AN INTERNAL ORDER PARAMETER FORMALISM FOR NON-RIGID MOLECULES

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INTRODUCTION

There has recently been much interest in describing orientational order in flexible molecules. The relevance of this problem is quite clear when considering that the molecules which form either thermotropic or lyotropic liquid crystals are in general not rigid. Typically we might have multi-ring molecules with some degree of internal rotation or molecules with floppy chain substituents. In addition to this, solutes with internal degrees of freedom dissolved in liquid crystals or membranes can be studied with various techniques (1). The assumption of rigidity (and quite often that of cylindrical symmetry) has usually been made in the past on the grounds of simplicity and of the inadequacy of experimental data in studying molecular structures at this level of sophistication. This latter point is no longer true; the quality and quantity of data becoming available, particularly from Nuclear Magnetic Resonance (2-4) techniques applied to isotopically substituted molecules now often demands going beyond the rigid molecule approximation.

The problem of a general formalism for describing orientational order in non-rigid particles is also becoming timely in the field of computer simulations (5). The first simulations of small alkyl chain systems and even of model bilayers are starting to appear (6). Once the attendant technical and computational problems are solved, these simulations can in fact give a huge amount of information. As an example, in a molecular dynamics simulation, all the positions and orientations of the submolecular fragments can be determined at every time step considered. Therefore, like in simulations of...
rigid particles the need arises of condensing this embarrassingly large amount of data in a set of quantities which on one hand contains the relevant information and on the other can hopefully be measured (7).

The description of orientational ordering in molecules with internal degrees of freedom has been considered by Emsley and Luckhurst (EL) using an equilibrium statistical mechanics approach (8) and by Burnell and de Lange (BL) using a time dependent picture (9). The two approaches are apparently quite different. EL have no time scale argument and express order parameters at Boltzmann averages in terms of a potential of mean torque depending on orientational as well as conformational degrees of freedom. They then partition this potential into an internal part \( U_{\text{int}}(h) \) depending only on the internal state of the molecule and an external part depending both on conformation \( h \) and orientation \( \omega \). They are then able to assign an ordinary orientational ordering matrix to every conformation \( h \). The orientational order parameter for the molecule is finally defined as an average over the singlet conformational distribution. In BL treatment the approach is kinetic. Rate equations for conformational changes are set up under assumptions of stochasticity and markovianity and order parameters are recovered as time averages in the limit of very long times. We do not enter here into a detailed comparison of the two methods or in a discussion of their equivalence or not (10). We notice, however, that in both approaches the underlying philosophy is that of treating a non-rigid molecule as a mixture of conformers, considered in turn as normal rigid molecules.

We wish to briefly outline here an alternative approach, which is a generalization of that presented in the previous chapter and which takes into account from the start the differences between a rigid and a non-rigid molecule. For simplicity we assume a flexible molecule to have only rotational internal degrees of freedom, i.e. a multi-rotor molecule. Apart from these internal degrees of freedom the molecule is rigid in the sense that the assumption of fixed bond lengths and bond angles is made here. This is justified for most relatively large molecules since changes of "shape" are largely determined by torsional as opposed to, say, vibrational degrees of freedom.

