$L \gg a$ ($a$ is a monomer size), the system displays $(d-1)$-dimensional properties (a "dimensional reduction"), and expansions about a $d$-dimensional reference state are inappropriate. These difficulties manifest themselves in renormalization group calculations having first-order (in the excluded volume) corrections to many quantities which become much larger than zeroth-order contributions in the $\langle \mathbf{R}^2 \rangle_f^{1/2} \gg L$ regime. The mathematical origin of this effect is that, as $\langle \mathbf{R}^2 \rangle^{1/2} \sim \mathcal{O}(L)$, the normal end-vector distribution scales as $G_\perp(R/L)$ rather than $G_\perp(R/\langle \mathbf{R}^2 \rangle^{1/2})$. See Dolan and Edwards[3] for a relevant discussion. An effective free energy functional method has been recently introduced by two of us [Nemirovsky, A. M.; Freed, K. F. *J. Phys. A: Math. Gen.*, in press; *Nucl. Phys. B*, in press] to remedy related problems in critical phenomena. We plan to utilize similar methods to study the "dimensionally reduced" regime of polymers strongly adsorbed onto surfaces and confined in some bounded geometries where $L \lesssim \mathcal{O}(\langle \mathbf{R}^2 \rangle_f^{1/2})$.

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# Conformational Entropy of Ring Polymers

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*Received November 26, 1985*

ABSTRACT: An expression for the partition function of ring polymers is derived for the treatment in which bond lengths and bond angles are kept fixed and only dihedral angles are variables. When there are $n$ rotatable backbone dihedral angles in a ring polymer, only $(n-6)$ of them are independent and the values of the remaining six angles can be determined as functions of $(n-6)$ angles chosen as independent variables. The conformational energy $E$ is then a function of these $(n-6)$ independent variables. However, the partition function is not given as an integral of $\exp(-\beta E)$ over the space of the $(n-6)$ variables. In fact this integral depends on the choice of $(n-6)$ independent variables, while the correct partition function should be independent of the choice. The derived expression is independent of the choice of independent variables.

The theoretical method of conformational energy analysis has been applied successfully to many problems of biopolymers, including proteins and peptides.[1] The method has been developed to calculate not only conformational energy but also conformational entropy by formulating the method of calculating the partition function.[2] When bond lengths and bond angles are kept fixed and only dihedral angles are treated as variables in such analyses, ring polymers require special considerations, because not all of the backbone dihedral angles are independent. When there are $n$ rotatable backbone dihedral angles in a ring polymer, only $(n-6)$ of them are independent and the values of the remaining six angles can be determined as functions of the $(n-6)$ angles chosen as independent variables. The problem of expressing dependent dihedral angles as explicit functions of independent dihedral angles was solved previously.[3] Therefore, conformational energy $E$ is then given as a function of the

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$(n-6)$ independent variables. However, the exact partition function is not given as an integral of $\exp(-\beta E)$ over the space of the chosen $(n-6)$ independent variables. In fact, this integral depends on the choice of the independent variables, while the true partition function should not. In this paper I will derive an explicit expression of the partition function of ring polymers which is correct and independent of the choice of independent variables.

## Derivation of the Basic Formula

The derivation is based on the result obtained in a previous paper,[2] in which the problem of treatments of the degrees of freedom of bond stretching and bond angle bending in chain molecules was studied. Here I shall summarize the result of this paper very briefly. If we fix the bond lengths and bond angles at the outset and treat them as constraints (the classical rigid model), the partition function is given by an integral of $(\det G)^{-1/2} \exp[-\beta E(Q)]$ over the space of dihedral angles $Q$ in a chain molecule, where the elements of the matrix $G$ are the coefficients in the quadratic expression (in terms of generalized momenta conjugate to $Q$) for the kinetic energy of the chain molecule and $E(Q)$ is the conformational energy of the molecule. If we conceptually allow bond lengths and bond angles to vary under an infinitely strong potential (the classical flexible model) and perform the integration of the Boltzmann factor over the momenta conjugate to the Cartesian coordinates, we obtain the partition function in the form of an integral of $\exp[-\beta E(Q)]$ over the space of the dihedral angles. The origin of the differences between these two forms of the partition function was explored and it was shown that, while both involve approximations, the latter is more accurate than the former.

