

# Reviews

## Foundations of Rotational Isomeric State Theory and General Methods for Generating Configurational Averages

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*Received January 15, 1974*

**ABSTRACT:** Recent methods for treating configuration-dependent properties of chain molecules are generalized and presented in a concise, systematic form. These methods involve, first, the formulation of a generator matrix  $\mathbf{F}_i$  that embodies all contributions associated with bond  $i$ ; it depends on the conformation of bond  $i$ . Serial multiplication of the  $\mathbf{F}_i$  appropriate to a specified conformation for  $i = 1$  to  $n$  yields the configuration-dependent property  $f$  for that conformation. The property  $f$  may be a scalar, a vector, or a tensor (e.g.,  $r^2$ ,  $\mathbf{r}$ , or  $\hat{\alpha}$ , respectively, where  $\mathbf{r}$  is the chain vector,  $r^2$  is its squared magnitude, and  $\hat{\alpha}$  is the anisotropic part of the polarizability tensor). Combination of these generator matrices with the statistical weight matrix  $\mathbf{U}_i$  yields the generator matrix  $\mathbf{F}_i = (\mathbf{U}_i \otimes \mathbf{E}_s) \cdot \|\mathbf{F}_i\|$  from which to obtain, again by serial multiplication, the average  $\langle f \rangle$  over all configurations of the chain;  $\mathbf{E}_s$  is the identity of the same order, (s) as  $\mathbf{F}_i$ , and  $\|\mathbf{F}_i\|$  is the diagonal development of the  $\mathbf{F}_i$  for the various rotational states. Generator matrices for quantities of higher orders, e.g., tensors  $\mathbf{r} \otimes \mathbf{r}$ ,  $\mathbf{r} \otimes \mathbf{r} \otimes \mathbf{r}$ , etc., and scalars  $r^4$ ,  $r^6$ , etc., are the self-direct products of the generator matrices  $\mathbf{F}_i$  for the primary quantities. General procedures are presented for condensing self-direct products as required to render practicable the computation of averages of quantities up to sixth or eighth orders. Further condensations applicable in the configurational averaging over symmetric chains are presented. The foregoing methods enjoy the utmost generality, being applicable to chains of any length, and to copolymers of any composition, including stereoirregular polymers. Their foundations in classical statistical mechanics are shown to be secure. A critique is presented of the rotational isomeric state scheme for implementing evaluation of integrals over the configuration space.

Theory pertaining to the configurational statistics of polymer chains and the many ramifications of this subject has been carried to an advanced stage during recent years.<sup>1-4</sup> Methods are now at hand for treating the configuration-dependent properties of virtually any chain in a realistic manner. These methods involve no mathematical approximations beyond the replacement of integrals over configuration space by sums over a discrete set of rotational isomeric states (RIS). In application, therefore, they are limited in accuracy only by choice of rotational states for the representation of the array of spatial configurations, and not at all by the usual compromises of mathematical exactness with the exigencies of practicability.

Molecular properties of a linear chain that depend upon its spatial configuration invariably comprise vector or tensor contributions from individual skeletal bonds and the groups associated with them; or, more frequently, they comprise products of such contributions from two or more bonds. These contributions must be summed over all bonds, all bond pairs, or all combinations of a higher order dictated by the given property. The most versatile method for evaluation of sums of this nature employs a *matrix generation* technique.<sup>4-6</sup> The required summations are executed through sequential multiplication of *generator matrices*. One such matrix is required for each bond, or for each repeat unit, of the chain. Upon elaboration of the generator matrices to include the statistical weights or appropriately chosen rotational isomeric states,<sup>4-7</sup> averages of various quantities over all configurations of the chain can be developed in the same manner. The procedure is mathematically exact. It is broadly applicable to chains of any length, to copolymers of any specified composition and to asymmetric (e.g., vinyl) chains of any stereochemical configuration and sequence, tactic or atactic.<sup>8</sup> Properties that may readily be evaluated include averages of the chain vector  $\mathbf{r}$  and its higher moments (scalar<sup>9-11</sup> and tensor<sup>6</sup>), the dipole moment, the squared radius of gyration and analogous higher moments of pair distances,<sup>4</sup> the mean-squared optical an-

isotropy  $\langle \gamma^2 \rangle$  relevant to depolarized light scattering,<sup>7,12</sup> the stress-optical parameter  $\Delta a$ ,<sup>3,4,13,14</sup> the Kerr constant for electric birefringence,<sup>15,16</sup> the optical rotatory power,<sup>17</sup> and the dichroic ratio.<sup>4,18</sup>

Since their inception,<sup>4,5</sup> matrix generation techniques have been greatly simplified and broadened in scope.<sup>6,7,11</sup> It is the main purpose of this paper to present a concise resume of these methods in a coherent form that embodies refinements introduced over the past 5 years.

These methods, and others that have been used as well,<sup>2</sup> have their foundations in classical statistical mechanics. The validity of treating the configurational statistics of macromolecules on this basis has been questioned, quantum mechanical procedures being advocated in their stead.<sup>19,20</sup> Quite apart from whatever validity these criticisms might have, they serve to point out that the statistical mechanical foundations of the methods currently employed may not have been adequately set forth. These foundations are therefore examined in the opening section of the paper.

Representation of the spatial configurations of macromolecules in terms of discrete rotational states in accordance with the RIS scheme has proved to be an exceedingly useful device.<sup>1-4</sup> It is essential to the matrix generation method and has been employed as well in most other theoretical formulations dealing with the configurational statistics of chain molecules. It admits of close correlation with molecular features dictating the character of bond rotational potentials; its heuristic value in this respect is strongly in its favor. Yet, the prevalence of the notion that rotational states must be identified with energy minima in conformation space has obscured the broader potentialities of the RIS scheme as a means for evaluating configurational integrals through summation over discrete states. Although it is often both justified and expedient to identify rotational isomeric states with energy minima, this is not a requirement of RIS methods.<sup>21</sup> By increasing the number of states, and hence decreasing the intervals in rotation

angle between them, any desired degree of accuracy may in principle be attained. In practice, the accuracy of calculated results is limited much more by the crudity of estimates of conformational energies, and by uncertainties in other quantities (e.g., bond dipole moments, polarizabilities, etc.), than by limitations imposed through the adoption of a small number of rotational states.

The efficacy of the RIS scheme as an instrument for establishing connections between the conformational energy and the properties of the macromolecule that must be averaged over all of the configurations is discussed at the close of the first section.

### Statistical Mechanical Foundations of Macromolecular Configuration Theory and Methods

As pointed out above, current configurational statistical theory of polymer chains is founded upon classical statistical mechanics. Justification for this intuitively satisfactory premise has been called into question<sup>19,20</sup> on the grounds that the frequencies of some of the modes of motion within the chain are well beyond the classical limit. This undeniable fact appears to have been construed to imply that a comprehensive theory of macromolecular configurations should be developed in the terms of quantum statistical mechanics.<sup>19,20</sup> The ultimate rectitude of the latter is incontestable, but drastic approximations are necessary in order to implement its application to a macromolecule in the liquid state. Measures adopted to circumvent the difficulties confronting rigorous application of quantum statistical mechanics may entail errors far more serious than any approximations involved in resort to classical statistical mechanics, as we point out below.

The motions of the macromolecule are subject to influences of the neighboring molecules, consisting of solvent or of other polymer molecules, which invariably make up its environment. Conformational modes of the macromolecule are especially vulnerable to restrictions imposed by its neighbors. Hence, treatment of the system as a whole is obligatory. The Hamiltonian representing the system must include kinetic energies of the surrounding molecules as well as the intermolecular potential energies involving them. Under the terms of quantum mechanics, the kinetic energies of the neighboring species are not separable.

If, these circumstances notwithstanding, one adopts a course paralleling the treatment of gaseous molecules, then it is natural to proceed in terms of normal modes for the isolated macromolecule. Integration of the partition function over those momenta deemed to be in the classical range yields the familiar determinant of the matrix of the quadratic form representing the kinetic energy in the normal coordinates. This intractable quantity, cited by Saitô and coworkers<sup>19</sup> and discussed by Gô, Gô, and Scheraga,<sup>20</sup> is a function of the configuration, and it occurs as a factor in their partition functions. It defies evaluation for anything as complex as a macromolecule.

Thus, resolution of the motions of the macromolecule into normal modes, as if it was a dynamically independent body, not only is incorrect; treatment in this manner leads to insuperable difficulties as well. As we show below, classical statistical mechanics offers a practicable alternative basis for the treatment of conformations of macromolecules, including the motions associated therewith. The need to retain the aforementioned factor within the integrand of the configuration integral in normal coordinates, on the grounds that this factor is a function of the coordinates, turns out to be spurious.

**Random Coil.** Our first concern is with the irregularly configured macromolecule interspersed with other mole-

cules which we choose to designate as "solvent." These neighboring species may, however, consist in part or entirely of other randomly coiled macromolecules.

The conformational motions of the macromolecule, *i.e.*, those that are primarily associated with bond torsions, are "soft" in the sense that their frequencies are low and their amplitudes at ordinary thermal energy are fairly large. The associated displacements of peripheral atoms would, in general, exceed 0.5 Å if they were not impeded by surrounding solvent. Clearly, the momenta for motions of this amplitude will be markedly affected by solvent molecules. To treat them in the manner of the internal motions of an isolated molecule, represented by a Hamiltonian that includes only intramolecular momenta and coordinates, obviously is quite wrong.

On the other hand, modes of higher frequency above the range where classical excitation obtains (*i.e.*, higher than about 400 cm<sup>-1</sup> at  $T = 300$  K) are affected negligibly by intermolecular collisions. Their amplitudes are small, being  $< \sim 0.1$  Å at thermal energies. Inasmuch as the "lattice" frequencies are on the order of 20 cm<sup>-1</sup>, an internal normal mode of 200 cm<sup>-1</sup> (well within the classical range) would be perturbed by less than 1 cm<sup>-1</sup>, as Prigogine and Bellemens<sup>22</sup> have pointed out. Hence, in absence of strong interactions like hydrogen bonds, the effect of the solvent environment on the motional modes of higher frequency should be negligible. This certainly holds in the range where quantization must be taken into account, *i.e.*, at frequencies beyond the limit for convergence to classical mechanics.

As will be intuitively evident from the facts recited above, the analysis of conformations and the performance of configurational averaging over conformation space should fall within the domain of classical statistical mechanics. The following development serves to validate this assertion unambiguously. We consider a chain of  $n + 1$  point masses connected by  $n$  chemical bonds. Pendant hydrogen atoms may, in interests of simplicity, be absorbed into these mass points; modes dominated by motions of hydrogen atoms, being of high frequency, are immune to effects of solvent and of conformation as well. Bond lengths and bond angles may be considered to be fixed within narrow limits. The conformation is then defined by the torsional rotations  $\phi_2, \phi_3, \dots, \phi_{n-1}$  about internal bonds of the chain skeleton. Since internal modes of associated solvent molecules are inconsequential, we ignore them and include only their translational coordinates and momenta.