To begin with let us consider the definition of the positional-orientational state of a molecule, assuming, as usual in the statistical mechanics of fluids (11), that it can be treated as a classical particle. The state of a rigid particle is specified as seen in the previous chapter by a position vector \( r \) and by three orientational parameters e.g. three Euler angles (12) or four quaternions linked by a normalization relation (7,13). This set of quantities defines the origin and
the orientation of a coordinate frame fixed on the molecule (the molecular frame). We call the set of three parameters mentioned above the orientation $\omega$ of the particle. Typically we could choose the origin of the molecular frame on the centre of mass. We would then select three orthogonal axis in such a way as to put in evidence the symmetry of the molecule. For example, if the molecule contains a ternary or higher rotation axis, we might define this as the molecular $z$ axis. Other symmetry elements could be exploited quite similarly using Group Theory (14). If, as it is often the case, the molecule does not have enough symmetry to unequivocally determine the particle fixed frame, we could typically choose the molecule frame as the one diagonalizing a certain molecular tensor of interest. For instance in treating dispersion interactions it might be convenient to adopt as a molecular system the principal axis system of the polarizability tensor. In Liquid Crystals applications it is often expedient to choose the molecular frame as that diagonalizing the second rank ordering tensor. It is clear that this type of operational definition is not unique and if symmetry is not high enough, different choices of tensor of interest could lead to different molecular frames. The arbitrariness in selecting a molecular system clearly represents no problem at all as long as each system can be precisely defined, as is the case for a rigid molecule. As an example in electron resonance it is common to work with at least two systems: a local one diagonalizing the magnetic interaction of interest (hyperfine, $g$, ...) and a molecular system, diagonalizing the diffusion tensor. The same simple description does not apply to more complex molecules with mobile parts. In view of what we have said, defining an orientation requires the possibility of introducing a prescription for attaching a coordinate frame to the molecule. If the definition of molecular frame as that diagonalizing a certain tensor is adopted, it is apparent that an internal rotation will in general change the axis system even if overall tumbling has not taken place. In the most general case the state of a non rigid molecule can be described by a set of vectors defining the position in space of all the constituent atoms. Fortunately, however, this situation is more general than is normally needed, since a molecule contains collections of atoms whose relative positions are fixed. We call these rigid fragments. If we can attach a coordinate frame to every rigid fragment, then the state of a molecule can be given as the collection of orientations and positions of the rigid fragments in the laboratory frame $r_1$, $\omega_1$, $r_2$, $\omega_2$, ..., where the subscripts label the various rigid parts. This description, although formally complete, has perhaps the disadvantage of not making immediately clear the relation between different parts of the same molecule.

We might also take the view that every conformation is like
a rigid molecule with its own molecular frame and its orientation with respect to the laboratory frame. However, we would still have the problem, when taking averages is required, of expressing every property of interest for the various conformations in the same coordinate frame, in order to sum the (suitably weighted) conformational contributions. This means in practice that a common molecular frame has to be chosen, and it has to be placed in a rigid part of the molecule. If it is not possible to assume that enough rigidly connected atoms exist to define such a frame, another, more general description will have to be adopted. It seems therefore that the possibility of defining something we can call the orientation of a non rigid molecule is linked to the possibility of defining in it a rigid part. Taking this view it is quite natural then to define the state of the flexible molecule by giving on one hand the position and orientation of its chosen rigid part with respect to the laboratory frame and on the other the orientations of the internally moving parts with respect to the molecular rigid frame.

In the next Section this approach will be examined in detail for the simplest case of a molecule formed by two rigid parts mobile one with respect to the other, and the concept of internal order parameter will be introduced. The relation to experimentally observable quantities will then be discussed and we shall look at the limiting situation where orientational and conformational degrees of freedom are decoupled. We shall then briefly make contact between the present formalism and that of Emsley and Luckhurst. The formalism will then be generalized to more complex molecules formed of various rotating units.

THE INTERNAL ORDER PARAMETER FORMALISM

To be specific let us consider a molecule formed of two rigid distinguishable parts M1 and M2 connected by a bond and rotating one with respect to the other. This could be for instance an unsymmetrically substituted biphenyl.

Let us take one of the fragments, M1, say, as the "rigid" part, where we place the molecular frame. The second part of the molecule can rotate through an angle $\phi$ around an axis $r$. We now imagine the molecule embedded in a uniform isotropic or anisotropic fluid phase. Thus the molecule we consider could be a mesogen in its nematic or isotropic phase or it could equally well be a solute molecule dissolved in such a phase.

The singlet distribution function (15) can be written as

$$f(r_1, \omega_1, r_2, \omega_2) = f_r(\omega_1, \omega_2)$$
where the dependence on the inter-fragment vector \( \mathbf{r} \) is parametric as \( \mathbf{r} \) is taken to be constant while internal or external reorientation takes place. We shall omit writing down explicitly this dependence on the internal axis orientation and distance parameter \( \mathbf{r} \) from now on, when there is no risk of confusion. In the biphenyl type molecule mentioned above the internal rotation axis \( \mathbf{r} \) is along the para axis. It should be noticed that by writing the distribution as a function of the two labelled orientations \( \omega_1 \) and \( \omega_2 \) we have made use of the physical distinguishability of the two groups i.e. that it is possible to devise an experiment that can tell which part we are looking at. If, on the contrary, there is permutation symmetry \( P_{1,2} \) for the two parts we should consider just one-independent orientation \( \omega \) and write Eq. (1) as \( f(\omega, \phi) \). We now go back to Eq. (1) and rewrite the one particle distribution in a suitable composite basis set. In practice we expand the external orientation dependence in terms of Wigner rotation matrices and the internal rotation in Fourier series. We find