Therefore I will derive the correct expression of the partition function of ring chain molecules by treating them as classical flexible molecules, i.e., by conceptually allowing bond lengths and bond angles to vary under an infinitely strong potential. Let us consider a ring chain molecule consisting of $n$ main-chain atoms whose position vectors will be expressed by $\mathbf{r}_i$, $i = 1, 2, ..., n$. The $n$th atom is linked to the first one to close a ring. Thus the conformational energy $E$ consists of two terms

$$E(\mathbf{r}_1,\mathbf{r}_2,...,\mathbf{r}_n) = E_0(\mathbf{r}_1,\mathbf{r}_2,...,\mathbf{r}_n) + E_1 \tag{1}$$

$$E_1 = (\epsilon_1/2)\sum_{i=1}^{n}(d_i - d_{i0})^2 + (\epsilon_2/2)\sum_{i=1}^{n}(\theta_i - \theta_{i0})^2 \tag{2}$$

The first term, $E_0$, is the usual conformation-dependent term and is eventually a function of dihedral angles $\omega_1, \omega_2, ..., \omega_n$, even though it is expressed in eq 1 as a function of the position vectors of the backbone atoms at the moment. The second term, $E_1$, pertains to variation in bond lengths, $d_i$, and bond angles, $\theta_i$. We will take $\epsilon_1$ and $\epsilon_2$ as very large positive quantities, so that deviations of $d_i$ and $\theta_i$ from fixed "standard" values $d_{i0}$ and $\theta_{i0}$, respectively, become negligible. Here definitions of bond length $d_i$, bond angle $\theta_i$, and dihedral angle $\omega_i$ are given in Figure 1. Note that for defining $d_n$, $\theta_{n-1}$, $\theta_n$, $\omega_{n-2}$, $\omega_{n-1}$, and $\omega_n$, position vectors $\mathbf{r}_1$, $\mathbf{r}_2$, and $\mathbf{r}_3$ are formally read as $\mathbf{r}_{n+1}$, $\mathbf{r}_{n+2}$, and $\mathbf{r}_{n+3}$. Now the partition function is given by

$$Z = \int d\mathbf{r}_1 ... d\mathbf{r}_n \exp[-\beta E(\mathbf{r}_1, ..., \mathbf{r}_n)] \tag{3}$$

Our problem is to reduce this expression to that of integration over the space of dihedral angles. We do this by changing the variable of integration in two steps. At first we change as $(\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_n) \rightarrow (\mathbf{r}_1, \mathbf{x}_1, \mathbf{x}_2, ..., \mathbf{x}_{n-1})$ where

$$\mathbf{x}_i = \mathbf{r}_{i+1} - \mathbf{r}_i \qquad (i = 1, 2, ..., n-1) \tag{4}$$

Here $\mathbf{x}_i$ is a bond vector pointing from the $i$th to the $(i+1)$th atom. The position vector of the first atom, $\mathbf{r}_1$, is retained to define the overall translational degrees of freedom of the molecule. Then the bond vectors are expressed in terms of Eulerian angles ($\Phi$, $\Theta$, and $\Psi$) and the internal variables (bond lengths, bond angles, and dihedral angles).

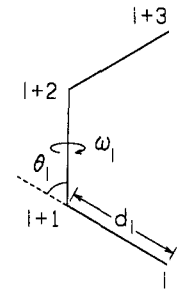


**Figure 1.** Definition of bond length $d_i$, bond angle $\theta_i$, and dihedral angle $\omega_i$.

$$\mathbf{x}_1 = R(\Phi)T(\Theta)\mathbf{d}_1$$

$$\mathbf{x}_2 = R(\Phi)T(\Theta)R(\Psi)T(\theta_1)\mathbf{d}_2$$

$$\mathbf{x}_i = R(\Phi)T(\Theta)R(\Psi)T(\theta_1)\prod_{j=1}^{i-2}R(\omega_j)T(\theta_{j+1})\mathbf{d}_i \qquad (i = 3, 4, ..., n-1) \tag{5}$$

where

$$\mathbf{d}_k = \begin{pmatrix} d_k \\ 0 \\ 0 \end{pmatrix} \tag{6}$$

$$R(\omega) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & \cos\omega & -\sin\omega \\ 0 & \sin\omega & \cos\omega \end{pmatrix} \tag{7}$$

$$T(\theta) = \begin{pmatrix} \cos\theta & -\sin\theta & 0 \\ \sin\theta & \cos\theta & 0 \\ 0 & 0 & 1 \end{pmatrix} \tag{8}$$