We begin by formulating the classical partition function  $Q_{\text{class}}$  for a canonical ensemble of systems, each system comprising a macromolecule and its complement of  $N_s$  solvent molecules contained within a volume  $V$ . With the choice of cartesian coordinates for all chain atoms (mass points) and solvent molecules, the momenta are separable from the coordinates. Integration over the former in customary fashion yields

$$Q_{\text{class}} = (h/\sqrt{2\pi\bar{m}kT})^{3N} Z_N \quad (1)$$

where  $N$  is the total number of particles inclusive of both solvent molecules and chain atoms (and also substituents, other than H, if present),  $\bar{m}$  is the mass of a particle appropriately averaged over chain atoms and solvent, and  $Z_N$  is the configuration partition function given by

$$Z_N = \int_V \dots \int_V \exp[-U(\mathbf{x}^{(N)})/kT] d\mathbf{x}^{(N)} \quad (2)$$

where  $\mathbf{x}^{(N)}$  symbolizes the  $3N$  cartesian coordinates for the system and  $U(\mathbf{x}^{(N)})$  is the potential energy for the system in the specified configuration. The  $3(n - 1)$  internal coordinates,  $\mathbf{x}_{\text{int}}$ , specifying the positions of the  $n + 1$  skeletal atoms of the chain relative to one another may be sepa-

rated from the  $3N_s + 6$  external coordinates specifying the locations of the  $N_s$  solvent molecules, the location of a reference point within the macromolecule, and the orientation of the macromolecule. Integration over these external coordinates yields

$$Z_N = C_{\text{int}} \int \dots \int \exp[-\bar{U}(\mathbf{x}_{\text{int}})/kT] d\mathbf{x}_{\text{int}} \quad (3)$$

where  $\mathbf{x}_{\text{int}}$  represents the  $3(n-1)$  internal (cartesian) coordinates and  $\bar{U}(\mathbf{x}_{\text{int}})$  is a potential of mean force defined by

$$C_{\text{int}} \exp[-\bar{U}(\mathbf{x}_{\text{int}})/kT] = \int_V \dots \int \exp[-U(\mathbf{x}^{(N)})/kT] d\mathbf{x}_{\text{ext}} \quad (4)$$

Here  $\mathbf{x}_{\text{ext}}$  represents the  $3(N-n+1)$  external coordinates;  $C_{\text{int}}$  is a constant having the dimensions (volume) $^{N-n+1}$ .

We next transform from the  $n-1$  cartesian internal coordinates  $\mathbf{x}_{\text{int}}$  to the set of spherical polar coordinates consisting of  $n$  bond lengths  $l$ ,  $n-1$  bond angle supplements  $\theta$ , and  $n-2$  torsional angles. Integration over the sets of variables  $|l|$  and  $|\theta|$  yields

$$Z_N = C_{|\phi|} Z_{|\phi|} \quad (5)$$

where

$$Z_{|\phi|} = \int \dots \int \exp(-\bar{U}|\phi|/kT) d|\phi| \quad (6)$$

$|\phi|$  being the set of torsional angles, and  $\bar{U}|\phi|$  is defined by

$$C_{|\phi|} \exp(-\bar{U}|\phi|/kT) = C_{\text{int}} \int \dots \int \exp[-\bar{U}(\mathbf{x}_{\text{int}})/kT] \times d|l|d|\theta| = \int_V \dots \int \exp[-U(\mathbf{x}^{(N)})/kT] d\mathbf{x}_{\text{ext}} d|l|d|\theta| \quad (7)$$

The constant  $C_{|\phi|}$  has the dimensions (volume) $^N$ . Thus,  $Z_{|\phi|}$  is the classical mechanical configuration partition function for the macromolecules expressed as the integral over the conformational variables, and  $\bar{U}|\phi|$  is the potential of mean force with respect to the variables  $|\phi|$  that specify the conformation. It is in the nature of a free energy for the specified conformation. Effects of solvent and of possible variations in bond lengths  $l$  and bond angle supplements  $\theta$  with conformation are included in  $\bar{U}|\phi|$ , as is apparent from the equation, eq 7, that defines the potential of mean force.

The foregoing formulation errs in ignoring the fact that some of the motional modes of the macromolecule possess frequencies beyond the classical range. The error may be amended by introducing the factor

$$\Gamma = \prod_{\zeta=1}^{3(n-1)} \gamma_{\zeta} \quad (8)$$

where  $\gamma_{\zeta}$  is the ratio of the quantum mechanical partition function for normal mode  $\zeta$  to its classical partition function. Thus,  $\gamma_{\zeta} = y (\sinh y)^{-1}$  with  $y = h\nu_{\zeta}/2kT$ . The product is over all normal modes of the macromolecule. No harm is done by defining  $\Gamma$  in terms of normal modes of the macromolecule with disregard for the influence of the solvent; the nonclassical modes ( $y > \sim 1$ ) for which  $\gamma_{\zeta}$  is appreciably smaller than unity are unperturbed by the solvent, and modes possibly subject to such influence are well within the classical range ( $y < 1$ ), where the ratio  $\gamma_{\zeta}$  differs negligibly from unity. The appropriately revised configuration partition function is therefore

$$Z_N = \Gamma C_{|\phi|} Z_{|\phi|} \quad (9)$$

The only modes (apart from those dominated by motions of hydrogens, which modes we have eliminated at the outset) for which  $\gamma_{\zeta}$  is significantly smaller than unity are those at the high frequency ends of the bond stretching and in-plane bending branches.<sup>23,24</sup> The frequencies of these vi-

brations are known to be virtually unaffected by conformation and environment.<sup>24</sup> Hence, for our purpose  $\Gamma$  may be regarded as a constant that depends neither on conformation nor on the solvent. It follows that the classical partition function  $Z_{|\phi|}$  may be used, without hazard of sensible error, in the analysis of the configuration statistics, and configuration-dependent quantities may be averaged over classical configuration space, the fact notwithstanding that some of the modes of the macromolecule occur in the quantum mechanical range.

It is obligatory in the development of the configuration partition function  $Z_{|\phi|}$  to take account of possible differences in intermolecular interactions in the various conformations. Such differences are incorporated, according to the format of theory, in the potential of mean force  $\bar{U}|\phi|$  together with the intramolecular energy. Much evidence exists indicating intermolecular interactions to be about the same in competing conformations of the random coil and the differences cited to be negligible. The density of packing with neighboring molecules should be little affected by changes in conformation; ordinarily the same species of molecules will be mutually involved in the interactions in the various conformations. Hence, similar intermolecular forces are operative. Only in the event of strong polar interactions is it plausible to expect a significant discrimination between conformations, and even in such circumstances the effects of discrimination will be discernible only if certain conformations are appreciably more conducive to the interactions than others.

The validity of these assertions is attested by the insensitivity of the average spatial configuration of the random coil to the solvent in which it is dissolved,<sup>4</sup> apart from effects of excluded volume. Moreover, the configuration of the random coil in the undiluted amorphous polymer<sup>25-28</sup> coincides with that of the same polymer in a  $\theta$  solvent where the excluded volume perturbation should be null.<sup>25,29</sup> Thus, considerations of a theoretical nature<sup>29</sup> supported by compelling experimental evidence indicate the intermolecular (free) energy usually to be little dependent on the conformation of the random coil. The intermolecular contribution to  $\bar{U}|\phi|$  may be considered constant, and it is legitimate, in general, to confine attention to the intramolecular interactions. Treatments of the configurational statistics of the random coil are enormously simplified in consequence of this generalization. The scope of results obtained is enlarged by their applicability to the macromolecule in the bulk amorphous state as well as to its configuration in a dilute solution.

**Cooperative Conformational Changes.** Conformational transitions such as occur in the melting of a crystalline polymer or of an isolated helix involve circumstances not encountered in the equilibria between various conformations accessible to the random coil. The conclusions reached above must therefore be reexamined.

We note at the outset, however, that classical statistical mechanics remains valid as a basis for treating the changes involved. Frequencies of "internal" modes beyond the classical range will be little affected by the transition between helix or crystal and coil. The factor  $\Gamma$  in eq 9 ordinarily should be substantially unaltered by passage from helix to coil or from the crystalline to the amorphous state.

Complications arise principally as a consequence of the differences between the intermolecular interactions in the crystalline or in the helical state on the one hand and in the random coil, or the amorphous state, on the other. These differences, often large, stem mainly from the greater density of packing in the ordered form. They may be augmented by the regularity of arrangement of molecules in the crystal, affording a more efficient arrangement of the inter-

acting groups. In contrast to circumstances normally prevailing in the random coil, it is not legitimate to consider the intermolecular interactions to be equivalent in the competing states: crystalline, or helical, and coil.

The difference between the intermolecular energy in the two states separated by the cooperative transition conceivably may be estimated with sufficient accuracy by one of the various empirical functions now in vogue for calculating the interactions between nonbonded atoms or groups. But the difficulty is more pervasive. If thermodynamical relations between the two states are to be established, their respective configuration partition functions must be adjoined.

For the crystal, treatment in terms of vibrational modes seems compelling, at least for those modes that are predominantly intramolecular. If some of the modes involving torsional motions are thus dealt with, the opportunity to express the skeletal conformations in cartesian coordinates is forfeited and the separation of the classical momentum integral as described in the preceding section cannot be effected. Treatment of *all* conformational motions in terms of normal modes is then obligatory. Inasmuch as intermolecular (phonon) motions are not separable, unambiguously, from the "soft" intramolecular motions of large amplitude, their treatment in like manner is indicated. The task takes on the scope of a complete evaluation of the thermodynamic functions of the crystal on the basis of structural information (possibly supplemented by spectroscopic data) along with semiempirical expressions for conformational energies and intermolecular interactions.

Estimation of the configuration partition function for the crystal at an acceptable level of approximation by proceeding along the lines indicated above may be within reach of achievement in favorable instances. But what of the random coil? In absence of an adequate theory of the liquid state, no corresponding basis exists for treating the random coil in an equivalent manner. Intermolecular motions and interactions in the liquid of which the random coil is a part, must be taken into account in order to match the treatment of the crystal. The gap of density cited above accentuates the difficulty.

The difficulties are only partially resolved in the case of a dispersed helix, such as the polypeptide  $\alpha$  helix in equilibrium with the random coil. The lure of analysis in terms of normal vibrational modes of the helix can be avoided by confining attention to the classical configuration integrals for both helix and coil; the momentum integrals may be handled classically as above, and hence cancel upon equating functions for the two forms. The conformational energies of each should, of course, be estimated using the same energy functions, with due account of the hydrogen bonds in the helix. Difficulties of estimating hydrogen-bond energies, and limitations of the semiempirical expression for interactions of nonbonded atoms, especially as applied to conformations so disparate as the helix and the coil, seem to preclude a reliable evaluation of the relative energies of helix and coil. Alternatively, the magnitude of this difference may be adjusted arbitrarily on the basis of experimental evidence.