\[
f(\omega, \phi) = \sum L \left( \frac{(2L + 1)/16\pi^3}{f_{mnq}^L} D_{\mathbf{L}}^{L\ast} (\omega) \exp(-i\phi), \right.
\]

where \( q = 0, \pm 1, \pm 2, \ldots \) and as usual the sum is extended to all the coefficients not appearing on the left hand side. The angle \( \phi, 0 \leq \phi \leq 2\pi \) is the dihedral rotation angle around \( \mathbf{r} \).

The orthogonality relation of the chosen basis immediately allows definition of the expansion coefficients as

\[
f_{mnq}^L = \langle D_{m,n}^L (\omega) \exp(i\phi) \rangle
\]

where the angular brackets denote an orientational average over the distribution \( f(\omega, \phi) \). As usual (15) the singlet distribution expansion coefficients are related to the order parameters for the system. We have here three types of order parameters, i.e.

(i) Purely Orientational Order Parameters

\[
\langle D_{m,n}^L (\omega) \rangle = f_{mn\phi}^L.
\]

This type of expansion coefficient is essentially an ordinary orientational order parameter for the molecular frame. It gives the average orientation of the chosen rigid part of the molecule with respect to the director frame. For a truly rigid molecule the ordering matrix is of course unique and the parameters determined give information on the total ordering
matrix. Thus in the rigid molecule limit if we wish to employ symmetry to reduce the number of independent parameter it is the overall point symmetry of the molecule that should be employed and not the local one. If, instead, the rigid fragment is connected to the rest of the molecule via a single bond (i.e. if it is an internal rotor) then local symmetry operations may become feasible and be applied. As an example in the two ring type molecules already mentioned if the fragment where the molecular frame has been planted possesses $D_2$ symmetry, then the distribution in Eq. (2) can be simplified using this local symmetry independently of the second ring orientation. This amounts to saying that feasible local symmetry operations of this kind can be treated exactly as we have seen in the previous lecture. In the example given we shall have the restriction that \( L \) has to be even in Eq. (2). The possibility of having independent fragments implies, however, that in a flexible molecule the orientation of one sub-unit does not automatically determine the orientation of the other fragments.

We also notice that the expansion in Eq. (2) separates completely the laboratory frame operations from the internal motion. The rotation $\hat{R}_{\text{lab}}(\omega) \equiv \hat{R}_{\text{lab}}(\hat{M} \cdot L)$ is that affected by mesophase symmetry operations. Thus, for example, we have for uniaxial mesophases

$$ f_{\text{lab}}^{\text{L}} = f_{\text{lab}}^{\text{L}} \hat{5}_{\text{eq}} \hat{5}_{\text{eq}} \hat{5}_{\text{eq}} $$

whatever the conformation. Similarly if the phase has a plane of symmetry perpendicular to the director then \( L \) has to be even. Other operations can be applied as already seen in the previous chapter.

(ii) Purely Internal Order Parameters

We define purely internal order parameters as the averages

$$ \langle \exp(\text{i}q\phi) \rangle = \langle \frac{1}{q} \text{tr} \hat{5}_{\text{eq}} \hat{5}_{\text{eq}} \hat{5}_{\text{eq}} \rangle $$

These parameters describe the ordering of the second part of the molecule with respect to the first one irrespective of the overall orientation. They can be different from zero even in the isotropic phase if there is some preferential orientation of the second fragment around the internal axis. The internal order parameters for a rigid molecule with the second fragment at an angle $\phi$ from the first one will just be $\exp(iq\phi)$. By suitable definition of axis system this becomes just one. A flexible molecule can be defined as a molecule with internal order parameters deviating from the theoretical rigid value whatever
the frame. At the other extreme, we have \( f_{\phi \phi \phi} = 0 \) when the distribution \( f(\omega, \phi) \) does not depend on the internal angle \( \phi \). Apart from the trivial case of a cylindrical fragment this indicates a uniaxial distribution of the second sub-unit around the rotation axis. The coefficient \( f_{\phi \phi \phi} = 0 \) thus indicates complete internal disorder around the rotation axis. Notice that no time argument is involved in going from a rigid to an internally disordered molecule. Internal order parameters are determined by the energy barrier to rotation. Thus if the energy barrier is \( U(\phi) \) the internal order parameters are obtained from the Boltzmann expression