Equations 5–8 serve also as precise definitions of the Eulerian angles and internal variables. The Eulerian angles define overall orientation of the molecule by defining the directions of the first two bond vectors $\mathbf{x}_1$ and $\mathbf{x}_2$. However, six additional internal variables appearing explicitly or implicitly in eq 1 and 2, i.e., $d_n$, $\theta_{n-1}$, $\theta_n$, $\omega_{n-2}$, $\omega_{n-1}$, and $\omega_n$, are not yet defined in the above equations. To define them, the ranges of eq 4 and 5 are now extended to $i = 1, 2, ..., n+2$ and $i = 3, 4, ..., n+2$, respectively. Note that, in this process of extension of the ranges of equations, we introduced three more internal variables, $d_{n+1}$, $d_{n+2}$, and $\theta_{n+1}$, three bond vectors, $\mathbf{x}_n$, $\mathbf{x}_{n+1}$, and $\mathbf{x}_{n+2}$, and three position vectors, $\mathbf{r}_{n+1}$, $\mathbf{r}_{n+2}$, and $\mathbf{r}_{n+3}$. Corresponding to the introduction of these new quantities, we rewrite eq 3 as follows:

$$Z = \int d\mathbf{r}_1 ... d\mathbf{r}_n\, d\mathbf{r}_{n+1}\, d\mathbf{r}_{n+2}\, d\mathbf{r}_{n+3}\delta(\mathbf{r}_{n+1} - \mathbf{r}_1)\delta(\mathbf{r}_{n+2} - \mathbf{r}_2)\delta(\mathbf{r}_{n+3} - \mathbf{r}_3) \exp(-\beta E) \tag{9}$$

where $\delta$ is the delta function. This mathematical procedure may be interpreted as treating the ring chain molecule as if it were a linear chain molecule but with constraints of imposing the last three atoms to coincide with the first three atoms, respectively (Figure 2).

Now we carry out the first change of variables of integration. Because the Jacobian for this change is unity, we have

$$Z = \int d\mathbf{r}_1\, d\mathbf{x}_1 ... d\mathbf{x}_{n+2}\delta(\sum_{i=1}^{n}\mathbf{x}_i)\delta(\mathbf{x}_{n+1} - \mathbf{x}_1)\delta(\mathbf{x}_{n+2} - \mathbf{x}_2) \exp(-\beta E) \tag{10}$$

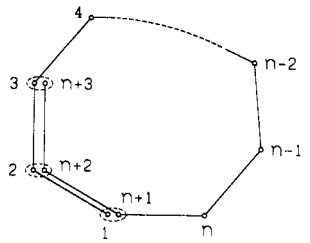


**Figure 2.** Illustration of eq 9.

Because the conformational energy $E$ can be expressed in terms of only bond vectors, the integration with respect to $\mathbf{r}_1$ can be carried out to produce a constant volume, $V$, of a space in which the molecule is contained. Then we carry out the second change of variables of integration for which the Jacobian, $J$, was previously shown[2] to be

$$J = \sin\Theta \prod_{i=1}^{n+1} \sin\theta_i \prod_{i=1}^{n+2} d_i^2 \tag{11}$$