The conformational energy of the random polypeptide chain is separable into independent contributions of individual residues,<sup>30</sup> each such contribution being a function of the torsion angles  $\phi$  and  $\psi$  for the single bonds adjoining the  $\alpha$ -carbon of the given residue. Hence, the configuration integral may be evaluated in the conventional manner (see below) from integrals over the familiar conformational energy surfaces for the respective residues.<sup>4,30</sup>

Interactions in the  $\alpha$  helix extend over the greater range embracing several units of the chain. Hence, the partition

function cannot be resolved as above into independent factors for each of its residues. Taking advantage of the fact that the minimum of energy is narrowly confined to a restricted domain of configurational space, Gō and Scheraga<sup>31</sup> employ a harmonic approximation for the conformational energy. The resulting quadratic form in the displacements of the torsional angles from those for the lowest energy may be diagonalized, and the configuration integral for the helix is readily obtained from the eigenvalues.<sup>31</sup>

The foregoing procedure detailed by Gō and Scheraga,<sup>31</sup> and involving evaluation of the configuration integrals for random coil and helix as outlined here, is conceptually sound. Its proper implementation requires, however, that potentials of mean force be employed instead of conformational energies that take account only of intramolecular interactions. The interactions of the respective forms, helix and coil, with surrounding solvent cannot here be dismissed, as is warranted for competing conformations of the random coil (see preceding section), on the grounds that they are equivalent. Owing to disparities in shape, density, and hydrogen bonding, the mutual influences operative between solvent and solute must be expected to differ substantially for the helix and the coil. These differences are not accountable merely in terms of specific interactions between neighbors. They involve more recondite aspects of the liquid state as well. In fact, on careful inspection, establishment of the required connections between the helical and coil forms will be found to be confronted by difficulties resembling those cited above for the melting of a crystal.

The foregoing difficulties are not necessarily insuperable. Attention is directed to them with the intention of pointing out that treatment of cooperative conformational transitions is beset with complications that do not affect analysis of the random coil. Evaluation of the configuration partition functions for the two states in ways that are suitable for each, respectively, and that also yield mutually comparable results is essential for an acceptable treatment of cooperative conformational transitions.

**Rotational Isomeric State Scheme.** The total conformational energy for a random chain usually (but not always<sup>4,32</sup>) can be resolved into contributions each of which depends on a consecutive pair of bond rotations  $\phi$ .<sup>2-4</sup> The surface that represents the energy as a function of two such variables can be computed in some instances by semiempirical methods, but with a degree of reliability not well established. If the function so represented is known with sufficient accuracy, then it remains to evaluate the averages of certain quantities (such as transformation matrices) needed for treating various properties of the chain molecule.

In the RIS scheme, integrals over the energy surface are approximated by summations over a discrete set of states. These should be judiciously chosen with regard to features of the surface, and especially with regard to its symmetry.<sup>21</sup> If the conformational energy surface has been computed and if it is deemed to be of sufficient accuracy and reliability to warrant estimation of statistical weights from it, then these should be evaluated from the configuration integrals over the respective ranges of conformation associated with each of the several states; it may not suffice to evaluate the statistical weight solely on the basis of the energy at the minimum within the given range. All regions of accessible energy must be represented by the set of rotational isomeric states.

It is important also that the rotational states be chosen in such manner as to be consonant with the objective of equitable representation of the conformation space. A proper set of states may coincide with the positions of minima of the surface, but identification of rotational states on this basis is not required.<sup>4,21</sup> Serious errors may in fact result

from blindly assigning states at certain minima while ignoring other regions of the configuration space of comparable energy but devoid of minima.<sup>21</sup> Such a procedure biases the evaluation of a configuration-dependent quantity by giving undue weight to regions that happen to exhibit minima at the expense of those that do not display this incidental feature. It is important to bear in mind that the RIS scheme serves as a means by which to evaluate continuous integrals, *i.e.*, integrals over the configuration space as a whole.

In instances where the conformational energy surface is diffuse and is not characterized by a simple set of well-defined minima, a more detailed representation of the conformation space is clearly indicated. Choice of states at closer intervals (*e.g.*, at 30°, or even at 10°) has proved advantageous in treating the properties of polypeptides<sup>30</sup> and polynucleotides.<sup>33</sup>

A measure of circumspection obviously is necessary in the selection of rotational isomeric states, and the RIS scheme is susceptible to errors of judgment in this regard. Allegra and coworkers<sup>34</sup> have developed a more objective procedure involving double Fourier expansion of the statistical weight  $\exp[-E(\phi_i, \phi_{i+1})/kT]$  for rotations about consecutive bonds  $i$  and  $i + 1$  over the full ranges, 0 to  $2\pi$ , of the pair of angles. Designation of rotational states is thus avoided. The Fourier coefficients play a role analogous to that of the matrix of statistical weights in the RIS scheme. Allegra and coworkers claim their method to be superior to the RIS scheme when the Fourier expansions are carried to about ten terms in each of the two torsion angles  $\phi$  before truncation; in the RIS calculations carried out for comparison, three rotational states were assigned for each angle  $\phi$ .

If it is important to compare the advantages of the two methods, then the number of rotational states in the RIS scheme should be comparable to the number of terms included in the Fourier expansion. In the limit where these numbers are made sufficiently large, the two methods must yield identical results. The comparative advantages of the two methods in this respect are overshadowed by the reality that the conformational energy surface is not determinable with an accuracy that would justify pressing either method to its limit. For most chains, three states suffice for representation in the RIS scheme well within the limits of reliability in the estimation of conformational energies.

Inasmuch as the Fourier expansion procedure relies on eigenvalues of the matrix of Fourier coefficients, it is applicable only to uniform chains of great length. The RIS scheme enjoys the considerable advantage of greater versatility, being applicable to finite chains, to copolymers of any description and to stereoirregular polymers of any tactic sequence. It also provides a consistent basis for treating a wide variety of properties, including higher moments of the chain vector  $\mathbf{r}$  and more complicated quantities involving this vector, as we show in the following sections of this paper. If the range of interdependence of skeletal rotation angles exceeds two bonds, as assumed above, the RIS scheme can be adapted thereto by restructuring (and enlarging) the statistical weight matrix.<sup>4,32</sup>

As noted earlier, the RIS scheme has the advantage of being directly cognate to physical features of the particular chain and the hindrances affecting rotation about its skeletal bonds. The choice of rotational states usually is dictated by circumstances that can be comprehended by inspection of a suitable model. Consequently, configurational characteristics of polymer chains can be interpreted directly and rationally in terms of molecular characteristics; conformational energies calculated by current empirical methods, though helpful, are not essential for this purpose. Also, corresponding conformations in different polymer chains can

be compared meaningfully, and a high degree of correlation has been demonstrated.<sup>4</sup>

For a number of simple chains, conformational energy calculations have thus far failed to reproduce observed characteristics. Polyoxymethylene, polyoxyethylene and poly(dimethylsiloxane) are examples.<sup>4</sup> The RIS scheme may nevertheless be applied to treatment of their configurational statistics and of configuration-dependent properties.<sup>4</sup> In such instances the statistical weights, or the corresponding conformational energies, must be evaluated from observed configuration-dependent properties. Contrary to the usual view of the RIS scheme as an intermediary in the process of deducing molecular properties from energies calculated according to "theory," the RIS scheme may be employed inductively to characterize the conformation on the basis of experimental information.

### Configuration-Dependent Quantities for Chains of Specified Conformation

Properties of chain molecules that depend on configuration include the dimensions of the spatial configuration as measured by the chain displacement vector  $\mathbf{r}$  connecting its ends, or by any of various products that may be formed from  $\mathbf{r}$ ; the radius of gyration or other moments formed from higher even powers of the distances between all pairs of atoms; molecular dipole moments; and optical anisotropies. Evaluation of these properties requires summation over contributions from the individual bonds or groups comprising the chain. These contributions, being vectors or tensors identified with the respective skeletal bonds numbered 1 to  $n$ , are conveniently expressed in local reference frames. A cartesian coordinate system is therefore defined for each skeletal bond. It is customary to take the axis  $X_i$  for system  $i$  along skeletal bond  $i$ , the  $Y_i$  axis in the plane defined by bonds  $i - 1$  and  $i$  and the  $Z_i$  axis in the perpendicular direction that completes a right-handed reference frame.<sup>4</sup>

Also in keeping with previous conventions,<sup>4</sup> we let  $\mathbf{T}_i$  denote the matrix of the transformation between reference frames  $i + 1$  and  $i$ . It is a function of  $\theta_i$  and  $\phi_i$ . Throughout this section we take the set of parameters  $\{l, \theta, \phi\}$  for all bonds to be fixed;  $\{l\}$  and  $\{\theta\}$  are fixed by the structure and  $\{\phi\}$  by arbitrary assignment.

Typically, the sums to be evaluated consist of terms involving serial products of transformations  $\mathbf{T}_i$ , or their self-direct products (see below), as required to combine the contributions associated with two or more bonds of the chain. These serial products may be generated by matrix multiplication of suitably constructed matrices, one such matrix being formulated for each bond of the chain. Evaluation of the required sum for a given property then reduces to serial multiplication of generator matrices, one for each bond 1 to  $n$ .

**Chain Displacement Vector.** The chain vector  $\mathbf{r}$  with components  $x, y, z$ , being the sum of skeletal bond vectors  $\mathbf{l}_i$ , is given by

$$\mathbf{r} = \begin{bmatrix} x \\ y \\ z \end{bmatrix} = \mathbf{l}_1 + \mathbf{T}_1 \mathbf{l}_2 + \mathbf{T}_1 \mathbf{T}_2 \mathbf{l}_3 + \dots + \mathbf{T}_1 \mathbf{T}_2 \dots \mathbf{T}_{n-1} \mathbf{l}_n \quad (10)$$

where each bond vector  $\mathbf{l}_i$  is expressed in its own frame of reference; *i.e.*

$$\mathbf{l}_i = \text{col}(l_i, 0, 0) = \begin{bmatrix} l_i \\ 0 \\ 0 \end{bmatrix} \quad (11)$$

Since bond 1 has no predecessor, axes  $Y_1$  and  $Z_1$  are not

specified by the definitions above; hence  $\phi_1$  is not defined and specification of  $\mathbf{T}_1$  is incomplete. In order to amend this deficiency,<sup>6</sup> we supply an imaginary zeroth bond and direct it parallel to bond 2. Then  $\phi_1 = 0$ , the conformation of bond 1 being regarded as trans. In effect, the directions of bonds 1 and 2 fix the reference frame in which  $\mathbf{r}$  is expressed according to eq 10.

