twist of $[\boldsymbol{X}_{i+1}]$ about the x_i-axis, when observed from the $[\boldsymbol{X}_i]$-system.

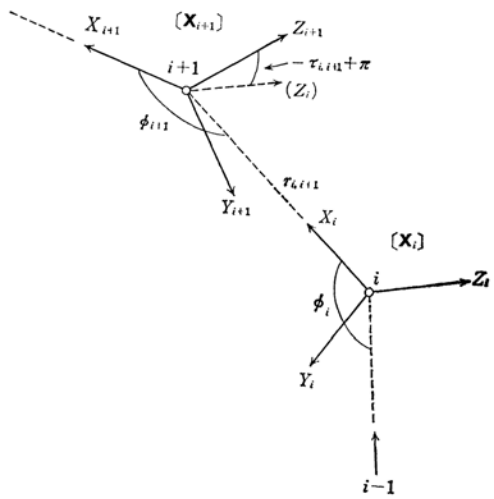

Fig. 1. The coordinate system $[\boldsymbol{X}_i]$.

When we designate the coordinates of an arbitrary point referred to the coordinate systems $[\boldsymbol{X}_i]$ and $[\boldsymbol{X}_{i+1}]$ as $\boldsymbol{X}_i$ and $\boldsymbol{X}_{i+1}$, respectively, a transformation between them is carried out[2] as

$$\boldsymbol{X}_i = \boldsymbol{A}_{i,i+1} \cdot \boldsymbol{X}_{i+1} + \boldsymbol{B}_{i,i+1}, \tag{1}$$

where

$$\boldsymbol{A}_{i,i+1} = \boldsymbol{A}^{\tau}{}_{i,i+1} \cdot \boldsymbol{A}^{\phi}{}_{i+1} \tag{1a}$$

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1) W. Cochran, F. H. C. Crick and V. Vand, *Acta Cryst.*, **5**, 581 (1952).
2) T. Shimanouchi and S. Mizushima, *J. Chem. Phys.*, **23**, 707 (1955).
3) T. Miyazawa, *J. Poly. Sci.*, **55**, 215 (1961).

$$\boldsymbol{A}^{\phi}{}_{i+1} = \begin{bmatrix} -\cos\phi_{i+1} & -\sin\phi_{i+1} & 0 \\ \sin\phi_{i+1} & -\cos\phi_{i+1} & 0 \\ 0 & 0 & 1 \end{bmatrix} \quad (1b)$$

$$\boldsymbol{A}^{\tau}{}_{i,i+1} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & -\cos\tau_{i,i+1} & \sin\tau_{i,i+1} \\ 0 & -\sin\tau_{i,i+1} & -\cos\tau_{i,i+1} \end{bmatrix} \quad (1c)$$

and

$$\boldsymbol{B}_{i,i+1} = (r_{i,i,+1}\, 0, 0)^{\dagger}, \quad (1d)$$

where the symbol † indicates transposed, r the bond length, ϕ the bond angle, and τ the dihedral angle.

In general, the same type of the relation mentioned above applies to atoms situated n-bonds apart;

$$\boldsymbol{X}_i = \boldsymbol{A}_{i,i+n}\cdot\boldsymbol{X}_{i+n} = \boldsymbol{B}_{i,i+n}, \quad (2)$$

where $\boldsymbol{A}_{i,i+n}$ and $\boldsymbol{B}_{i,i+n}$ are given by the following recurrence formula,[2]

$$\boldsymbol{A}_{i,i+n} = \boldsymbol{A}_{i,i+n-1}\cdot\boldsymbol{A}_{i+n-1,i+n} \quad (2a)$$

$$\boldsymbol{B}_{i,i+n} = \boldsymbol{A}_{i,i+n-1}\cdot\boldsymbol{B}_{i+n-1,i+n} + \boldsymbol{B}_{i,i+n-1}. \quad (2b)$$

On expressing repeating units by the subscript k, and atoms in a recurring unit by i, the relation (2) is rewritten as

$$\boldsymbol{X}_{(k\,i)} = \boldsymbol{A}_{(k\,i)(k'\,i')}\boldsymbol{X}_{(k'\,i')} + \boldsymbol{B}_{(k\,i)(k'\,i')}, \quad (3)$$

where $\boldsymbol{A}_{(k\,i)(k'\,i')}$ and $\boldsymbol{B}_{(k\,i)(k'\,i')}$ are given by recurrence formulas similar to Eqs. (2a) and (2b), respectively.