\[
\begin{align*}
\phi_{\phi \phi}^S &= \int d\phi \exp(iq\phi) \exp(-U(\phi)/kT)/ \int d\phi \exp(-U(\phi)/kT),
\end{align*}
\]

where \( U(\phi) \) is the internal potential of mean torque and \( kT \) are respectively the Boltzmann constant and the absolute temperature. In an isotropic system and if the medium effect on the barrier can be neglected the \( U(\phi) \) is the potential obtainable in principle from an ab-initio or semi-empirical theoretical calculation (16-19). In turn the determination of the parameters \( \phi_{\phi \phi}^S \) can provide information on the internal barrier.

(iii) Mixed Internal-External Order Parameters

The third type of coefficients in Eq. (2) are

\[
\begin{align*}
\langle \phi_{m,n}^L (\omega) \exp(iq\phi) \rangle &= \phi_{mnq}^L
\end{align*}
\]

These terms describe coupling between internal and external degrees of freedom. They can be used to recover purely orientational order parameters for the second sub-unit from those of the first one. In fact, writing down explicitly the transformations between frames we have

\[
\begin{align*}
\phi_{m,n}^L (M2-L) &= \sum_p \phi_{m,p}^L (M1-L) D_{p,n}^L (M2-M1) \\
&= \sum_p R_{p,n}^L (M2-M1) \phi_{m,p}^L (M1-L) \exp(-iq\phi) \\
&= \sum_p R_{p,n}^L (M2-M1) \phi_{m,p}^L (M1-L) \\
&= \sum_p \phi_{m,p}^L (M2-M1) f_{nm}^L
\end{align*}
\]

where we have introduced the notation
\[ p_{a,b}^L(\alpha, \beta) = \exp(-i\alpha\sigma) d_{a,b}^L(\beta) \]  

(10)

to indicate the transformation defining the rotation axis. Notice that here \(-L \leq p, n \leq L\) so that only a subset of mixed order parameters is needed in obtaining the ordering matrix for the second ring. Eq. (9) constitutes a sort of sum rule for the mixed order parameters. For a rigid molecule Eq. (9) reduces to

\[ \langle q_{m,n}^L \rangle = \sum_p \langle q_{m, p}^L \rangle \langle p_{n, (M1-M2)}^L \rangle \]  

(11)

since the transformation linking the two frames is a time independent one. In this case the orientation \(\omega = (M1-L)\) is sufficient to completely define the state of the particle. Eq. (11) simply gives the relation between the orientational order parameter when expressed in the two frames.

For a molecule where the internal rotation axis coincides with the molecular frame z axis, we have \(r_{pn}(0, 0) = \delta_{pn}\) and

\[ \langle q_{mn}^L \rangle = \langle q_{mn}^L \rangle \exp(-i\eta\theta) \]  

(12)

so that in this case the sum rule reduces to just one term. We have already mentioned when looking at purely orientational parameters that in the present treatment the different frame transformations employed to specify the orientational and internal state are clearly distinct, thus making it possible to apply symmetry simplifications referring to internal or external degrees of freedom. We have also said that mesoscale center symmetry does not put restrictions on the internal order parameters. Here, however, we have the possibility of implementing fragment symmetry. In simple cases this can be done by direct inspection. For example the order parameters for a molecule with a para (i.e. along the z axis) biaxial substituent are

\[ f_{mnq} \; q = 0, \pm 2, \pm 4, \ldots \]

Similarly if we have a methyl substituent, or generally a substituent with \(C_3\) symmetry around the internal rotation axis, then \(q = 0, \pm 3, \ldots \). In more complex cases the methods developed
within the group theory of non rigid molecules can be employed (20-22). Our purpose here is not that of giving a systematic treatment for various rotor symmetries but it is interesting that the formalism allows full exploitation of local symmetry if needed.