In the interests of simplifying expressions to follow, serial products such as  $\mathbf{T}_1\mathbf{T}_2 \dots \mathbf{T}_j$  will be written  $\mathbf{T}_1^{(j)}$ . The serial index of the first factor of the serial product is identified by the subscript and the number of factors by the superscript in parentheses. With this convention, eq 10 is replaced by

$$\mathbf{r} \equiv \mathbf{r}_{0n} = \sum_{j=1}^n \mathbf{T}_1^{(j-1)} \mathbf{l}_j \quad (12)$$

Serial generation of the sum of terms in eq 10 or 12 requires performance of all operations pertaining to bond  $i$  at step  $i$ . These operations include (a) perpetuation of the serial product  $\mathbf{T}_1 \dots \mathbf{T}_{i-1}$  by appending  $\mathbf{T}_i$ , (b) completion of a term by appending  $\mathbf{l}_i$ , and (c) retention of all terms similarly completed at previous stages through acquisition of a vector  $\mathbf{l}_h$ , where  $h < i$ . Two classes of terms may be distinguished at a given stage  $i-1$ : the first (1) consists of a single member, namely, the incompleting serial product  $\mathbf{T}_1^{(i-1)}$  cited above, and the second (2) is the sum of completed terms

$$\mathbf{r}_{0,i-1} = \sum_{h=1}^{i-1} \mathbf{T}_1^{(h-1)} \mathbf{l}_h$$

Let these classes of terms be presented as the two "elements" (actually submatrices) of the matrix  $\mathbf{M}_{i-1}$  defined by

$$\mathbf{M}_{i-1} = [\mathbf{T}_1^{(i-1)}, \mathbf{r}_{0,i-1}]$$

Performance of operation (a) on the first element generates the corresponding element (or submatrix) of  $\mathbf{M}_i$ , and performance of the operation (b) on this element yields the term required to be added to  $\mathbf{r}_{0,i-1}$  to obtain  $\mathbf{r}_{0,i}$ .

A generator matrix  $\mathbf{A}_i$  may be formulated<sup>6</sup> such that its first row is addressed to the incompleting serial product, i.e., to the first element of  $\mathbf{M}_{i-1}$ , on which it must perform the operations (a) and (b), and whose second row is dedicated to retention of the terms in the second element of  $\mathbf{M}_{i-1}$  as required according to (c) above. Thus, we let

$$\mathbf{A}_i = \begin{bmatrix} \mathbf{T} & \mathbf{l} \\ 0 & \mathbf{1} \end{bmatrix}_i \quad (13)$$

where the subscript  $i$  appended to the brackets will be understood to denote the serial indices of the quantities  $\mathbf{T}$  and  $\mathbf{l}$  within. Then

$$\mathbf{M}_i = \mathbf{M}_{i-1} \mathbf{A}_i$$

Let an initial matrix  $\mathbf{A}_1$  be defined as the first row of  $\mathbf{A}_1$ , the latter matrix being defined according to eq 13; i.e.

$$\mathbf{A}_1 = [\mathbf{T} \ \mathbf{l}]_h \quad (14)$$

Then, with  $h = 1$ , the serial product  $\mathbf{A}_1\mathbf{A}_2^{(n-2)}$  gives  $\mathbf{M}_{n-1}$ . Postmultiplication by the last column of  $\mathbf{A}_n$ , which we denote by

$$\mathbf{A}_n = \begin{bmatrix} \mathbf{l} \\ 1 \end{bmatrix}_k \quad (15)$$

with  $k$  set equal to  $n$ , yields<sup>6</sup>

$$\mathbf{r} = \mathbf{A}_1\mathbf{A}_2^{(n-2)}\mathbf{A}_n \quad n \geq 2 \quad (16)$$

i.e.,  $\mathbf{r}$  is obtained as a serial product of generator matrices.

This result admits of immediate generalization to

$$\mathbf{r}_{hk} = \mathbf{A}_{h+1}\mathbf{A}_{h+2}^{(k-h-2)}\mathbf{A}_k \quad k - h \geq 2 \quad (17)$$

for the vector spanning the sequence of  $k - h$  bonds connecting atom  $h$  with  $k$ . For  $h = 0$  and  $k = n$ , this result reduces to eq 16 with  $\mathbf{r} \equiv \mathbf{r}_{0n}$ .

The exclusion from eq 16 and 17 of the trivial case of a chain or sequence of unit length can be amended by an alternative, but less versatile, formulation (see footnote 35). These results are completely general. No restrictions apply to the character of the chain; bonds and bond angles may be specified in any manner whatsoever.

The foregoing treatment of the chain vector  $\mathbf{r}$  represents the simplest application of the matrix generation method. The generator matrix  $\mathbf{A}_i$ , like others to follow, is irreducible to diagonal form.

**Square of the Magnitude of the Chain Vector.** The square of the magnitude of  $\mathbf{r}$  is given by

$$r^2 = \sum_{h=1}^n l_h^2 + 2 \sum_{h < j} \mathbf{l}_h^T \mathbf{T}_h \mathbf{T}_{h+1} \dots \mathbf{T}_{j-1} \mathbf{l}_j \quad (18)$$

where  $\mathbf{l}_h^T$  is the transposed, or row form of bond vector  $\mathbf{l}_h$ , and  $l_h$  is its magnitude. Each term of the double sum is the scalar product of a pair, e.g.,  $h, j$ , of bond vectors. Like preceding expressions, this one is completely general.

Pursuant to the formulation of a generator matrix suitable for evaluation of eq 18, we observe that at step  $i > 1$  three classes of terms occurring in eq 18 must be advanced from stage  $i-1$  to  $i$ . These classes, distinguished according to the location of  $i$  relative to  $h$  and  $j$  in eq 18, are: (1) those for which  $i \leq h \leq j$ , (2) those with  $h < i \leq j$ , and (3) those having  $h \leq j < i$ . Terms of the first category acquire the initial factor  $\mathbf{l}_h^T$  at or beyond stage  $i$ ; class (2) comprises terms that have acquired this factor but not  $\mathbf{l}_j$  before stage  $i$ ; and terms of class (3) have acquired both  $\mathbf{l}_h^T$  and  $\mathbf{l}_j$  prior to stage  $i$  and hence are complete. The generator matrix with rows addressed to terms of categories (1), (2), and (3), respectively, is

$$\mathbf{G}_i = \begin{bmatrix} 1 & 2\mathbf{l}^T \mathbf{T} & l^2 \\ 0 & \mathbf{T} & \mathbf{l} \\ 0 & 0 & 1 \end{bmatrix}_i \quad (19)$$

The row matrix with elements (submatrices) representing the three classes of terms at stage  $i-1$  is

$$\mathbf{M}_{i-1} = \left[ 1, \ 2 \sum_{h=1}^{i-1} \mathbf{l}_h^T \mathbf{T}_h^{(i-h)}, \ \sum_{h=1}^{i-1} l_h^2 + 2 \sum_{h=1}^{i-1} \sum_{j=2}^{i-1} \mathbf{l}_h^T \mathbf{T}_h^{(j-h)} \mathbf{l}_j \right]$$

Postmultiplication of this row by  $\mathbf{G}_i$  yields the succeeding matrix  $\mathbf{M}_i$ . In the process, each of the terms of the second element is extended by the factor  $\mathbf{T}_i$  and the new term  $2\mathbf{l}_i^T \mathbf{T}_i$  is added to them; the set of terms completed by the factor  $\mathbf{l}_i$  is added to those comprising the third element of  $\mathbf{M}_{i-1}$ . The third element becomes the repository for the terms required by eq 18, the full set being acquired when  $i$  reaches  $n$ .

It follows at once that<sup>4,11</sup>

$$r^2 = \mathbf{G}_1 \mathbf{G}_2^{(n-2)} \mathbf{G}_n \quad n \geq 2 \quad (20)$$

where  $\mathbf{G}_1$  and  $\mathbf{G}_n$  are, respectively, the first row of  $\mathbf{G}_1$  and the final column of  $\mathbf{G}_n$ . In general

$$\mathbf{G}_h = [1 \ 2\mathbf{l}^T \mathbf{T} \ l^2]_h \quad (21)$$

$$\mathbf{G}_k = \begin{bmatrix} l^2 \\ \mathbf{l} \\ 1 \end{bmatrix}_k \quad (22)$$



$$r_{hk}^2 = \mathbf{G}_{[h+1]} \mathbf{G}_{h+2}^{(k-h-2)} \mathbf{G}_k \quad k-h \geq 2 \quad (23)$$

Thus, serial multiplication of  $\mathbf{G}$  matrices in the manner stipulated by eq 20 generates the terms of eq 18 identically. Equation 23 likewise generates the terms for the  $hk$  sequence. (An alternative procedure is given in footnote 35.)

**Radius of Gyration.** The radius of gyration  $s$  for a chain of  $n$  bonds is given by

$$s^2 = (n+1)^{-2} \sum_{0 \leq h < k \leq n} r_{hk}^2 \quad (24)$$

the sum being over all pairs of chain atoms. Substitution of eq 23 for  $r_{hk}^2$  with  $k-h \geq 2$  gives

$$s^2 = (n+1)^{-2} \left[ \sum_{h < k-1} \mathbf{G}_{[h+1]} \mathbf{G}_{h+2}^{(k-h-2)} \mathbf{G}_k + \sum_{k=1}^n l_k^2 \right] \quad (25)$$

The required generator matrix is

$$\mathbf{S}_1 = \begin{bmatrix} 1 & \mathbf{G}_1 & l^2 \\ 0 & \mathbf{G} & \mathbf{G}_1 \\ 0 & 0 & 1 \end{bmatrix}_i \quad (26)$$

$$= \begin{bmatrix} 1 & 1 & 2\mathbf{T}\mathbf{T} & l^2 & l^2 \\ 0 & 1 & 2\mathbf{T}\mathbf{T} & l^2 & l^2 \\ 0 & 0 & \mathbf{T} & 1 & 1 \\ 0 & 0 & 0 & 1 & 1 \\ 0 & 0 & 0 & 0 & 1 \end{bmatrix}_i \quad (27)$$

with  $\mathbf{S}_{[1]}$  and  $\mathbf{S}_n$  defined as the first row of  $\mathbf{S}_1$  and last column of  $\mathbf{S}_n$ , respectively. Then

$$s^2 = (n+1)^{-2} \mathbf{S}_{[1]} \mathbf{S}_2^{(n-2)} \mathbf{S}_n \quad n \geq 2 \quad (28)$$

**Quantities of Higher Orders.** The dyadic product  $\mathbf{r}\mathbf{r}^T$  is the matrix of the symmetric second order tensor formed from the components  $x, y, z$  of  $\mathbf{r}$ . That is

$$\mathbf{r}\mathbf{r}^T = \begin{bmatrix} x^2 & xy & xz \\ yx & y^2 & yz \\ zx & zy & z^2 \end{bmatrix}$$

The direct product of  $\mathbf{r}$  with itself gives the  $9 \times 1$  vector comprising the same elements taken in reading order, row by row, and arranged as a column; i.e.,

$$\mathbf{r} \otimes \mathbf{r} = \text{col}(x^2, xy, \dots, z^2) \equiv \text{col}(\mathbf{r}\mathbf{r}^T) \quad (29)$$

where  $\otimes$  denotes the direct product.