2. Helix Parameters

We next consider a relation between the coordinates of two equivalent atoms which belong to adjacent two units. Let us consider that each of these coordinates is given in terms of the coordinate system on the 0th atom in each unit, namely $[\boldsymbol{X}_{(k,0)}]$ and $[\boldsymbol{X}_{(k+1,0)}]$. The relation is given as

$$\boldsymbol{X}_{(k,0)} = \boldsymbol{A}_{(k,0)(k+1,0)}\boldsymbol{X}_{(k+1,0)} + \boldsymbol{B}_{(k,0)(k+1,0)}. \quad (4)$$

The subscript 0 is a common sulffix in the equation; it is omitted in the following discussion in this section.

One can find an axis about which a translational rotation can superpose the coordinate system $[\boldsymbol{X}_{k+1}]$ upon that of $[\boldsymbol{X}_k]$. This is the helix axis. The helix-coordinate system about this axis is defined as shown in Fig. 2. In that rectangular coordinate system, $[\boldsymbol{\xi}_k]=(\xi_k, \eta_k, \zeta_k)$, ξ_k-axis points to the origin of the $[\boldsymbol{X}_k]$, ζ_k-axis is on the helix axis, and η_k-axis is taken so as to make the coordinate system right handed. Coordinates of an arbitrary point ξ_k and ξ_{k+1} which refer to $[\boldsymbol{\xi}_k]$-system and $[\boldsymbol{\xi}_{k+1}]$-system, respectively, are transformed into each other by the following equation[2],

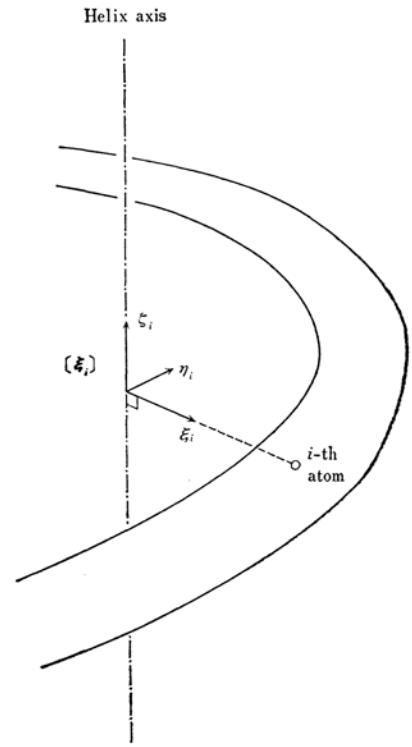

Fig. 2. The coordinate system $[\boldsymbol{\xi}_i]$.

$$\boldsymbol{\xi}_k = \boldsymbol{N}\boldsymbol{\xi}_{k+1} + \boldsymbol{L}, \quad (5)$$

where $\boldsymbol{N} = \begin{bmatrix} \cos\theta & -\sin\theta & 0 \\ \sin\theta & \cos\theta & 0 \\ 0 & 0 & 1 \end{bmatrix}$, (5a)

$\boldsymbol{L} = (0, 0, \mathrm{d})^{\dagger}$,

θ: translation angle,

d: translation distance along the helical axis per repeating unit.

The translation angle is taken to be positive at the right handed screw direction looking from k to $k+1$. This helix coordinate system is expressed in terms of the set of internal coordinates by introducing the transforming matrix $\boldsymbol{T}$.[4] Namely,

$$\boldsymbol{\xi}_k = \boldsymbol{T}\boldsymbol{X}_k + \boldsymbol{S} \quad (6a)$$

$$\boldsymbol{\xi}_{k+1} = \boldsymbol{T}\boldsymbol{X}_{k+1} + \boldsymbol{S} \quad (6b)$$

$$\boldsymbol{S} = (\rho,\ 0,\ 0)^{\dagger} \quad (6c)$$

where ρ is the radial distance from the helical axis to an atom $(k,\ 0)$. Thus, from Eqs. (4), (5) (6a), and (6b), we obtain[2]