**Observables for a Molecule with One Internal Rotor**

We now examine here the experimental determination of the various types of order parameters introduced. Let us consider the measurement of a tensor property \( F \) with irreducible components \( F^{(2, m)} \). The observable averaged component of \( F \) along the director in the laboratory frame will be in a uniaxial phase,

\[
\langle e^{(2, x)} \rangle = \sum_{m} \langle 0 | (M_1 - L)^{x} \rangle_{m} F^{(2, m)} \rangle_{M_1} . \tag{13}
\]

The property \( F \) can be a true overall molecular property, defined for a certain molecular conformation, e.g. polarizability or dipole moment. However, it can also be a sub-molecular, local property, such as the nuclear dipolar coupling \( T^{(2, m)} \) between two nuclei \( i \) and \( j \) of importance in NMR. In the latter case we may have various possibilities.

i) The two nuclei \( i \) and \( j \) belong to the fragment where the molecular frame has been planted. If this is the case the \( T^{(2, m)} \) are constant whatever the conformation and we have

\[
\langle e^{(2, x)} \rangle_{ij} = \sum_{m} \langle 0 | (M_1 - L)^{x} \rangle_{m} T^{(2, m)}_{ij} ; i, j \text{ on } M_1 . \tag{14}
\]

Thus the experiment can give the ordering matrix of the rigid part, provided enough couplings are available. The situation here is just the same as that of a truly rigid molecule as we discussed earlier on.

ii) The two nuclei both belong to the second ('moving') part of the molecule. The molecular frame couplings \( T^{(2, m)}_{ij} \) exhibit in this case a dependence on the internal rotation angle \( \theta \), but it is not difficult to show that this dependence can be removed. In fact

\[
\langle e^{(2, x)} \rangle_{ij} = \sum_{m} \langle 0 | (M_1 - L)^{x} \rangle_{m} T^{(2, m)}_{ij} ; i, j \text{ on } M_2 . \tag{15a}
\]
\[ \sum_{m,n} <D^2_{mn} (M1-L)^a D^2_{mn} (M2-M1)^a > T^{(2,n)}_{ij} \]  
\[ \sum_{m,n} (-)^m R^2_{mn} (M2-M1)^a f^2_{0-mn} T^{(2,n)}_{ij} \]

where the dependence on internal motion has been removed by transforming \( T^{(2,n)}_{ij} \) to a frame M2 fixed on the second fragment. Coupling the two Wigner rotation matrices with the closure relation, Eq. (15) becomes

\[ \sum_{n} <D^2_{nn} (M2-L)^a > T^{(2,n)}_{ij} ; i,j \text{ on M2} \]  

These type of couplings therefore give information about the alignment of the second fragment in the laboratory frame.

iii) Each of the two nuclei belongs to a different sub-unit. This is the most interesting situation from the point of view of getting information on intramolecular rotation, i.e. the distinguishing property of our flexible molecules. We have

\[ T^{(2,n)}_{ij} = \sum_{m} D^2_{mn} (M1-L)^a T^{(2,m)}_{ij} \text{ (16)} \]

where the coupling \( T^{(2,m)}_{ij} \) is now a function of the internal rotation angle \( \theta \). By Fourier expansion of the tensor component \( T^{(2,m)}_{ij} (\theta) \) we can write

\[ T^{(2,m)}_{ij} (\theta) = \sum_{q} (T^{(2,m)}_{ij})_q \exp (iq\theta) \text{ (17)} \]

The couplings \( T^{(2,m)}_{ij} (\theta) \) and therefore the Fourier components \( (T^{(2,m)}_{ij})_q \) can of course be computed when the geometry of the fragment is known. Substitution of Eq. (16) thus gives

\[ <T^{(2,n)}_{ij}> = \sum_{m} \sum_{q} <D^2_{mn} (M-L)^a \exp (iq\theta) > (T^{(2,m)}_{ij})_q \text{ (18a)} \]
\[ = \sum_{m} \sum_{q} (-)^m f^2_{0-mn} (T^{(2,m)}_{ij})_q \text{ (18b)} \]

where \( m = 0, \pm 1, \pm 2; q = 0, \pm 1, \pm 2, \ldots \). We see therefore that this type of coupling contains information on internal order parameters. Dipolar couplings between different pairs of nuclei
and \( j \) can be expressed in terms of the same set of order parameters \( \{ \phi \}_{m,n} \). Notice, however, that the Fourier series in \( \phi \) is, strictly an infinite one and the number of parameters is not limited by an orthogonality selection rule as in the rigid solute case. On the other hand the convergence of the Fourier expansion of \( \Psi^{(n)}(\mathbf{R}) \) will limit the number of relevant terms. If enough coupling \( \phi \) can be collected a fitting procedure similar to that employed in the rigid molecule limit (3) can be used to extract a set of order parameters. Notice that if this can be pursued then a model for internal or overall reorientation does not have to be assumed. The determination of a set of order parameters would in turn allow methods mutuated from information theory (24-25) to be used for finding an approximate form of the single particle distribution as we shall briefly discuss later.