It follows from the generating scheme for  $\mathbf{r}$  as expressed by eq 16 together with the theorem on direct products<sup>36</sup> that

$$\mathbf{r} \otimes \mathbf{r} = (\mathbf{A} \otimes \mathbf{A})_{[1]} (\mathbf{A} \otimes \mathbf{A})_2^{(n-2)} (\mathbf{A} \otimes \mathbf{A})_n \quad n \geq 2 \quad (30)$$

Tensors of higher order can be developed analogously. Introducing the symbolism  $\mathbf{r}^{\times p}$  for the self-direct product of degree  $p$ , we have for the column form of the tensor of order  $p$  formed from  $x, y$ , and  $z$

$$\mathbf{r}^{\times p} = \mathbf{A}_{[1]}^{\times p} (\mathbf{A}^{\times p})_2^{(n-2)} \mathbf{A}_n^{\times p} \quad (31)$$

(See also footnote 35.)

Some of the elements of  $\mathbf{r}^{\times p}$  are identically equal for  $p > 1$ ; they differ only in the order of their factors  $x, y$ , and  $z$ . Such redundant elements may be combined in interests of concision without sacrifice of content. In this way the order of the vector  $\mathbf{r}^{\times p}$  may be reduced from  $3^p$  to  $(p+2)!/p!2!$ .

Similar redundancy occurs in the self-direct products of the generator matrices in eq 31. It may be eliminated ac-

cording to the following procedure enunciated by Nagai<sup>10,37</sup> and formulated algebraically by Flory and Abe.<sup>11</sup> Let the rows and columns of  $\mathbf{A}$  be indexed by digits 1-4. The rows and columns of  $\mathbf{A}^{\times p}$  are indexed by numbers formed from  $p$  digits 1-4. Two or more rows are said to correspond to one another if their indexes are formed from the same set of digits, but in permuted order. Corresponding columns are defined in like manner. Condensation may be effected by combining (i.e., adding) corresponding rows.<sup>11,37</sup> This operation is performed for each set of corresponding rows. Corresponding columns are rendered identical by this process. Redundant columns beyond the first indexed by the given set of digits are deleted. The pre- and postmultipliers  $\mathbf{A}_1^{\times p}$  and  $\mathbf{A}_j^{\times p}$  are reduced according to the same rules for deleting columns and for combining rows, respectively. In this way the square order of  $\mathbf{A}^{\times p}$  is reduced from  $4^p$  to  $(p+3)!/p!3!$ , and of course the order of  $\mathbf{r}^{\times p}$  is reduced as stated above. It will be apparent that computation for higher values of  $p$  (e.g., for  $p = 6-8$ ), which would otherwise be prohibitive, are enormously simplified in this way.

The higher even moments of the magnitude  $r$  of  $\mathbf{r}$  may be formulated by a procedure involving further use of direct products. Thus, it is permissible to consider  $r^4$  as the self-direct product of  $r^2$ . For the even moments in general

$$r^p = (r^2)^{\times p/2}$$

where  $p/2$  is an integer  $>0$ . Hence, from eq 20 one obtains

$$r^p = \mathbf{G}_{[1]}^{\times p/2} (\mathbf{G}^{\times p/2})_2^{(n-2)} \mathbf{G}_n^{\times p/2} \quad n \geq 2 \quad (32)$$

Condensation of the self-direct products of the generator matrices may be carried out in the manner prescribed above.

Higher moments  $S_p$  analogous to the square of the radius of gyration, may be defined as the sums of even powers  $p$  of the distance  $r_{hk}$  between all pairs  $hk$  of chain atoms; i.e.

$$S_p = (n+1)^{-2} \left[ \sum_{h < k-1} r_{hk}^p + \sum_{k=1}^n l_k^p \right] \quad (33)$$

where  $p$  is an even integer. They may be elaborated from the quantities  $r_{hk}^p$  formulated after the manner of eq 32 for  $r_{0n}^p \equiv r^p$ .<sup>4</sup>

**Other Quantities.** The dipole moment  $\mu$  for the molecule is given by eq 16 in conjunction with eq 13-15 with  $\mathbf{l}_i$  therein replaced by the dipole contribution  $\mathbf{m}_i$  of group  $i$ . The squared magnitude  $\mu^2$  of  $\mu$  is given by eq 19-22 with corresponding alterations.

The squared optical anisotropy  $\gamma^2$  that determines the contribution to depolarized light scattering by each molecule in a system of independent and uncorrelated molecules is defined by

$$\gamma^2 = (3/2) \text{trace}(\hat{\alpha}\hat{\alpha}) \quad (34)$$

where  $\hat{\alpha}$  is the anisotropic part of the molecular polarizability tensor  $\alpha$ ; the former tensor,  $\hat{\alpha}$ , is obtained from the latter by subtraction of the trace of  $\alpha$ . If the symmetric tensor  $\hat{\alpha}$  is expressed instead as a  $9 \times 1$  column vector, denoted by  $\hat{\alpha}^C$  with elements taken in "reading order" as above, then the scalar product of  $\hat{\alpha}^C$  with itself yields the same result; i.e.

$$\gamma^2 = (3/2) \hat{\alpha}^R \hat{\alpha}^C \quad (35)$$

$\hat{\alpha}^R$  being the row form of this vector. If  $\hat{\alpha}$  can be regarded as the sum of contributions  $\hat{\alpha}_i$  from the respective groups, or units, then<sup>12</sup>

$$\gamma^2 = \frac{3}{2} \sum_i \hat{\alpha}_i^2 + 3 \sum_{h < j} \hat{\alpha}_h^R (\mathbf{T} \otimes \mathbf{T})_h^{(j-h)} \hat{\alpha}_j^C \quad (36)$$

where  $\hat{\alpha}_i^R$  and  $\hat{\alpha}_j^C$  are expressed in their respective reference frames. The generator matrix is easily established to

be<sup>7</sup>

$$\mathbf{P}_i = \begin{bmatrix} 1 & 2\hat{\alpha}^R(\mathbf{T} \otimes \mathbf{T}) & \hat{\alpha}^2 \\ 0 & \mathbf{T} \otimes \mathbf{T} & \hat{\alpha}^C \\ 0 & 0 & 1 \end{bmatrix} \quad (36')$$

and

$$\gamma^2 = (3/2)\mathbf{P}_{[1} \mathbf{P}_2^{(n-2)} \mathbf{P}_n] \quad (37)$$

where  $\mathbf{P}_{[1}$  and  $\mathbf{P}_n]$  are the first row of  $\mathbf{P}_1$  and the last col-

umn of  $\mathbf{P}_n$ , respectively. The stress-optical coefficient obtained from measurements of the strain birefringence exhibited by a cross-linked network depends on the quantity  $\Delta a$  given by<sup>3,4,13,14</sup>

$$\Delta a = (3/2)\langle \mathbf{r}^T \hat{\alpha} \mathbf{r} \rangle_0 / \langle r^2 \rangle_0 \quad (38)$$

where vector  $\mathbf{r}$  refers to a representative chain of the network and  $\hat{\alpha}$  denotes the anisotropic part of the polarizability tensor for such a chain. The angle brackets subscripted 0 denote the average over all configurations for the unperturbed chain. Our concern at this juncture is limited to the quantity  $\mathbf{r}^T \hat{\alpha} \mathbf{r}$  for a specified configuration. Its evaluation is illustrative of the application of matrix generation methods to more complicated sums.

On the assumption that bond polarizability tensors for the bonds, or groups, comprising the chain are additive

$$\mathbf{r}^T \hat{\alpha} \mathbf{r} = \sum_h \sum_j \sum_k \mathbf{l}_h^T \hat{\alpha}_j \mathbf{l}_k \quad (39)$$

where  $\hat{\alpha}_j$  is the contribution associated with bond  $j$  and the sums are over all bonds 1 to  $n$  of the chain. The products of transformation matrices  $\mathbf{T}$  required to establish identity of reference frames for the three quantities in each term are here omitted for simplicity. Two alternative renditions of this expression are

$$\mathbf{r}^T \hat{\alpha} \mathbf{r} = \Sigma \hat{\alpha}^R [(\Sigma \mathbf{l}_h^T) \otimes (\Sigma \mathbf{l}_k)] \quad (39')$$

$$= [(\Sigma \mathbf{l}_h^T) \otimes (\Sigma \mathbf{l}_k)] \Sigma \hat{\alpha}_j^C \quad (39'')$$

where  $\hat{\alpha}_j^R$  and  $\hat{\alpha}_j^C$  are the row and column forms of  $\alpha_j$ , respectively. Which of the three expressions is preferred depends on the serial order of  $h, j$ , and  $k$ .

For the construction of a generator matrix,  $\mathbf{Q}_i$  for bond  $i$ , the following six categories of terms must be distinguished according to the serial order of  $i, j, h, k$

- (1)  $i \leq h, j, k$
- (2)  $h < i \leq j, k$
- (3)  $j < i \leq h, k$
- (4)  $h, k < i \leq j$
- (5)  $h, j < i \leq k$
- (6)  $h, j, k < i$

The generator matrix shall consist of six rows addressed respectively to elements comprising terms in these six categories. Each such row is required to include elements chosen

neously interchanging the corresponding columns.) Then for the specified configuration

$$\mathbf{r}^T \hat{\alpha} \mathbf{r} = \mathbf{Q}_{[1} \mathbf{Q}_2^{(n-2)} \mathbf{Q}_n] \quad (41)$$

where  $\mathbf{Q}_{[1}$  is the first row of  $\mathbf{Q}_1$  and  $\mathbf{Q}_n]$  is the last column of  $\mathbf{Q}_n$ .

The dipole orientational contribution to the Kerr constant for electric birefringence depends on the quantity  $\mu^T \hat{\alpha} \mu$  where  $\mu$  is the dipole moment of the molecule in the specified configuration.<sup>15,16</sup> This quantity can be generated using eq 40 and 41, with  $\mathbf{l}_i$  in eq 40 replaced by the dipole moment  $\mathbf{m}_i$  associated with skeletal bond  $i$ .

The coefficient of strain dichroism falls within the scope of the same formalism.<sup>4,18</sup> The transition moment replaces  $\hat{\alpha}$  in eq 40.

Patterson<sup>38</sup> has formulated generator matrices for the quantities that occur in the complete theory of light scattering presented by Nagai.<sup>39</sup> These quantities depend on sums of terms such as  $(\hat{\alpha}_i \mathbf{r}_{ij}^T \hat{\alpha}_j \mathbf{r}_{ij})$ ,  $(r_{ij}^2 \hat{\alpha}_i^R \hat{\alpha}_j^C)$ , and  $(\mathbf{r}_{ij}^T \hat{\alpha}_i \hat{\alpha}_j \mathbf{r}_{ij})$  over all pairs  $i, j$ . The last of these terms is the product of two tensors with a vector and with its transpose.