$$\boldsymbol{N} = \boldsymbol{T}\cdot\boldsymbol{A}_{k,k+1}\cdot\boldsymbol{T}^{\dagger} \quad (7)$$

and

4) This $\boldsymbol{T}$ matrix is the transpose of the "$\boldsymbol{T}$" used by Shimanouchi and Mizushima.[2]

$$(\boldsymbol{N}-\boldsymbol{I})\boldsymbol{S}+\boldsymbol{L}=\boldsymbol{T}\cdot\boldsymbol{B}_{k,k+1} \tag{8}$$

$\boldsymbol{I}$: unit matrix.

The elements, t_{ij}, of the matrix $\boldsymbol{T}$ are related to the parameters defining a helix: θ, d, and ρ, by the following equations

$$\rho(\cos\theta-1)=t_{11}b_1+t_{12}b_2+t_{13}b_3, \tag{9a}$$

$$\rho\sin\theta=t_{21}b_1+t_{22}b_2+t_{23}b_3, \tag{9b}$$

$$d=t_{31}b_1+t_{32}b_2+t_{33}b_3, \tag{9c}$$

where b's are the elements of $\boldsymbol{B}_{k,k+1}=(b_1, b_2, b_3)\dagger$.

Shimanouchi and Mizushima[2] gave the following three equations:

$$d^2=[b_1(a_{13}+a_{31})+b_2(a_{23}+a_{32})+b_3(a_{33}-a_{11}-a_{22}+1)]^2/(3-a_{11}-a_{22}-a_{33})\times(a_{33}-a_{11}-a_{22}+1), \tag{10}$$

and

$$\cos\theta=(a_{11}+a_{22}+a_{33}-1)/2, \tag{11}$$

$$\rho^2=(b_1^2+b_2^2+b_3^2-d^2)/(3-a_{11}-a_{22}-a_{33}), \tag{12}$$

where a_{ij}'s are the elements of $\boldsymbol{A}_{k,k+1}$.

The two equations (10) and (11) are useful for calculating the residue translation distance (d) along the helix axis and the residue rotation angle (θ) around the axis from a given set of bond lengths, bond angles, and dihedral angles. We like to add a new equation here,

$$2d\sin\theta=(a_{21}-a_{12})b_3+(a_{13}-a_{31})b_2+(a_{32}-a_{23})b_1, \tag{13}$$

so that the sign of θ can be uniquely determined. (This equation (13) can be derived as shown in Appendix I from Eqs. (7) and (9c) by the use of the fact that $\boldsymbol{T}$ is an orthogonal matrix with $|\boldsymbol{T}|=1$.) Let d be positive on going from k to $k+1$. Then, $0<\theta<\pi$, when the right side value of Eq. (13) is positive; and $-\pi<\theta<0$, when the right side value of Eq. (13) is negative. It should be mentioned here that Miyazawa[3] gave equations corresponding to Eqs. (10), (11), (12), and (13) in some different forms.

3. Structure Parameter for Each Atom

On the basis of what have been described, the cylindrical-polar coordinates of each atom in a helical polymer are now to be given. Let us set the origin of the coordinates so that $\theta_{0,0}=0$, $d_{0,0}=0$, $\rho_{0,0}=\rho$ for the 0th atom in the 0th residues. Our problem is now reduced to the problem of obtaining the (ξ, η, ζ) values of the ith atom in the kth residue in terms of the $[\boldsymbol{\xi}_{0,0}]$ coordinate system. This is given as

$$\begin{bmatrix}\rho_{ki}\cos\theta_{ki}\\ \rho_{ki}\sin\theta_{ki}\\ d_{ki}\end{bmatrix}=\begin{bmatrix}\xi_{ki}\\ \eta_{ki}\\ \zeta_{ki}\end{bmatrix}\equiv\boldsymbol{\xi}_{00}{}^{ki}=\boldsymbol{T}\boldsymbol{X}_{00}{}^{ki}+\boldsymbol{S}. \tag{14}$$