The arguments of the $\delta$ functions in eq 10 are now given as follows:

$$\sum_{i=1}^{n} \mathbf{x}_i = R(\Phi)T(\Theta)R(\Psi)\mathbf{a}$$

$$\mathbf{x}_{n+1} - \mathbf{x}_1 = R(\Phi)T(\Theta)R(\Psi)\mathbf{b}$$

$$\mathbf{x}_{n+2} - \mathbf{x}_2 = R(\Phi)T(\Theta)R(\Psi)\mathbf{c} \tag{12}$$

where

$$\mathbf{a} = \mathbf{d}_1 + \sum_{i=2}^{n} \prod_{j=1}^{i-1} T(\theta_j)R(\omega_j)\mathbf{d}_i$$

$$\mathbf{b} = U\mathbf{d}_{n+1} - \mathbf{d}_1$$

$$\mathbf{c} = UT(\theta_{n+1})\mathbf{d}_{n+2} - T(\theta_1)\mathbf{d}_2 \tag{13}$$

with

$$U = \prod_{j=1}^{n} T(\theta_j)R(\omega_j) \tag{14}$$

To derive these equations we used the following equations:

$$R(\Psi)\mathbf{d}_1 = \mathbf{d}_1$$

$$R(\omega_{i-1})\mathbf{d}_i = \mathbf{d}_i \qquad (i = 2, ..., n+1) \tag{15}$$

By using eq 11 and 12, we can now rewrite eq 10 as follows:

$$Z = V\int J\, d\Phi\, d\Theta\, d\Psi\, dd_1 \ldots dd_{n+2}\, d\theta_1 \ldots d\theta_{n+1}\, d\omega_1 \ldots d\omega_n \delta(\mathbf{a})\delta(\mathbf{b})\delta(\mathbf{c}) \exp(-\beta E) \tag{16}$$

By the direct substitution of eq 12 into eq 10 we have the $\delta$ functions in the forms of $\delta(R(\Phi)T(\Theta)R(\Psi)\mathbf{a})$, etc. However, as shown in Appendix A, the matrices $R(\Phi)T(\theta)R(\Psi)$ can be dropped. Now the conformational energy $E$ can be expressed in terms of only internal variables. Therefore the integration with respect to the Eulerian angles can be carried out to give a factor of $8\pi^2$. After that we carry out integration with respect to $d_1, ..., d_n, \theta_1, ..., \theta_n$ by making use of the assumption that $\epsilon_1$ and $\epsilon_2$ in eq 2 are very large positive quantities. Thus, we obtain

$$Z = 8\pi^2 V(2\pi/\beta)^n(\epsilon_1\epsilon_2)^{-n/2}\prod_{i=1}^{n} d_{i0}^2 \sin\theta_{i0} \int d_{n+1}^2 d_{n+2}^2 \sin\theta_{n+1}\, dd_{n+1}\, dd_{n+2}\, d\theta_{n+1}\, d\omega_1 \ldots d\omega_n \delta(\mathbf{a})\delta(\mathbf{b})\delta(\mathbf{c}) \exp(-\beta E_0) \tag{17}$$

We now note that a set of equations

$$\mathbf{b} = \mathbf{0} \tag{18}$$

$$\mathbf{c} = \mathbf{0} \tag{19}$$

is equivalent to a set of following equations:

$$d_{n+1} = d_{10}$$

$$d_{n+2} = d_{20}$$

$$\theta_{n+1} = \theta_{10} \tag{20}$$

and

$$U = I \tag{21}$$

where $I$ is the $3 \times 3$ identity matrix. The last equation means that an orthogonal matrix given by eq 14 is in fact the identity matrix.

We now notice that eq 21 and

$$\mathbf{a} = \mathbf{0} \tag{22}$$

are exactly the set of equations used in the previous paper[3] to derive an explicit expression for the values of six dependent dihedral angles in terms of $(n-6)$ dihedral angles chosen as independent variables. At this point let us decide that we take the first $(n-6)$ dihedral angles as independent variables and express the last six dihedral angles as functions of these independent variables. Then six equations

$$\omega_i = \omega_{i0} \qquad (i = n-5, n-4, ..., n) \tag{23}$$

are equivalent with eq 21 and 22, where $\omega_{i0}$ are values of dihedral angles $\omega_i$ in exactly closing ring structures which are expressed as functions of the first $(n-6)$ dihedral angles.