**Statistical Mechanical Averages Over Configuration Space.** Let  $\mathbf{U}_i$  represent the matrix of statistical weights  $u_{\zeta\eta,i}$  applicable to rotational isomeric states  $\zeta, \eta = \alpha, \beta, \dots, \nu$  for bonds  $i-1$  and  $i$ , respectively. The configuration partition function  $Z$  for the chain molecule is given by the serial product of these matrices, *i.e.*

$$Z = \mathbf{U}_1^{(n)} \quad (42)$$

where

$$\mathbf{U}_1 = \text{row}(1, 0, \dots, 0) \quad (43)$$

and

$$\mathbf{U}_n = \text{col}(1, 1, \dots, 1) \quad (44)$$

The matrix generation methods presented above for evaluating properties of chain molecules in specified configurations are readily elaborated to yield the corresponding statistical mechanical averages over all configurations as represented in terms of a suitable set of rotational isomeric states. The procedure is general.<sup>6,7,11</sup>

Consider a configuration-dependent molecular property  $f = f(\{\phi\})$ . We assume that this property can be expressed as a sum of contributions each attributable to, or associated with, an individual skeletal bond of the chain. For a specified configuration  $\{\phi\}$  the property  $f(\{\phi\})$  can be generated



by serial multiplication of generator matrices  $\mathbf{F}_i$  of order  $s$ . For the purpose of generating, in a similar fashion, the average  $\langle f \rangle$  of  $f$  over all configurations of the chain, we formulate the generator matrix

$$\mathfrak{F}_i = \begin{bmatrix} u_{\alpha\alpha}\mathbf{F}(\alpha) & u_{\alpha\beta}\mathbf{F}(\beta) & \dots & \dots \\ u_{\beta\alpha}\mathbf{F}(\alpha) & u_{\beta\beta}\mathbf{F}(\beta) & \dots & \dots \\ \vdots & \vdots & \ddots & \vdots \\ \vdots & \vdots & \vdots & u_{\nu\nu}\mathbf{F}(\nu) \end{bmatrix}_i \quad (45)$$

for  $1 < i < n$ . Terminal matrices similarly obtained by introducing elements of  $\mathbf{U}_1$  and  $\mathbf{U}_n$  into the appropriate generator matrices, are

$$\mathfrak{F}_{[1]} = [\mathbf{F}_{[1]} \ 0 \ 0 \ \dots \ 0] \quad (46)$$

$$\mathfrak{F}_{[n]} = \text{col}(\mathbf{F}_{[n]}\mathbf{F}_{[n]} \ \dots \ \mathbf{F}_{[n]}) \quad (47)$$

where  $\mathbf{F}_{[1]}$  and  $\mathbf{F}_{[n]}$  are the first row and last column of  $\mathbf{F}_1$  and  $\mathbf{F}_n$ , respectively. Rotational state designations are not required in the terminal matrices  $\mathfrak{F}_{[1]}$  and  $\mathfrak{F}_{[n]}$  inasmuch as neither the row  $\mathbf{F}_{[1]}$  nor the column  $\mathbf{F}_{[n]}$  depends on the conformation. This is implicit in the fact that neither  $\phi_1$  nor  $\phi_n$  is defined (except in the arbitrary specification of  $\phi_1$  for the purpose of establishing an initial reference frame for representation of chain vector  $\mathbf{r}$ ; see above). The generator matrices  $\mathfrak{F}$  are more succinctly defined by

$$\mathfrak{F}_i = (\mathbf{U}_i \otimes \mathbf{E}_s) \|\mathbf{F}_i\| \quad 1 < i < n \quad (48)$$

where  $\|\mathbf{F}_i\|$  is the diagonal array of the generator matrices  $\mathbf{F}_i(\alpha), \dots, \mathbf{F}_i(\nu)$  for the rotational states  $\alpha \dots \nu$ , and  $\mathbf{E}_s$  is the matrix identity of the order  $s$  of matrix  $\mathbf{F}_i$ . Terminal matrices are given by

$$\mathfrak{F}_{[1]} = \mathbf{U}_1 \otimes \mathbf{F}_{[1]} \quad (49)$$

$$\mathfrak{F}_{[n]} = \mathbf{U}_n \otimes \mathbf{F}_{[n]} \quad (50)$$

It will be apparent from the organization of elements within the generator matrices  $\mathfrak{F}_i$  that serial multiplication of these matrices from 1 to  $n$  generates the complete set of products  $\mathbf{F}_{[1]}\mathbf{F}_2 \dots \mathbf{F}_{n-1}\mathbf{F}_{[n]}$ , one for each and every configuration of the chain specified by the set of rotational states for all internal bonds. Each such product yields the value of  $f = F(\{\phi\})$  for the configuration  $\{\phi\}$  it represents. The serial multiplication of the  $\mathfrak{F}_i$  matrices simultaneously generates the product of the statistical weights  $u_{\zeta\eta}$  that expresses the statistical weight  $\Omega_{\{\phi\}}$  for each configuration, and it joins this product as a multiplier of  $f_{\{\phi\}}$  for the same configuration. Thus, the serial product  $\mathfrak{F}_{[1]}\mathfrak{F}_2^{(n-2)}\mathfrak{F}_{[n]}$  comprises the sum of the complete set of terms  $\Omega_{\{\phi\}}f_{\{\phi\}}$  for each configuration. Division by the sum  $Z$  of the statistical weights  $\Omega_{\{\phi\}}$  for every configuration yields  $\langle f \rangle$ . That is

$$\langle f \rangle = \mathfrak{F}_{[1]}\mathfrak{F}_2^{(n-2)}\mathfrak{F}_{[n]}Z^{-1} \quad (51)$$

This result is easily modified to express the average of a scalar configuration-dependent property  $f_{hk}$  that comprises contributions only from bonds  $i$  in the interval  $h < i < k$ . Then

$$f_{hk} = \mathbf{F}_{[h+1]}\mathbf{F}_{h+2}^{(k-h-2)}\mathbf{F}_{[k]}$$

and the average over all configurations of the chain as a whole is given by<sup>40</sup>

$$\langle f_{hk} \rangle = Z^{-1}\mathbf{U}_1^{(h)}\mathfrak{F}_{[h+1]}\mathfrak{F}_{h+2}^{(k-h-2)}\mathfrak{F}_{[k]}\mathbf{U}_{k+1}^{(n-k)} \quad (52)$$

where

$$\mathfrak{F}_{[h+1]} = \mathbf{U}_{h+1}\|\mathbf{F}_{[h+1]}\| \quad (53)$$

$$\mathfrak{F}_{[k]} = (\mathbf{U}_k \otimes \mathbf{E}_s)\|\mathbf{F}_{[k]}\| = \mathbf{U}_k \otimes \mathbf{F}_{[k]} \quad (54)$$

(For an alternative formulation, see footnotes 35 and 40.) These specifications for the terminal matrices follow directly from eq 48 if it is observed that  $\mathbf{F}_{[h+1]}$  is of order  $1 \times s$  and, hence, that  $\mathbf{E}_s$  in eq 48 must be replaced by unity for the purpose of defining  $\mathfrak{F}_{[h+1]}$ . In general, the "elements"  $\mathbf{F}_{[h+1]}$  in eq 53 may depend on the rotational state of bond  $h + 1$ . If, however, the contribution of the bond is directed along the bond, as in the case of the bond vector or its products, then the  $\nu$  "elements" comprising  $\|\mathbf{F}_{[h+1]}\|$  are identical, and eq 53 simplifies to

$$\mathfrak{F}_{[h+1]} = \mathbf{U}_{h+1} \otimes \mathbf{F}_{[h+1]} \quad (53')$$

The  $\nu$  columns that are the "elements" comprising  $\|\mathbf{F}_{[k]}\|$  are necessarily identical. It is on this account that  $\mathfrak{F}_{[k]}$  simplifies unambiguously to the final expression in eq 54, which corresponds to eq 50. Adaptation of the procedure to a vectorial quantity  $\mathbf{f}_{hk}$  is straightforward.

The foregoing methods are applicable to all of the quantities treated or mentioned in the preceding section; i.e., to  $\mathbf{r}$ ,  $r^2$ ,  $s^2$ ,  $\mu^2$ ,  $\gamma^2$ ,  $\Delta a$  and to the higher moments that may be obtained from these quantities. These methods are exact. They are applicable to chains of any conceivable length, and to copolymers and stereoirregular polymers of any specified constitution and/or sequence. The orders of the generator matrices,  $\nu s \times \nu s$ , are not excessive. The matrices required for generating  $\mathbf{r}$ ,  $r^2$ ,  $s^2$ ,  $\gamma^2$ , and  $\Delta a$  are of square orders  $s = 4, 5, 7, 11$ , and  $26$ , respectively. If, as is often the case, three rotational states suffice, then the square orders of the generator matrices for the statistical mechanical averages of these quantities are 12, 15, etc.

Higher moments such as  $\mathbf{r}^{\times p}$  and  $(r^2)^{p/2}$  require the larger generator matrices obtained as the self-direct products of  $\mathbf{A}$  and  $\mathbf{G}$ , respectively. These may be condensed by the methods cited above to orders  $(s + p - 1)!/p!(s - 1)!$ , with savings in computational effort that are indispensable for  $p > 3$ . Through use of the condensed matrices, corresponding economies are realized in generating the configuration averages. The matrix  $\mathbf{P}_i$  for generating  $\gamma^2$  can be condensed similarly from square order  $s = 11$  to 8.<sup>7</sup> The order of the matrix  $\mathbf{Q}_i$ , given in eq 40, for generating  $\Delta a$  can be reduced similarly from  $s = 26$  to  $s = 20$ .

If all bonds of the chain are identical, the serial subscripts 2 to  $n - 1$  may be omitted, and the serial product in eq 51 may be replaced by the unsubscripted matrix  $\mathfrak{F}$  raised to the power  $n - 2$ . Thus,

$$\langle f \rangle = \mathfrak{F}_{[1]}\mathfrak{F}^{n-2}\mathfrak{F}_{[n]}Z^{-1} \quad (51')$$

Owing to the fact that the generator matrices  $\mathfrak{F}$ , like their antecedents  $\mathbf{F}$ , are irreducible to diagonal form, eigenvalue methods cannot be employed for the reduction of the serial products in eq 51'. The matrix generation methods are therefore incompatible with the more conventional procedures whereby averages are expressed in terms of eigenvalues of the statistical weight matrix. These latter procedures are necessarily restricted to uniform chains consisting of identical units which repeat regularly throughout the chain. They are restricted also to chains of great length for which terms in the largest eigenvalue suffice.<sup>4</sup> If the repeat unit comprises a succession of two or more skeletal bonds, terms representing various combinations of the several bonds are required and the formulation in terms of the largest eigenvalue for the product of statistical weight matrices representing the sequence of bonds spanning the repeat unit is correspondingly complicated. Practicable eigenvalue formulations of higher moments and other quantities of greater complexity are unknown. Even in the case

of a simple chain of uniform structure and great length, any advantages of eigenvalue methods from a computational standpoint are marginal at best. The matrix multiplication procedures offer overriding advantages of simplicity, flexibility, and much greater scope.