**LIMITING CASES**

A particularly simple limiting case arises when the probability of finding the molecule at a certain orientation \( \omega \) and internal angle \( \phi \) can be written as a product of orientational and conformational probabilities, i.e. when the two motions can be considered to be independent. In this case the mixed order parameters decouple:

\[
\frac{\Psi^{(n)}}{\phi_{m,n}} = \left< \phi_{m,n}^{(n)}(\omega) \exp(i\phi) \right> = \left< \phi_{m,n}^{(n)}(\omega) \right> \left< \exp(i\phi) \right>.
\]

An order parameter for the second fragment becomes

\[
\left< \phi_{m,n}^{(n)}(n+1-L) \right> = \sum_{p} \left< \phi_{m,p}^{(p)}(n+1-L) \phi_{p,n}^{(n+1-L)} \right>
\]

\[
= \sum_{p} \left< \phi_{m,p}^{(p)}(n+1-L) \right> \left< \phi_{p,n}^{(n+1-L)} \right> \left< \exp(-i\phi) \right>.
\]

Comparison with the rigid molecule expression Eq. (11) shows that Eq. (20) differs only by the substitution of \( \exp(-i\phi) \) by \( \left< \exp(-i\phi) \right> \) i.e. a rotation averaged over internal motions is substituted for the constant rotation. In this sense we can speak of an effective "averaged" molecule or pseudomolecule (8,23). We can see this also from the limiting expression for the coupling between nuclei on different frames, Eq. (16), which becomes
\[
\langle \mathrm{T}^{(2;1)} \rangle_{ij} = \sum_{m} \langle \mathrm{T}^{(2;1)}_{m} \rangle_{ij}.
\]

Notice that no argument about the relative speed of internal and overall rotation has been introduced.

RELATION TO EMSLEY–LUCKBURST FORMALISM

The EL formalism is treated in chapter 5. Here we consider the expression for \(\langle \Delta_{zz} \rangle\) the component along the director of a partially averaged second rank tensor quantity \(A\) in the EL formalism, i.e.

\[
\langle \Delta_{zz} \rangle = \sum_{a,b} \int dh P(h) A_{ab}(h) S_{ab}(h) ; a,b = X,Y,Z
\]

where \(A_{ab}(h)\) and \(S_{ab}(h)\) are respectively the molecular property of interest and the ordering matrix calculated for the molecule in a conformation \(h\), treated as a rigid particle. For a single rotor molecule the conformational label \(h\) reduces to the internal rotation angle \(s\). If we now expand the \(s\) dependence of the ordering matrix and of the \(A\) tensor components in the molecular frame as

\[
A_{ab}(s) = \sum_{n} (A_{ab})_{n} \exp(i n s),
\]

we find

\[
\langle \Delta_{zz} \rangle = \sum_{n,n'} \sum_{a,b} (A_{ab})_{n} (S_{ab})_{n'} f^i_{s;n;n'},
\]

where the parameters \(f^i_{s;n;n'}\), expansion coefficients of the internal distribution \(P(s)\), correspond to our definition of purely internal order parameters. We see therefore that EL expressions can be written down in the present formalism. However, in the internal order parameters treatment the conformational information is disentangled from the rest. This shows the various types of different order parameters involved and their relation, if any.

MULTI-ROTOR MOLECULES

We consider a molecule with various rotating fragments as a system formed of N linked bodies of unspecified symmetry. Within the assumption of fixed bond length and valence angles we can
think in terms of a molecular model where each sub-unit has one or more pins (bonds) $r_i$ placed at a certain fixed orientation with respect to the local fragment frame $\mathbf{M}_i$. The next body in the chain, if any, can be thought of as having a socket which fits in the previous pin (26). We can have various types of branched or linear systems according to the links realized between the bodies.