As a whole, a set of nine constraints of eq 18, 19, and 22 are equivalent with another set of nine constraints of eq 20 and 23. Therefore we can replace the three $\delta$ functions in eq 17 as follows:

$$\delta(\mathbf{a})\delta(\mathbf{b})\delta(\mathbf{c}) = J_0^{-1}\delta(d_{n+1} - d_{10})\delta(d_{n+2} - d_{20})\delta(\theta_{n+1} - \theta_{10}) \prod_{i=n-5}^{n} \delta(\omega_i - \omega_{i0}) \tag{24}$$

where $J_0$ is the Jacobian needed, as shown in Appendix A, for the change of $\delta$ functions. The explicit form of the Jacobian is given as follows:

$$J_0 = d_{n+1}^2 d_{n+2}^2 \sin\theta_{n+1} J_1 \tag{25}$$

$$J_1 = \begin{vmatrix} \mathbf{e}_{n-4}\times(\mathbf{r}_1-\mathbf{r}_{n-4}) & \mathbf{e}_{n-3}\times(\mathbf{r}_1-\mathbf{r}_{n-3}) & \mathbf{e}_{n-2}\times(\mathbf{r}_1-\mathbf{r}_{n-2}) & \mathbf{e}_{n-1}\times(\mathbf{r}_1-\mathbf{r}_{n-1}) & 0 & 0 \\ \mathbf{e}_{n-4} & \mathbf{e}_{n-3} & \mathbf{e}_{n-2} & \mathbf{e}_{n-1} & \mathbf{e}_n & \mathbf{e}_1 \end{vmatrix} \tag{26}$$

where $\mathbf{e}_i$ is a unit vector pointing from atom $i$ to atom $(i+1)$. Rotation of the dihedral angle $\omega_{i-1}$ takes place around a bond oriented along this direction. This expression is derived in Appendix B. By substituting eq 25 into eq 17 and by carrying out integration with respect to $d_{n+1}$, $d_{n+2}$, $\theta_{n+1}$, $\omega_{n-5}$, ..., $\omega_n$, we have the following expression:

$$Z = \text{const} \int d\omega_1 \ldots d\omega_{n-6} |J_1|^{-1} \exp(-\beta E_0) \tag{27}$$

The const is the same constant factor as in front of the integration sign in eq 17. This equation, which is expressed as an integral with respect to arbitrarily chosen six variable dihedral angles, is invariant with respect to the choice of variables of integration because the expression is exactly the same with eq 3 in the limit of large values of $\epsilon_1$ and $\epsilon_2$. The latter equation is, of course, independent of the choice. The invariance of the integration from the choice of the independent variables is assured by the presence of the absolute value of the Jacobian in eq 27. The reason the abolute value of $J_1^{-1}$ appears in eq 27 is given below.

A set of values of $\omega_{n-5,0}, ..., \omega_{n0}$ is a solution of eq 21 and 22 for a given set of values of independent variables. $\omega_1, ..., \omega_{n-6}$. Solutions of eq 21 and 22 define an $(n-6)$-di-

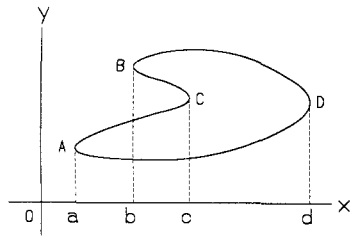


**Figure 3.** Simple illustrative example to explain the appearance of the absolute value of $J_1^{-1}$ in eq 26. The integral in eq A26 is to be carried out along the closed curve in this figure.

mensional supersurface in the $n$-dimensional space of $\omega_1$, ..., $\omega_n$. The supersurface encloses one or more continuous regions of the $n$-dimensional space in which the sign of the product of components of vectors **a**, **b**, and **c**, or identically the sign of product of $(\omega_i - \omega_{i0})$ for $i = n-5, ..., n$, is always negative. There is, in general, an even number of solutions of eq 21 and 22 for a given set of values of independent variables. The number of solutions depends on the values of independent variables. Sets of independent variables at which the number of solutions is constant form continuous domains in the space of the independent variables. On the boundary between such domains a pair of solutions merge into one, so that the number of solutions becomes, in general, odd. Very near the boundary just before a pair of solutions merge into one, the values of $\omega$, which are treated as dependent variables, vary very much for small changes of the values of independent variables. This makes $J_1$ vanish on the boundary. The sign of $J_1$ is different on a pair of solutions which merge into one on the boundary. When $J_1$ is negative, integration of eq 17 with respect to $\omega_{n-5}$, ..., $\omega_n$ is to be carried out along the direction in which the sign of the products mentioned above changes from positive to negative. When $J_1$ is positive, the direction is opposite. Because of this direction of integration, the absolute value of $J_1^{-1}$ appears in eq 27. Because what is mentioned in this paragraph is a bit abstract, an illustrative simpler example is given in Appendix C to explain the situations occurring here.