In general, the generator matrix  $F$  is considered to depend on the rotational state, or conformation, only through the transformation matrix  $T$  that invariably occurs within  $F$ . (See matrices  $A$ ,  $G$ ,  $S$ ,  $P$ , and  $Q$  of the preceding section.) The contribution associated with each bond  $i$  (e.g.,  $l_i$ ,  $m_i$ , or  $\hat{\alpha}_i$ ) is considered to be locally invariant to conformation; i.e., the contribution is assumed to be independent of the rotational state when this contribution is expressed in the reference frame of bond  $i$ . Inspection of the constitution of the generator matrix as expressed in eq 45 shows clearly that this assumption is needlessly restrictive. Obviously, the contribution of bond  $i$  to  $F_i$  could be varied with the rotational state of this bond in any conceivable manner. Moreover, possible variations of the contribution (e.g., of  $\hat{\alpha}_i$ ) with the rotational state of the preceding bond (i.e., bond  $i - 1$ ) could also be taken into account by replacing the entries  $F_i(\eta)$  in each column  $\eta$  of  $F_i$ , as expressed by eq 45, with  $F_i(\zeta, \eta)$  where  $\zeta$  is the row index denoting the state of the preceding bond. (Equation 48 would then be rendered void.)

These potentialities of the matrix generation scheme have not been exploited owing to lack of information in the detail required for assigning local contributions in the higher order of refinement suggested above. The capacity and flexibility of these methods exceeds requirements as determined by current knowledge of molecular parameters.

We have pointed out earlier in this paper that the number of rotational states for a bond may, if warranted, be increased beyond the usual number of three in order to achieve closer approximation to the integrals over configuration space. In fact, such refinements seldom are required. Often, the nature of the bond torsional potentials and conformational interactions are such as to restrict the rotations to no more than three well-defined states.<sup>4</sup> Even in instances where physical circumstances suggest subdivision of the primary set of three states, inaccuracy of ancillary information, notably the conformational energy, seldom warrants refinement beyond that attainable by compromising locations and statistical weights of the primary set of three states. In any event, the adequacy of the smaller number of states may easily be put to test by investigating the effect of increasing the number of states on the results of computations. The states must, however, be selected in such a way as to preserve equitable representation of the accessible ranges of angle.<sup>21</sup>

The range over which bond rotations are interdependent seldom goes beyond first neighbors. However, in those instances where the range is greater, the statistical weight matrix may be revised to relate the conformation for two (or more) bonds to the conformation assigned to the preceding pair (or triad, etc.). Such elaboration is, of course, at the expense of enlargement of the statistical weight matrix.

### Symmetric Chains

If the skeletal bonds of the chain are devoid of intrinsic chirality,<sup>41</sup> then right- and left-handed rotations of the same magnitude have equal *a priori* probabilities. Hence, for every rotational state  $\eta$  chosen at  $\phi_\eta$  in the range  $0 < \phi_\eta < \pi$  an equivalent state must be included at  $-\phi_\eta$ . We denote this pair by  $\eta^+$  and  $\eta^-$ , or jointly by  $\eta^\pm$ . Whether or not states should be assigned at  $\phi = 0$  and/or at  $\phi = \pi$  will be determined by the character of the bond and the associated conformational energy. The set of states may be repre-

sented generally as  $0, \alpha^\pm, \beta^\pm, \dots, \pi$ , with assignments at the extremities,  $0$  and  $\pi$ , to be determined by circumstances in given examples.

The statistical weight matrix, and the generator matrices  $F_i$  derived from it, may be condensed by combining states of opposite signs in an appropriate manner.<sup>10,11,42</sup> General procedures<sup>7,11</sup> to this end are presented below.

For the reduction of the order of the statistical weight matrix, we define matrices  $X^0$  and  $Y^0$  as follows:

$$X^0 = \begin{matrix} & 0 & \alpha^+ & \alpha^- & \beta^+ & \beta^- & \dots \\ \begin{matrix} 0 \\ \alpha^\pm \\ \beta^\pm \\ \vdots \end{matrix} & \begin{bmatrix} 1 & 0 & 0 & 0 & 0 & \dots \\ 0 & \frac{1}{2} & \frac{1}{2} & 0 & 0 & \dots \\ 0 & 0 & 0 & \frac{1}{2} & \frac{1}{2} & \dots \\ \vdots & \vdots & \vdots & \vdots & \vdots & \ddots \end{bmatrix} \end{matrix} \quad (55)$$

$$Y^0 = \begin{matrix} & 0 & \alpha^\pm & \beta^\pm & \dots \\ \begin{matrix} 0 \\ \alpha^+ \\ \alpha^- \\ \beta^+ \\ \beta^- \\ \vdots \end{matrix} & \begin{bmatrix} 1 & 0 & 0 & \dots \\ 0 & 1 & 0 & \dots \\ 0 & 1 & 0 & \dots \\ 0 & 0 & 1 & \dots \\ 0 & 0 & 1 & \dots \\ \vdots & \vdots & \vdots & \ddots \end{bmatrix} \end{matrix} \quad (56)$$

The order of indexing states indicated on the columns of  $X^0$  and on the rows of  $Y^0$  corresponds to the order of indexing in  $U_i$ . We note that

$$Y^0 X^0 = \begin{bmatrix} 1 & 0 & 0 & 0 & 0 & \dots \\ 0 & \frac{1}{2} & \frac{1}{2} & 0 & 0 & \dots \\ 0 & \frac{1}{2} & \frac{1}{2} & 0 & 0 & \dots \\ 0 & 0 & 0 & \frac{1}{2} & \frac{1}{2} & \dots \\ 0 & 0 & 0 & \frac{1}{2} & \frac{1}{2} & \dots \\ \vdots & \vdots & \vdots & \vdots & \vdots & \ddots \end{bmatrix} \quad (57)$$

In the familiar case of the three rotational states  $t$ ,  $g^+$ , and  $g^-$ , which may be identified with  $0$ ,  $\alpha^+$ , and  $\alpha^-$  in the scheme above, the orders of  $X^0$  and  $Y^0$  are  $2 \times 3$  and  $3 \times 2$ , respectively;  $Y^0 X^0$  is  $3 \times 3$ ; and the statistical weight matrix is expressed with full generality by<sup>4</sup>

$$U_i = \begin{bmatrix} 1 & \sigma & \sigma \\ 1 & \sigma\psi & \sigma\omega \\ 1 & \sigma\omega & \sigma\psi \end{bmatrix}_i \quad (58)$$

With retention of the previous definitions of  $U_1$  and  $U_n$  (see eq 43 and 44), the following invariances to multiplication by  $Y^0 X^0$  are readily verified

$$\left. \begin{aligned} U_1 Y^0 X^0 &= U_1 \\ X^0 U_i Y^0 X^0 &= X^0 U_i \\ Y^0 X^0 U_n &= U_n \end{aligned} \right\} \quad (59)$$

It follows that the matrix  $Y^0 X^0$  may be interdigitated between successive  $U$  matrices of the serial product in eq 42 without affecting the result.<sup>11</sup> Reapportioning factors, we obtain in place of this equation

$$Z = U_1^\dagger U_2^{(n-2)} U_n^\dagger \quad (60)$$

where

$$U_i^\dagger = U_i Y^0 = [1 \quad 0] \quad (61)$$

$$U_i^\dagger = X^0 U_i Y^0 = \begin{bmatrix} 1 & 2\sigma \\ 1 & \sigma(\psi + \omega) \end{bmatrix} \quad (62)$$

$$U_n^\dagger = X^0 U_n = \begin{bmatrix} 1 \\ 1 \end{bmatrix} \quad (63)$$

It will be apparent that the invariance relations, eq 59, hold for any number of states chosen to conform with the requirements of symmetry and assigned a pattern of statistical weights, expressed in  $U_i$ , in conformity therewith. The condensation consists in the replacement of each pair of states  $\eta^\pm$  by a single state  $\eta$ . The results achieved by the operations specified in eq 61-63 are easily obtained by simply adding the columns for  $\alpha^+$  and  $\alpha^-$ , the columns for  $\beta^+$  and  $\beta^-$ , etc., and then deleting redundant rows. The operations are presented in algebraic form above in order to facilitate their adaptation to the condensations of the  $\mathcal{F}$  matrices below.

Before undertaking to effect the corresponding condensation of the generator matrices, represented generically by  $\mathcal{F}_i$ , one should examine the symmetry characteristics of the corresponding matrix  $F_i$  used in the construction of  $\mathcal{F}_i$ . We assume that the contribution from bond  $i$  to the property  $f$  is locally invariant, and, consequently, that the dependence of  $F_i$  on the conformation resides solely in the transformation  $T_i$ , and/or its self-direct products. (As noted earlier, this assumption is needlessly restrictive with respect to the preceding mathematical format, although it has been adopted invariably in applications to date. It is a requirement for the following treatment, however.) Hence, those elements of  $F_i$  which are not identically zero must fall into two classes according to their symmetry with respect to reversal of the sign of  $\phi_i$ . On this basis the characters of the elements of  $G_i$ , for example, are expressed by

$$G_i \sim \begin{bmatrix} + & + & + & 0 & + \\ 0 & + & + & 0 & + \\ 0 & + & + & - & 0 \\ 0 & - & - & + & 0 \\ 0 & 0 & 0 & 0 & + \end{bmatrix}_i \quad (64)$$

where 0, +, and - denote, respectively, null elements, even elements that are unchanged by replacing  $\phi$  by  $-\phi$ , and odd elements whose signs are reversed by such replacement. Then,  $G_0 = G_+ + G_-$ , where  $G_0$ ,  $G_+$ , and  $G_-$  are the generator matrices for the  $t$ ,  $g^+$  and  $g^-$  states. In general, for any configuration-dependent property  $f$ , and any number of rotational states

$$F_0 = (1/2)(F_{g^+} + F_{g^-}) \quad (65)$$

It follows as a consequence of the character of  $F$  cited above that a diagonal elementary matrix  $E_-$  may be defined such that

$$F_{g^\mp} = E_- F_{g^\mp} E_- \quad (66)$$

and, of course,  $E_- E_- = E_+$ , where  $E_+$  is the identity of the same order ( $s$ ) as  $E_-$ . Further, let

$$E_0 = (1/2)(E_+ + E_-) \quad (67)$$

i.e., the negative elements, -1, of  $E_-$  are replaced by 0 in  $E_0$ , elements 1 being unchanged. In the case of the  $G_i$  matrix for generation of  $r^2$ , for example

$$\begin{aligned} E_\pm &= \text{diag}(1, 1, 1, \pm 1, 1) \\ E_0 &= \text{diag}(1, 1, 1, 0, 1) \end{aligned} \quad (68)$$

The transformation, eq 66, is easily verified for  $F = G$  by inspection of expression 64. In the case of the matrix  $P_i$  for

generating  $\gamma^2$ , the required operators are<sup>7</sup>

$$E_\pm = \text{diag}(1, 1, 1, \pm 1, 1, \pm 1, 1, 1) \quad (69)$$

provided that the order of  $P_i$  has been reduced to  $8 \times 8$  by condensation of the self-direct product  $T \otimes T$  included in  $P_i$  as defined by eq 36.