The methods required for molecules of different connectivity are quite similar. Here we shall therefore treat for convenience a simply connected system of $N$ rotors (cf. Fig. (1)).

![Figure 1. A simply connected multi-rotor molecule.](image)

Here we imagine the molecular "rigid" frame to be fixed on the first ($M_1$) fragment, although another sub-unit could equally well have been chosen, at least in general.

The system considered includes the case of a macromolecule with a chain attached or a nematogen with a methylene chain substituent. It also includes the case of polyphenyl type molecules.

The conformational-orientational state of a molecule of this kind can be given by specifying the rigid geometry (bond angles and bond lengths) once and for all and by giving the set of internal orientations $(\omega_1, \phi_2, \phi_3, \ldots, \phi_N)$. In the same sense the conformation alone is specified by $(\phi_2, \phi_3, \ldots, \phi_N)$. The singlet distribution function can now be written by generalizing Eq. (2) as

$$f(\omega, \phi_2, \phi_3, \ldots, \phi_N) = (2L + 1)((8\pi^2)/(2\pi)^{N-1}))^{1/2} \frac{\sqrt{L}}{\sqrt{L} \pi_{mn}^{Lm}(\omega_1)} \exp(-\mu \cdot \delta),$$

(24)
where we have introduced the notation

\[ Q = (q_2, q_3, \ldots, q_N) \]  
\[ \Phi = (\varphi_2, \varphi_3, \ldots, \varphi_N) \]  

for the collection of labels \( q_i \) and of angles \( \varphi_i \) respectively. The coefficients in the expansion are explicitly

\[ e_{mn}^{Lm,n_1,n_2,n_3,\ldots,n_N} = \langle \Phi_m | \exp(i(q_2\varphi_2+q_3\varphi_3+\ldots+q_N\varphi_N)) \rangle \]  

They represent generalized order parameters for the flexible molecule. A simple extension of the concepts introduced in the previous Sections allows interpreting these parameters as giving the correlation between the orientation of the various fragments.

Instead of keeping the treatment general let us now consider a specific example i.e. that of a molecule formed by three biaxial fragments M1, M2, M3 with a common rotation axis. This could be for example a suitably substituted terphenyl. The singlet distribution in a uniaxial phase will be

\[ f(\varphi_1, \varphi_2, \varphi_3) = \sum_{L} \frac{1}{2L+1} \langle \Phi_1^{L} | \exp(iq_2\varphi_2-iq_3\varphi_3) \rangle \]  

where \( L \) is even. We also have \( n, q_2 \) and \( q_3 \) even. If the distribution is even in \( \varphi_2 \) and \( \varphi_3 \) the order parameters should be invariant to a change in sign of \( q_2 \) and \( q_3 \). In order to consider the independent order parameters we can therefore limit ourselves to positive values of \( q_2, q_3 \) and of course of \( n \).

Let us now consider again the experimentally determinable properties for the various rings. We consider dipolar couplings again even if other properties could of course be examined instead. We have:

i) First unit

\[ \langle T_{2,1} \rangle = \sum_{i,j} \langle 0_{n_1} | (M1-L) | T_{2,1} \rangle \]  

\[ = \sum_{i,j} \langle 0_{n_1,n_2} | T_{2,1} \rangle \]  

\[ = \langle 0_{n_i} | T_{2,1} \rangle \]  

\[ = \langle 0_{n} | T_{2,1} \rangle \]  

\[ = \langle 0_{n} | T_{2,1} \rangle \]  

\[ = \langle 0_{n} | T_{2,1} \rangle \]  

(28)
ii) Second unit

\[
\langle T(t_{ij}) \rangle = \sum_i \sum_j \langle \Theta^{(i)}_{pq}(M1-L) \Theta^{(j)}_{pq}(M2-M1) \rangle T^{(i, j)}_{ij} \quad \text{i,j on M2}
\]

\[
= \sum_i \sum_j \langle \Theta^{(i)}_{pq}(M2-M1) \Theta^{(j)}_{pq}(M1-L) \exp(-i \phi_{ij}) \rangle T^{(i, j)}_{ij}
\]

\[
= \sum_i \langle \Theta^{(i)}_{pq}(M1-L) \exp(-i \phi_{ij}) \rangle T^{(i)}_{ij}
\]

\[
= \sum_i \sum_j \langle s^{(i, j)}_{0n,-n} \rangle T^{(i, j)}_{ij}
\]  