Herer ρ_{ki}, θ_{ki} and d_{ki} are the cylindrical-polar coordinates of the ith atom in the kth residue. (ρ_{ki} does not depend upon k and may be rewritten as ρ_i). $\boldsymbol{X}_{00}{}^{ki}$ is the (x, y, z) values of the $(k\ i)$ atom in terms of the $[\boldsymbol{X}_{00}]$ coordinate system. The coordinates of the $(k\ i)$ atom in terms of the $[\boldsymbol{X}_{ki}]$ coordinate system should be $(0, 0, 0)\dagger$, that is

$$\boldsymbol{X}_{ki}{}^{ki}=\begin{bmatrix}0\\ 0\\ 0\end{bmatrix}. \tag{15}$$

On substituting this in Eq. (3),

$$\boldsymbol{X}_{00}{}^{ki}=\boldsymbol{B}_{(0,0)(k,i)}. \tag{16}$$

Therefore,

$$\boldsymbol{\xi}_{00}{}^{ki}=\boldsymbol{T}\boldsymbol{B}_{(0,0)(k,i)}+\boldsymbol{S}. \tag{17}$$

Since $\boldsymbol{B}_{(0,0)(k,i)}$ and $\boldsymbol{S}$ are known as given by Eqs. (2b), (6c), and (12), our last task is now to calculate $\boldsymbol{T}$. (These $\boldsymbol{T}$ and $\boldsymbol{S}$ matices in Eq. (17) are common for any atom i in this helical molecule, regardless of whether it is in the main-chain or in the sidechain.)

4. Calculation of the T Matrix

Elements of the transformation matrix $\boldsymbol{T}$ are determined from Eqs. (7) and (8). On rewriting Eq. (7),

$$\boldsymbol{A}_{k,k+1}=\boldsymbol{T}\dagger\boldsymbol{N}\boldsymbol{T}. \tag{18}$$

By diagonalizing $\boldsymbol{N}$, we obtain,

$$\boldsymbol{N}=\boldsymbol{U}_0{}^{-1}\boldsymbol{\Lambda}\boldsymbol{U}_0, \tag{19}$$

where

$$\boldsymbol{\Lambda}=\begin{bmatrix}e^{-i\theta}&0&0\\ 0&e^{i\theta}&0\\ 0&0&1\end{bmatrix}. \tag{19a}$$

$\boldsymbol{U}_0$ is put tentatively as unitary matrix aside from its arbitrariness:

$$\boldsymbol{U}_0=\begin{pmatrix}\frac{1}{\sqrt{2}}&-\frac{i}{\sqrt{2}}&0\\ -\frac{i}{\sqrt{2}}&\frac{1}{\sqrt{2}}&0\\ 0&0&1\end{pmatrix}, \tag{20}$$

where $\boldsymbol{U}_0{}^{-1}=\boldsymbol{U}_0{}^*$ and $*$ indicates Hermitian conjugate. From Eqs. (18) and (19),

$$\boldsymbol{A}_{(k,0)(k+1,0)}=\boldsymbol{T}\dagger\boldsymbol{U}_0{}^*\boldsymbol{\Lambda}\boldsymbol{U}_0\boldsymbol{T}=\boldsymbol{U}^*\boldsymbol{\Lambda}\boldsymbol{U} \tag{21}$$

where

$$\boldsymbol{U}=\boldsymbol{U}_0\boldsymbol{T}, \tag{21a}$$

Each of the rows of the matrix $\boldsymbol{U}^*$ can be obtained as eigenvectors where they still have an arbitrary phase factor in the form $e^{i\alpha}$. But, when we use the condition that the elements of the matrix $\boldsymbol{T}$ obtained by Eq. (21) should be real, it is finally written as follows (see Appendix II),

$$\boldsymbol{T}=\begin{bmatrix} C[a_{31}\cos\beta+a_{13}\cos(\theta+\beta)] & C[a_{32}\cos\beta+a_{23}\cos(\theta+\beta)] & C[a_{33}\cos\beta-(a_{11}+a_{22})\cos(\theta+\beta)+\cos(2\theta+\beta)] \\ -C[a_{31}\sin\beta+a_{13}\sin(\theta+\beta)] & -C[a_{32}\sin\beta+a_{23}\sin(\theta+\beta)] & -C[a_{33}\sin\beta-(a_{11}+a_{22})\sin(\theta+\beta)+\sin(2\theta+\beta)] \\ \pm C'(a_{31}+a_{13}) & \pm C'(a_{32}+a_{23}) & \pm C'(a_{33}-a_{22}-a_{11}+1) \end{bmatrix} \quad (22)$$