The matrices required for condensation of  $\mathcal{F}_i$  are obtained by multiplying each of the columns of  $X^0$  and the rows of  $Y^0$  (see eq 55 and 56) by  $E_0$ ,  $E_+$ , or  $E_-$ , depending on the character of the column or row. Thus, in general

$$X = \begin{bmatrix} E_0 & 0 & 0 & 0 & 0 & \dots \\ 0 & (1/2)E_+ & (1/2)E_- & 0 & 0 & \dots \\ 0 & 0 & 0 & (1/2)E_+ & (1/2)E_- & \dots \\ \vdots & \vdots & \vdots & \vdots & \vdots & \ddots \end{bmatrix} \quad (70)$$

$$Y = \begin{bmatrix} E_0 & 0 & 0 & \dots \\ 0 & E_+ & 0 & \dots \\ 0 & E_- & 0 & \dots \\ 0 & 0 & E_+ & \dots \\ 0 & 0 & E_- & \dots \\ \vdots & \vdots & \vdots & \ddots \end{bmatrix} \quad (71)$$

Invariance relations, analogous to eq 59, hold as follows

$$\left. \begin{aligned} \mathcal{F}_{[1]} Y X &= \mathcal{F}_{[1]} \\ X \mathcal{F}_i Y X &= X \mathcal{F}_i \\ Y X \mathcal{F}_{[n]} &= \mathcal{F}_{[n]} \end{aligned} \right\} \quad (72)$$

It follows that<sup>7,11</sup>

$$\langle f \rangle = Z^{-1} \mathcal{F}_{[1]}^\dagger \mathcal{F}_2^{t(n-2)} \mathcal{F}_{[n]}^\dagger \quad (73)$$

where

$$\mathcal{F}_{[1]}^\dagger = \mathcal{F}_{[1]} Y \quad (74)$$

$$\mathcal{F}_i^\dagger = X \mathcal{F}_i Y \quad (75)$$

$$\mathcal{F}_{[n]}^\dagger = X \mathcal{F}_{[n]} \quad (76)$$

In the common case of three rotational states,  $t$ ,  $g^+$ ,  $g^-$ , the matrix  $\mathcal{F}_i^\dagger$  reduces to

$$\mathcal{F}_i^\dagger = \begin{bmatrix} E_0 F_0 & 2\sigma E_0 F_+ \\ E_0 F_0 & \sigma(\psi E_+ + \omega E_-) F_+ \end{bmatrix} \quad (77)$$

since  $E_0 F_0 E_0 = E_0 F_0$ . Thus, for three rotational states ( $\nu = 3$ ) the square orders of the  $\mathcal{F}_i$  are reduced by the factor  $2/3$ , i.e., by the same factor as  $U_i$ . In general, for a set of  $\nu - 1$  rotational states in addition to the trans state, the orders of both  $U_i$  and  $\mathcal{F}_i$  are reduced by the factor  $(\nu + 1)/2\nu$ .

The average of the higher moments of  $r$  and of  $r^2$ , i.e.,  $\langle r^{\times p} \rangle$  and  $\langle (r^2)^{p/2} \rangle$ , may be treated by a simple extension of the foregoing scheme. The order of the generator matrix  $\mathcal{Q}_{(p)}$  for  $r^{\times p}$  (see eq 48 with  $F_i$  identified with  $A_i^{\times p}$ ) can be reduced by the factor  $(\nu + 1)/2\nu$  as above by use of matrices  $X^{(\times p)}$  and  $Y^{(\times p)}$  obtained by replacing  $E_0$ ,  $E_+$ , and  $E_-$  in eq 70 and 71 by the respective self-direct products  $E_0^{\times p}$ ,  $E_+^{\times p}$ , and  $E_-^{\times p}$  where

$$E_\pm = \text{diag}(1, 1, 1, \pm 1, 1) \quad (78)$$

and  $E_0$  is defined according to eq 68. If, as expediency mandates, the self-direct product  $A^{\times p}$  has been condensed as

outlined in an earlier section of this paper, then  $\mathbf{E}_0^{\times p}$  and  $\mathbf{E}_{\pm}^{\times p}$  must be subjected to the same condensations according to the rules stated above. Thus, the reduction of the matrix orders for symmetric chains are superimposed on the condensations applicable to the self-direct products.

Analogous methods are applicable to the higher moments of  $r^2$ , i.e., to  $\mathcal{G}_{(p/2)}$  for generating  $\langle r^p \rangle$ , where  $p$  is a positive even integer. In this case,  $\mathbf{E}_0$  and  $\mathbf{E}_{\pm}$  are given by eq 68 and the required matrices  $\mathbf{X}^{(\times p/2)}$  and  $\mathbf{Y}^{(\times p/2)}$  are obtained by replacing  $\mathbf{E}_0$ ,  $\mathbf{E}_+$ , and  $\mathbf{E}_-$  in eq 70 and 71 by  $\mathbf{E}_0^{\times p/2}$ ,  $\mathbf{E}_+^{\times p/2}$ , and  $\mathbf{E}_-^{\times p/2}$ . These diagonal matrices are to be condensed to the same orders as  $\mathcal{G}_{(p/2)}$  in the matrix  $\mathcal{G}_{(p/2)}$ .

The generator matrices with orders reduced in the foregoing manner will be found to contain one or more null rows and corresponding null columns. The fourth row and fourth column of  $\mathcal{G}^\dagger$  are null, for example, as will be apparent from eq 77 with  $\mathbf{F} = \mathbf{G}$ . If this row and the corresponding column are deleted, then the square order of  $\mathcal{G}_i^\dagger$  for the case  $\nu = 3$  is reduced from  $10 \times 10$  to  $9 \times 9$ . Similarly, the third row and column of  $\mathcal{G}_i^\dagger$  are null and may be deleted. The order of  $\mathbf{P}_i$  is  $8 \times 8$ , after condensing the self-direct product  $\mathbf{T} \otimes \mathbf{T}$ . Hence,  $\mathcal{P}_i^\dagger$  in the case  $\nu = 3$  is of square order  $16 \times 16$ . Removal of its fourth and sixth rows and columns, which are null, reduces the square order of  $\mathcal{P}_i^\dagger$  to 14. Formal procedures for incorporating these reductions have been given previously.<sup>7,11</sup>

Null rows and columns also occur in the matrices  $\mathcal{G}_{(p)}$  and  $\mathcal{G}_{(p/2)}$  for generating the higher moments and may be deleted with some economy in computations. The pattern of propagation of these null rows and columns with increase in  $p$ , or in  $p/2$ , is complicated and apparently not amenable to presentation in simple mathematical form. The algebraic procedure previously offered<sup>11</sup> for elimination of these unnecessary rows and columns in  $\mathcal{G}_{(p/2)}$  for  $p/2 > 1$  is in error. If the orders of the matrices for generating the higher moments are to be reduced beyond reduction by the factor  $(\nu + 1)/2\nu$  according to the procedure presented here, such reduction is best carried out by inspection.

**Acknowledgment.** This work was supported by the Directorate of Chemical Sciences, U. S. Air Force Office of Scientific Research Grant No. AFOSR-73-2441A.

## References and Notes

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- (35) As an alternative to the designation of special generator matrices  $\mathcal{G}_{[h+1]}$  and  $\mathcal{G}_k$  for terminal members of the serial product, the square matrices defined according to eq 19 may be used for these as well as for internal members provided that the necessary alterations are introduced by insertion of appropriate operators preceding and following the serial product.<sup>7,11</sup> The square of the magnitude of the vector connecting atoms  $h$  and  $k$  is given on this basis by

$$r_{hk}^2 = \mathbf{C}_G^* \mathbf{C}_{h+1}^{(h-k)} \mathbf{C}_G \quad (23')$$

where  $\mathbf{C}_G$  = column  $(0, \dots, 0, 1)$  and  $\mathbf{C}_G^*$  = row  $(1, 0, \dots, 0)$ . This relation holds for all combinations  $1 \leq h < k \leq n$ ; hence, it offers the minor advantage of including "sequences" of unit length. Similarly

$$r_{hk} = \mathbf{C}_A^* \mathbf{A}_{h+1}^{(h-k)} \mathbf{C}_A \quad (17')$$

where  $\mathbf{C}_A$  = column  $(0, \dots, 0, 1)$  and  $\mathbf{C}_A^*$  = row  $(\mathbf{E}, 0)$ , with  $\mathbf{E}$  and  $0$  denoting the identity and the null column vector, respectively, both of order 3.

This scheme is readily extended to quantities of higher order treated in the following subsections. Thus, for example<sup>6</sup>

$$\mathbf{r}^{\times p} = (\mathbf{C}_A^*)^{\times p} (\mathbf{A}^{\times p})_1^{(n)} (\mathbf{C}_A)^{\times p} \quad n \geq 1 \quad (31')$$

Equations 37 and 41 for quantities derived from the optical anisotropy may be formulated similarly. The prefactor  $\mathbf{C}^*$  invariably is the operator that selects the first row (or pseudo-row of the order of the quantity being calculated), and  $\mathbf{C}$  is the postfactor that selects the final column.

The procedure outlined in this footnote is less satisfactory as a basis for elaborating the treatment of configurational averages in the following section of the paper. See footnote 40.

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- (40) Extending the scheme based on operators  $\mathbf{C}$  and  $\mathbf{C}^*$  set forth in footnote 35, we may replace  $\mathcal{F}_{[h+1]}$  and  $\mathcal{F}_k$  by use of the relations

$$\mathcal{F}_{[h+1]} = \mathcal{C}_F^* \mathcal{F}_{h+1} \quad h > 0 \quad (53'')$$

$$\mathcal{F}_k = \mathcal{F}_k \mathcal{C}_F \quad k < n \quad (54'')$$

where  $\mathcal{F}_{h+1}$  and  $\mathcal{F}_k$  are the (square) matrices defined according to eq 48 and  $\mathcal{C}_F$  and  $\mathcal{C}_F^*$  are operators given by  $\mathbf{E}_+ \otimes \mathbf{C}_F$  and  $\mathbf{E}_+ \otimes \mathbf{C}_F^*$ . The relations 53'' and 54'' follow directly from eq 53 and 54. These specifications are not directly applicable to terminal bonds, for which eq 46 and 47, or eq 49 and 50 or their equivalents, must therefore be retained. Thus, the same operators cannot be used for both terminal and internal bonds, and this fact detracts materially from the utility of the operator scheme described in this footnote and in footnote 35.

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