## Conclusion

We derived a basic formula of eq 27 with eq 26 for the expression of the conformational partition function of ring molecules. In eq 27, $\omega_1$, ..., $\omega_{n-6}$ are rotatable backbone dihedral angles that are chosen as independent variables. Values of six other rotatable backbone dihedral angles $\omega_{n-5}$, ..., $\omega_n$ are determined from the condition of exact ring closure as functions of the independent variables. The conformational energy $E_0$ in eq 27 is expressed as a function of these independent variables. Arbitrariness of the choice of independent variables is compensated by the appearance of the factor $|J_1|^{-1}$ in the integrand, which assures the independence of the calculated value of the partition function of the choice of independent variables.

**Acknowledgment.** This work has been supported by grants from Ministry of Education, Science and Culture, Japan, and Science and Technology Agency, Japan.

## Appendix

**A.** Here we prove a theorem on the use of the $\delta$ functions. We consider a real function $F(x,y)$ in an $(l+m)$-dimensional space of $x = (x_1, ..., x_l)$ and $y = (y_1, ..., y_m)$. We want to calculate an integral of this function over $m$-dimensional supersurface defined by

$$f_i(x;y) = 0 \qquad (i = 1, 2, ..., l) \tag{A1}$$

The integral, $I$, is defined by

$$I = \int dx_1 \dots dx_l\, dy_1 \dots dy_m \delta(f_1) \dots \delta(f_l) F(x,y) \tag{A2}$$

In order to carry out this integral, we change the variables of integration from $x$ to $f = (f_1, ..., f_l)$, the Jacobian for which is given by

$$J(x;f) = \det \begin{pmatrix} \partial x_1/\partial f_1 & \dots & \partial x_1/\partial f_l \\ \dots & & \dots \\ \partial x_l/\partial f_1 & \dots & \partial x_l/\partial f_l \end{pmatrix} \tag{A3}$$

Corresponding to this change of variables of integration, we define a real function $G(f,y)$ by

$$G(f,y) = F(x,y) \tag{A4}$$

Now the integral is given by

$$I = \int df_1 \dots df_l\, dy_1 \dots dy_m \delta(f_1) \dots \delta(f_l) J(x;f) G(f,y) = \int dy_1 \dots dy_m J(x;f) G(f,y)|_{f=0} \tag{A5}$$

The last equation indicates how the integral is given in terms of the chosen independent variables.

Let us then consider another set of equations

$$g_i(x;y) = 0 \qquad (i = 1, 2, ..., l) \tag{A6}$$

that defines the same supersurface as eq A1 does. This means that eq A1 and A6 are equivalent to each other. In terms of the functions in eq A6, the integral is given by

$$I = \int dy_1 \dots dy_m J(x;g) G(f,y)|_{f=0} \tag{A7}$$

By comparing eq A5 and A7, we see that we can express the integral as follows:

$$I = \int dy_1 \dots dy_m J(x;g) J(g;f) G(f,y)|_{f=0} = \int dx_1 \dots dx_l\, dy_1 \dots dy_m J(g;f) \delta(g_1) \dots \delta(g_l) F(x,y) \tag{A8}$$

This equation means that we must include the Jacobian for a change of functions that define the supersurface. This fact is used to derive eq 16 and 24. For deriving eq 16, we also used the fact that the determinant of an orthogonal matrix, which is the Jacobian involved, is unity.

**B.** Here we will derive eq 24. Two column vectors

$$\mathbf{i} = \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix} \quad \mathbf{j} = \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix} \tag{A9}$$

will be used in the derivation.