The constants C and C' are normalization factor, that is,

$$C = \{2(1-a_{33})\sin^2\theta\}^{-1/2} \quad (23a)$$

$$C' = \{(3-a_{11}-a_{22}-a_{33})(a_{33}-a_{22}-a_{11}+1)\}^{-1/2}. \quad (23b)$$

The sign left undetermined at the third row in Eq. (22) can be given by the condition $d \geqq 0$ from Eq. (9c). β in Eq. (22) has come from the phase factor that has not been determined yet. Since this term comes from Eq. (18) which does not involve the fact that the ξ_k-axis is directed to the origin of the system $[\boldsymbol{X}_k]$, the $[\boldsymbol{\xi}_k]$-system has a freedom of rotation about the helix axis. The freedom is to be removed by taking Eqs. (9a) and (9b) into account (see Appendix III). Thus,

$$\beta = -\frac{\theta+\gamma+\pi}{2} + m\pi, \qquad (m\text{: integer}) \quad (24)$$

where

$$\gamma = \tan^{-1}\frac{2uv\sin\theta+(v^2+2uw)\sin2\theta+2vw\sin3\theta+w^2\sin4\theta}{u^2+2uv\cos\theta+(v^2+2uw)\cos2\theta+2vw\cos3\theta+w^2\cos4\theta} \quad (24a)$$

$$u = a_{31}b_1 + a_{32}b_2 + a_{33}b_3 \quad (24b)$$

$$v = a_{13}b_1 + a_{23}b_2 - (a_{11}+a_{22})b_3 \quad (24c)$$

$$w = b_3. \quad (24d)$$

γ can be fixed in the region of $-\pi/2 — \pi/2$ if the sign of the following value is positive:

$$\cos\gamma = \frac{u^2+2uv\cos\theta+(v^2+2uw)\cos2\theta+2vw\cos3\theta+w^2\cos4\theta}{u^2+v^2+w^2+2(uv+vw)\cos\theta+2uw\cos2\theta} \quad (25)$$

and γ is in the other region when it happens to have a negative value. The ambiguity of the amount $m\pi$ in Eq. (24) leaves an undetermined sign at the first and second rows in the matrix $\boldsymbol{T}$. This is determined by the use of Eq. (9a) and the condition that $\rho(\cos\theta-1) \leqq 0$. The matrix $\boldsymbol{T}$ can then be produced without any ambiguity.

5. Summary with an Example

Suppose that, for poly-L-alanine, the bond lengths and bond angles are given as are shown in Fig. 3, and dihedral angles as follows:

$$\tau(\mathrm{CC_\alpha NC}) = 120°,$$

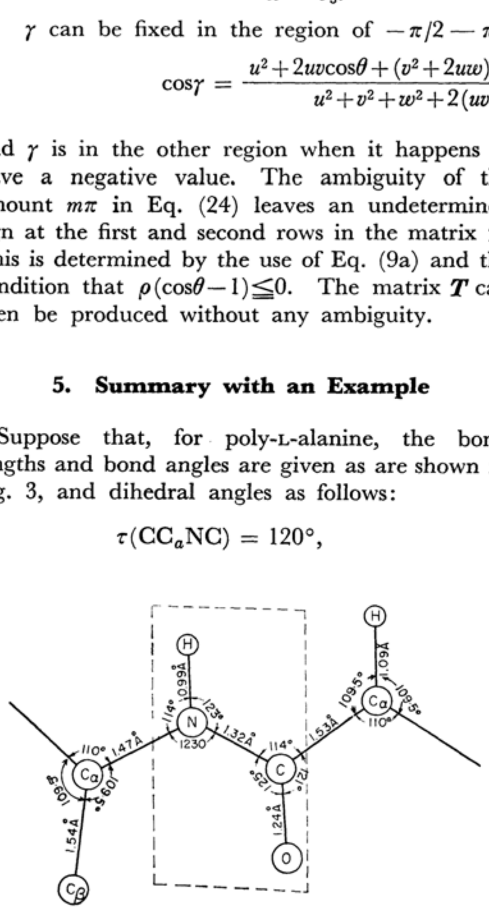

Fig. 3. The bond lengths and bond angles assumed for poly-L-alanine.