(29)

iii) Third unit

\[
\langle T(t_{ij}) \rangle = \sum_i \sum_j \langle \Theta^{(i)}_{pq}(M1-L) \Theta^{(j)}_{pq}(M2-M1) \Theta^{(j)}_{pq}(M3-M2) \rangle T^{(i, j)}_{ij} \quad \text{i,j on M3}
\]

\[
= \sum_i \sum_j \langle \Theta^{(i)}_{pq}(M2-M1) \Theta^{(j)}_{pq}(M3-M2) \exp(-i \phi_{ij}) \rangle T^{(i, j)}_{ij}
\]

\[
= \sum_i \langle \Theta^{(i)}_{pq}(M1-L) \exp(-i \phi_{ij}) \rangle T^{(i)}_{ij}
\]

\[
= \sum_i \sum_j \langle s^{(i, j)}_{0n,-n} \rangle T^{(i, j)}_{ij}
\]  

(30)

Examining Eqs. (28-30) we see that all the data relative to the three rings depend on the generalized order parameters

\[
f_{00,00}^2, f_{02,00}^2, f_{02,20}^2, f_{02,-2}^2
\]

Let us now consider an example of inter-fragment property, say the coupling \(\langle T(t_{ij}) \rangle\), where i is on M1 and j is on M2. We have, proceeding as usual

\[
\langle T(t_{ij}) \rangle = \sum_i \sum_j \langle \Theta^{(i)}_{0n}(M1-L) \Theta^{(j)}_{0n}(M2-M1) \rangle \quad \text{i on M1, j on M2}
\]

\[
= \sum_i \sum_j \langle \Theta^{(i)}_{0n}(M2-M1) \exp(i \phi_{ij}) \rangle \quad \text{i on M1, j on M2}
\]

\[
= \sum_i \sum_j \langle \Theta^{(i)}_{0n}(M1-L) \exp(-i \phi_{ij}) \rangle \quad \text{i on M1, j on M2}
\]

\[
= \sum_i \langle \Theta^{(i)}_{0n}(M1-L) \exp(-i \phi_{ij}) \rangle \quad \text{i on M1, j on M2}
\]

\[
= \sum_i \sum_j \langle s^{(i, j)}_{0n,0} \rangle \quad \text{i on M1, j on M2}
\]

(31)

Here \(q_2\) can be larger than two and order parameters like \(f_{00,0}^2, f_{00,0}^2\) etc. may enter. Thus on the one hand more information on internal reorientation is contained, on the other hand, the number of couplings obtainable experimentally is limited and therefore complete information on internal motion will not be available. A recourse to some model for conformational equilibrium can be invoked as in other approaches (8,9). Another
possibility is offered by information theory (24,25). This tells us that when the average value of a set of functions, here \( f_{\mathbf{n}} \), is determined, the best distribution we can choose is

\[
f(w_1, \ldots) = \exp \left\{ \sum_{\mathbf{n}, \mathbf{q}} c_{\mathbf{n}, \mathbf{q}} D_{\mathbf{n}}^2 (w_1) \exp(i\mathbf{q} \cdot \mathbf{\phi}) \right\}
\]  

(32)

where the sum in the exponent extends to the functions whose average is measured. The coefficients \( c_{\mathbf{n}, \mathbf{q}} \) are determined from the constraint that the available experimental data are reproduced. We see therefore that since this formalism identifies the order parameters for the system and their relation to experimentally available data it also offers a way to determine the best approximation to the orientational-conformational distribution available from NMR or other experimental techniques.

**SUMMARY**

We have briefly outlined a systematic approach to describing orientational and internal order in multi-rotor molecules. Contact with experiment has been made taking examples from NMR observables. The formalism can, however, be applied to other techniques and presents therefore a way of combining information on the system coming from the different approaches in a set of generalized order parameters. The quantities introduced should be particularly convenient to summarize the enormous quantity of configurational data obtained with simulation techniques in a relatively small set of parameters which can then be used to make contact with experiment. This systematic approach to the complete singlet distribution may be valuable when considering the amount of memory needed to store even a low resolution (large angular grid) multidimensional histogram even for a simple multi-rotor molecule.

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**REFERENCES**