The Jacobian $J_1$ is given as a determinant of a $9 \times 9$ matrix, whose elements are derivatives of three vectors **a**, **b**, and **c** with respect to $d_{n+1}$, $d_{n+2}$, $\theta_{n+1}$, $\omega_{n-5}$, ..., $\omega_n$. Because of the presence of the $\delta$ functions in eq 24, values of these derivatives are to be evaluated at a point at which eq 21 holds. Such values are given in the following. Those with respect to the first three variables vanish except for the following:

$$\partial \mathbf{b}/\partial d_{n+1} = \mathbf{i} \tag{A10}$$

$$\partial \mathbf{c}/\partial d_{n+2} = \cos\theta_{n+1}\mathbf{i} + \sin\theta_{n+1}\mathbf{j} \tag{A11}$$

$$\partial \mathbf{c}/\partial \theta_{n+1} = d_{n+2}(-\sin\theta_{n+1}\mathbf{i} + \cos\theta_{n+1}\mathbf{j}) \tag{A12}$$

These equations can be obtained easily from eq 6, 8, and 13. The derivatives with respect to $\omega_i$ are given as follows:

$$\partial \mathbf{a}/\partial \omega_i = \mathbf{f}_{i+1} \times (\mathbf{s}_1 - \mathbf{s}_{i+1}) \tag{A13}$$

$$\partial \mathbf{b}/\partial \omega_i = d_{n+1}\mathbf{f}_{i+1} \times \mathbf{i} \tag{A14}$$

$$\partial \mathbf{c}/\partial \omega_i = d_{n+2}\mathbf{f}_{i+1} \times (\cos\theta_{n+1}\mathbf{i} + \sin\theta_{n+1}\mathbf{j}) \tag{A15}$$

where $\mathbf{s}_i$ and $\mathbf{f}_i$ are the position vector of atom $i$ and the

unit vector pointing from atom $i$ to atom $(i + 1)$, both viewed in the local coordinate system located on the first atom, so that

$$\mathbf{e}_i = R(\Phi)T(\Theta)R(\Psi)\mathbf{f}_i$$
$$\mathbf{r}_i = R(\Phi)T(\Theta)R(\Psi)\mathbf{s}_i \quad \text{(A16)}$$

Derivation of eq A13, A14, and A15 will be given below. By substituting these expressions into a $9 \times 9$ determinant expression of $J_0$ and by carrying out some calculations, we can derive expressions of eq 25 and 26 but with $\mathbf{f}_i$ and $\mathbf{s}_i$ appearing in place of $\mathbf{e}_i$ and $\mathbf{r}_i$, respectively. However, the latter can be replaced by the former, because this replacement involves only a rotation and does not affect the value of the determinant.

Now we will derive eq A13, A14, and A15. For this purpose we need some preparation of algebra. We will make use of the following three generating matrices of rotation:

$$L_x = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & -1 \\ 0 & 1 & 0 \end{pmatrix} \quad L_y = \begin{pmatrix} 0 & 0 & 1 \\ 0 & 0 & 0 \\ -1 & 0 & 0 \end{pmatrix} \quad L_z = \begin{pmatrix} 0 & -1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \quad \text{(A17)}$$

These matrices generate rotation matrices. For example

$$R(\omega) = \exp(\omega L_x) \quad \text{(A18)}$$

We sometimes regard these three matrices as components of a three-dimensional vector $\mathbf{L}$. For example, a $3 \times 3$ matrix $q_xL_x + q_yL_y + q_zL_z$, where the coefficients are components of a usual three-dimensional vector $\mathbf{q}$, will be designated as $\mathbf{q}\cdot\mathbf{L}$. Now we quote three equaions valid for any $3 \times 3$ orthogonal (i.e., rotation) matrix $S$ and for any three-dimensional vectors $\mathbf{x}$ and $\mathbf{y}$.

$$S(\mathbf{x} \times \mathbf{y}) = S\mathbf{x} \times S\mathbf{y} \quad \text{(A19)}$$
$$(\mathbf{q}\cdot\mathbf{L})\mathbf{x} = \mathbf{q} \times \mathbf{x} \quad \text{(A20)}$$
$$S(\mathbf{q}\cdot\mathbf{L})S^{-1} = (S\mathbf{q})\cdot\mathbf{L} \quad \text{(A21)}$$

Validity of eq A19 is obvious. We can check eq A20 by explicit use of eq A17. We can prove eq A21 by observing that the following equation holds for an arbitrary vector $\mathbf{x}$:

$$S(\mathbf{q}\cdot\mathbf{L})S^{-1}\mathbf{x} = S\{\mathbf{q} \times (S^{-1}\mathbf{x})\} = (S\mathbf{q}) \times \mathbf{x} = \{(S\mathbf{q})\cdot\mathbf{L}\}\mathbf{x} \quad \text{(A22)}$$

In the first and third equalities we used eq A20. In the second equality we used eq A19.