$$\tau(\mathrm{C_\alpha NCC_\alpha}) = 0°,$$

$$\tau(\mathrm{NCC_\alpha C}) = 140°.$$

Let C_α atom as the zero-th atom in a kth residue. Then, the matrix elements of $\boldsymbol{A}_{(k,0)(k+1,0)}$ and $\boldsymbol{B}_{(k,0)(k+1,0)}$ are calculated by the use of Eqs. (2a) and (2b). Substituting the values of these elements into Eqs. (10), (11), (12), and (13), we obtain

$$d = 1.59_4 \text{ Å},$$

$$\theta = 103.7°,$$

and $\rho = 2.19_4$ Å.

Next, C and C' are to be calculated by Eqs. (23a) and (23b), then γ by Eqs. (24a)—(25), and β by Eq. (24). The $\boldsymbol{T}$ matrix elements are now calculated by Eq. (22). We are now ready to calculate the cylindrical-polar coordinates of any atom (i). By the use of Eq. (2b), $\boldsymbol{B}_{(k,0)(k,i)}$ matrix is obtained. $\boldsymbol{S}$ is known to be (2.19$_4$ Å, 0, 0). Therefore, $\boldsymbol{\xi}_{k0}{}^{ki}$ can be calculated (Eq. 17), from which ρ_i, θ_i, d_i values are derived by Eq. (14). What are obtained are as follows:

C_α:	$\rho=2.19_4$ Å	$\theta=0°$	$d=0$ Å
N:	1.40_3	28.1_7	0.89_8
carbonyl C:	1.62_3	76.4_7	0.48_6
O:	2.00_2	82.0_4	-0.68_0
H on N:	1.34_3	15.5_9	1.84_0
C_β:	3.20_1	-18.0_6	0.81_7
H on C_α:	2.94_9	14.8_1	-0.43_5

Appendix I. Derivation of Eq. (13)

From Eq. (7), we obtain the relations:

$$a_{12} = (t_{11}t_{12}+t_{21}t_{22})\cos\theta + (t_{21}t_{12}-t_{11}t_{22})\sin\theta + t_{31}t_{32} \tag{A1}$$

and

$$a_{21} = (t_{11}t_{12}+t_{21}t_{22})\cos\theta - (t_{21}t_{12}-t_{11}t_{22})\sin\theta + t_{31}t_{32}. \tag{A2}$$

From these two relations,

$$(a_{12}-a_{21})/2 = (t_{21}t_{12}-t_{11}t_{22})\sin\theta. \tag{A3}$$

The $\boldsymbol{T}$ matrix is an orthogonal matrix with $|\boldsymbol{T}|=1$; therefore, its adjoint matrix $\hat{\boldsymbol{T}}$ should be equal to $\boldsymbol{T}^{\dagger}$. Hence

$$t_{33} = t_{11}t_{22} - t_{12}t_{21}. \tag{A4}$$

From Eqs. (A3) and (A4),

$$t_{33} = (a_{21}-a_{12})/2\sin\theta. \tag{A5}$$

In similar ways, one can obtain the following two relations:

$$t_{32} = (a_{13}-a_{31})/2\sin\theta \tag{A6}$$

and

$$t_{31} = (a_{32}-a_{23})/2\sin\theta. \tag{A7}$$

On substituting these expressions for t_{33}, t_{32}, and t_{31} in Eq. (9c), we obtain Eq (13).

Appendix II. Derivation of Eq. (22)

From Eq. (21),

$$\boldsymbol{A}\boldsymbol{U}^* = \boldsymbol{U}^*\boldsymbol{\Lambda} \tag{A8}$$

This can be written as

$$\begin{bmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{bmatrix} \begin{bmatrix} l_{11} & l_{12} & l_{13} \\ l_{21} & l_{22} & l_{23} \\ l_{31} & l_{32} & l_{33} \end{bmatrix} = \begin{bmatrix} l_{11} & l_{12} & l_{13} \\ l_{21} & l_{22} & l_{23} \\ l_{31} & l_{32} & l_{33} \end{bmatrix} \begin{bmatrix} e^{-i\theta} & 0 & 0 \\ 0 & e^{i\theta} & 0 \\ 0 & 0 & 1 \end{bmatrix} \tag{A9}$$

where l's are the elements of the $\boldsymbol{U}^*$ matrix. Of these elements l_{11}, l_{21}, and l_{31} form the eigenvector for the eigenvalue $e^{-i\theta}$ of the $\boldsymbol{A}$ matrix. These values can be obtained by solving the simultaneous equations:

$$\left.\begin{aligned} a_{11}l_{11} + a_{12}l_{21} + a_{13}l_{31} &= e^{-i\theta}l_{11}, \\ a_{21}l_{11} + a_{22}l_{21} + a_{23}l_{31} &= e^{-i\theta}l_{21}, \\ \text{and} \quad a_{31}l_{11} + a_{32}l_{21} + a_{33}l_{31} &= e^{-i\theta}l_{31}, \end{aligned}\right\} \tag{A10}$$

as

$$l_{11} = C_1\begin{vmatrix} a_{12} & a_{13} \\ a_{22}-e^{-i\theta} & a_{23} \end{vmatrix}, \tag{A11}$$

$$l_{21} = C_1\begin{vmatrix} a_{13} & a_{11}-e^{-i\theta} \\ a_{23} & a_{21} \end{vmatrix}, \tag{A12}$$

and

$$l_{31} = C_1\begin{vmatrix} a_{11}-e^{-i\theta} & a_{12} \\ a_{21} & a_{22}-e^{-i\theta} \end{vmatrix}, \tag{A13}$$

where C_1 is a constant to be determined later. Since the $\boldsymbol{A}$ matrix is an orthogonal matrix with $|\boldsymbol{A}|=1$, its adjoint matrix $\hat{\boldsymbol{A}}$ should be equal to $\boldsymbol{A}^{\dagger}$. Therefore, we have

$$a_{12}a_{23} - a_{13}a_{22} = a_{31}, \tag{A14}$$

$$a_{13}a_{21} - a_{11}a_{23} = a_{32}, \tag{A15}$$

and

$$a_{11}a_{22} - a_{12}a_{21} = a_{33}. \tag{A16}$$

On substituting these into (A11), (A12), and (A13),

$$l_{11} = C_1(a_{31} + a_{13}e^{-i\theta}), \tag{A17}$$

$$l_{21} = C_1(a_{32} + a_{23}e^{-i\theta}), \tag{A18}$$

$$l_{31} = C_1[a_{33} - (a_{11}+a_{22})e^{-i\theta} + e^{-2i\theta}]. \tag{A19}$$

Because $\boldsymbol{U}^*$ should be a unitary matrix,

$$l_{11}l_{11}^* + l_{21}l_{21}^* + l_{31}l_{31}^* = 1. \tag{A20}$$

On substituting Eqs. (A17), (A18), and (A19) into Eq, (A20),

$$4C_1^*C_1(1-a_{33})\sin^2\theta = 1, \tag{A21}$$

or

$$C_1 = e^{-i\beta}\tfrac{1}{2}[(1-a_{33})\sin^2\theta]^{-1/2}. \tag{A22}$$

In an analogous way, the eigenvectors for the eigenvalue $e^{i\theta}$ can be obtained as

$$l_{12} = C_2(a_{31}+a_{13}e^{i\theta}), \tag{A23}$$

$$l_{22} = C_2(a_{32}+a_{23}e^{i\theta}), \tag{A24}$$

and

$$l_{32} = C_2[a_{33}-(a_{11}+a_{22})e^{i\theta}+e^{2i\theta}], \tag{A25}$$

where

$$C_2 = e^{i\beta'}\tfrac{1}{2}[(1-a_{33})\sin^2\theta]^{-1/2}. \tag{A26}$$

For the eigenvalue 1,

$$l_{13} = C_3(a_{31}+a_{13}), \tag{A27}$$

$$l_{23} = C_3(a_{32}+a_{23}), \tag{A28}$$

and

$$l_{33} = C_3(a_{33}-a_{11}-a_{22}+1), \tag{A29}$$

where

$$C_3 = e^{i\beta''}[(3-a_{11}-a_{22}-a_{33})(a_{33}-a_{22}-a_{11}+1)]^{-1/2} \tag{A30}$$