Now eq A13 can be derived as follows:

$$\begin{aligned} \partial\mathbf{a}/\partial\omega_i &= T_1R_1 \dots T_iR_iI_{-}^{-1}R_i'\mathbf{d}_{i+1,n} \\ &= T_1R_1 \dots T_iR_iL_x\mathbf{d}_{i+1,n} \\ &= T_1R_1 \dots T_iR_i(\mathbf{i} \times \mathbf{d}_{i+1,n}) \\ &= \mathbf{f}_{i+1} \times (\mathbf{s}_1 - \mathbf{s}_{i+1}) \end{aligned} \quad \text{(A23)}$$

where $R_i'$ is the derivative of $R_i$ with respect to $\omega_i$ and

$$\mathbf{d}_{i+1,n} = \mathbf{d}_{i+1} + \sum_{k=i+2}^{n} \prod_{j=i+1}^{k-1} T(\theta_j)R(\omega_j)\mathbf{d}_k \quad \text{(A24)}$$

We can derive eq A14 and A15 easily from the following equation and eq 13:

$$\begin{aligned} \partial U/\partial\omega_i &= T_1R_1 \dots T_iR_iR_i^{-1}R_i'T_{i+1} \dots R_n \\ &= T_1R_1 \dots R_iL_xR_i^{-1} \dots R_1^{-1}T_1^{-1}U \\ &= \{(T_1R_1 \dots R_i\mathbf{i})\cdot\mathbf{L}\}U \\ &= (\mathbf{f}_{i+1}\cdot\mathbf{L})U \end{aligned} \quad \text{(A25)}$$

**C.** Here we will give a simple illustrative example to explain the appearance of the absolute value of $J_1^{-1}$ in eq 27.

Let us consider the following integral of a real function $F(x,y)$ along a closed curve shown in Figure 3 by a solid line:

$$I = \int \mathrm{d}x\, \mathrm{d}y\delta(f(x,y))F(x,y) \quad \text{(A26)}$$

The closed curve is defined by

$$f(x,y) = 0 \quad \text{(A27)}$$

The value $f(x,y)$ is assumed to be negative inside the closed curve. By the solution of eq A27, $y$ can be expressed as a function of $x$. There are two solutions for eq A27 for values of $x$ in the range between a and b and between c and d. For values in the range between b and c, there are four solutions. The integration of eq A26 is to be carried out on the curve of eq A27 in the direction along which both variables $x$ and $y$ increase. Note that, when integration with respect to variable $y$ is carried out in this direction, the value of $f$ changes from positive to negative on AD and BC sections of the closed curve. On AC and BD sections it changes from negative to positive.

By chaning the variable of integration, we can express the integral as follows:

$$I = \int \mathrm{d}x\, \mathrm{d}f(\partial f/\partial y)^{-1}\delta(f)G(x,f) \quad \text{(A28)}$$

where

$$G(x,f) = F(x,y) \quad \text{(A29)}$$

The derivative $\partial f/\partial y$ is negative on AD and BC sections of the closed curve. On AC and BD sections it is positive. Because of the abovementioned direction of integration in variable $y$, integration with respect to $f$ near a point where $f = 0$ must be carried out in a direction along which $f$ changes from positive to negative on AD and BC sections of the closed curve. On AC and BD sections, the direction must be opposite. By carrying out integration with respect to $f$ in this way, we have

$$I = \int \mathrm{d}x\, |\partial f/\partial y|^{-1}G(x,f)|_{f=0} \quad \text{(A30)}$$

where the absolute value appears in the integrand. In a very similar situation the absolute value of $J_1^{-1}$ appears in eq 27.

## References and Notes


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