From these elements of $\boldsymbol{U}^*$, the elements of $\boldsymbol{U}$ can be obtained. By the use of the relation,

$$\boldsymbol{T} = \boldsymbol{U}_0^*\boldsymbol{U}, \tag{A31}$$

$\boldsymbol{T}$ matrix is now to be calculated. In this calculation we can easily find that the relations:

$$e^{i\beta'} = ie^{i\beta} \tag{A32}$$

and

$$e^{i\beta''} = \pm 1 \tag{A33}$$

are required so that all the elements of the $\boldsymbol{T}$ matrix are real. By substituting Eqs. (A32) and (A33) into Eqs. (A23)—(A30), and by the use of Eq. (A31), we can reach Eq. (22) in the text.

Appendix III. Derivation of Eq. (24)

From Eqs. (9a) and (9b), the following two relations are obtained:

$$\rho(\cos\theta-1) + i\rho\sin\theta = \rho(e^{i\theta}-1)$$
$$= (t_{11}+it_{21})b_1 + (t_{12}+it_{22})b_2 + (t_{13}+it_{23})b_3 \tag{A34}$$

and

$$\rho(\cos\theta-1) - i\rho\sin\theta = \rho(e^{-i\theta}-1)$$
$$= (t_{11}-it_{21})b_1 + (t_{12}-it_{22})b_2 + (t_{13}-it_{23})b_3. \tag{A35}$$

By substituting the $\boldsymbol{T}$ matrix elements given in Eq. (22) into these relations, we can rewrite them as

$$\rho(e^{i\theta}-1) = Ce^{-i\beta}\{(a_{31}+a_{13}e^{-i\theta})b_1+(a_{32}+a_{23}e^{-i\theta})b_2 + [a_{33}-(a_{11}+a_{22})e^{-i\theta}+e^{-2i\theta}]b_3\}, \quad \text{(A36)}$$

and

$$\rho(e^{-i\theta}-1)=Ce^{i\beta}\{(a_{31}+a_{13}e^{i\theta})b_1+(a_{32}+a_{23}e^{i\theta})b_2 + [a_{33}-(a_{11}+a_{22})e^{i\theta}+e^{2i\theta}]b_3\} \quad \text{(A37)}$$

Therefore, we have

$$\frac{e^{i\theta}-1}{e^{-i\theta}-1} = -e^{i\theta} = e^{-2i\beta}\frac{z^*}{z}, \quad \text{(A38)}$$

where

$$z = u + ve^{i\theta} + we^{2i\theta}, \quad \text{(A39)}$$

with u, v, and w defined as are given Eqs. (24b), (24c), and (24d) in the text. Let us put

$$e^{-i\gamma} = \frac{z^*}{z}. \quad \text{(A40)}$$

Then, Eq. (A38) becomes

$$-e^{i\theta} = e^{-2i\beta}e^{-i\gamma}, \quad \text{(A41)}$$

or

$$e^{i(\theta+\pi)} = e^{-i(2\beta+\gamma)}. \quad \text{(A42)}$$

Therefore,

$$\theta + \pi = -(2\beta+\gamma) + 2m\pi, \quad \text{(A43)}$$

where m is an integer. This is equivalent to Eq. (24) in the text. From Eq. (A40), we obtain

$$\cos\gamma = \frac{(z^*)^2+z^2}{2zz^*} \quad \text{(A44)}$$

and

$$\tan\gamma = -\frac{(z^*)^2-z^2}{i[(z^*)^2+z^2]}. \quad \text{(A45)}$$

On substituting Eq. (A39) into Eqs. (A44) and (A45), we have the two relations (25) and (24a) in the text.

Note. After the completion of this work, we have been informed that H. Sugeta and T. Miyazawa developed a method of calculating the $\boldsymbol{T}$ matrix elements which is somewhat different from our method given here.