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Objective Structures

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Abstract. An *objective atomic structure* is a collection of atoms represented by mass points or ions for which every atom sees precisely the same atomic environment, up to rotation (or, more generally, orthogonal transformations) and translation. An *objective molecular structure* is a collection of molecules in which corresponding atoms in each molecule see precisely the same environment up to orthogonal transformation and translation. Many of the most actively studied structures in science satisfy these conditions, including an arbitrary ordered periodic crystal lattice, the tails and also the capsids of certain viruses, carbon nanotubes, many of the common proteins and C_{60} . A single crystal rod that has been bent and twisted into helical form also satisfies the conditions in a certain sense. The quantum mechanical significance of objective structures is described and some general methods for generating such structures are developed. Using these methods, some unexpected objective structures are revealed. Methods for simplified atomic level calculations of the energy, equilibrium and dynamics of these structures are given.

Keywords: B. Atomistic structures, biological material; C. Numerical algorithms.

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1 Introduction

We will use the following terminology. An *objective atomic structure* is a collection of N mass points or ions in which the atomic environments of any two points can be precisely related to each other by an orthogonal transformation and translation. An *objective molecular structure* is a collection of N molecules, each of which consists of M atoms such that the full atomic environments of the i^{th} atom of any two molecules are precisely related to each other by an orthogonal transformation and translation. The terminology comes from the origins of these definitions from the invariance of the energy or free energy under objectivity transformations in fundamental theories of physics. This paper is a study of these structures.

The ideas in this paper were motivated by several lines of thought. In [16] Falk and James gave a simple formula (16) for the configuration of molecules of bacteriophage T4 tail sheath. This formula produces a structure that has precisely the property of being an objective molecular structure. Each molecule in the structure is a complicated folded protein consisting of a large number of atoms, yet the *relationships* between molecules are incredibly simple. It is these simple relationships that are embodied in the formula (16). It then was seen that this observation relates to the famous papers of Crick and Watson [10] and Caspar and Klug [7] and less well-known work of Crane [9] (cf. [6]). Caspar and Klug introduced the term *equivalence* to denote structures in which each subunit “is situated in the same environment”. This is similar to the notion here of an objective structure. Caspar and Klug then observed that this definition is too strict to apply to viral capsids, and they introduced the less restrictive concept of *quasi-equivalence*. They give several examples of quasi-equivalence: (1) the case of a long helical virus that is slightly bent, perturbing the exact concept of identical environments, and (2) the case of an icosahedral structure in which the faces of the icosahedron are further subdivided by equilateral triangles. In fact, (2) is an objective molecular structure according to our definition while (1) is not. Thus the concepts introduced here do not precisely coincide with those of Caspar and Klug, but there is sufficient overlap of the intuitive concepts that one can say that we have put one interpretation of the ideas of Caspar and Klug and Crane-Crick-Watson into precise analytical form. The calculations of this paper do not appear to shed light on the remarkable sequences of triangulation numbers associated with viral structure predicted by Caspar and Klug.

We show that there is very significant simplification of first principles calculations of the energy and also of the equilibrium equations of objective structures. First, for the calculation of the energy of an objective structure, there is a direct analog of what is commonly done in crystal lattices, that is, the calculation of the electronic density by using periodic boundary conditions on the unit cell of the lattice. For objective structures the unit cell is replaced by a certain fundamental domain and periodic boundary conditions are replaced by *objective boundary conditions*. This gives the energy as a function of the structural parameters, that is, the parameters that can be varied while keeping the structure an objective structure. Once this energy is determined as a function of the structural parameters, there is a second very significant simplification of the equations of equilibrium arising from the basic objectivity of quantum mechanics (Section 5). That is, for objective atomic structures and for some kinds of objective molecular structures, structural equilibrium implies equilibrium of all the atoms.

These simplifications of the equilibrium equations are unexpectedly related to work of Ericksen [14] on the large bending and torsion of beams based on nonlinear elasticity. Using the basic invariance group of nonlinear elasticity (objectivity), he constructs equilibrium solutions in nonlinear elasticity corresponding to a bent and twisted beam. The invariance allows him to reduce the 3-D Euler-Lagrange operator to a reduced operator on the cross-section. This reduction has deep connections to invariant solutions of partial differential equations and Noether's theorem. There are related results in Kirchhoff's rod theory with similar origins [8]. In a certain sense that we describe in Section 3.4, a bent and twisted beam at atomic level is an objective molecular structure, and the equilibrium equations can be similarly reduced to conditions on one layer of atoms that compose the beam, the analog, at atomic scale, of the determination of the warping function. We develop this example in the atomic level context, and we discuss the possible validity of an atomic level version of St. Venant's principle.

Much of what is known from experiment about the molecular structure of matter comes from x-ray crystallography on crystallized structures. However, as we explain in Section 6 many objective structures are not periodic, and also nonhelical. If such structures are forced via crystallization to adopt a 3-dimensional periodic structure, then they may well be distorted away from the relations associated with the definition of objective structures. Some of these relations are quite unexpected (Section 7). However, there are basic physical reasons why a molecular system of a few different kinds of atoms or molecules should adopt a objective atomic or molecular structure. In fact, we argue in Sections 5 and 6 that from a basic physics viewpoint it is not periodicity that makes crystalline substances so common in Nature but, rather, it is the concept embedded in the definition of an objective structure. Thus, it seems possible that various nonperiodic objective molecular structures might have been overlooked, or their special relationships not recognized, because the structure was determined experimentally by x-ray crystallography.

The Cauchy-Born rule, a rule that relates atomic to macroscopic deformation, has assumed a central importance in multiscale methods for crystalline materials in recent years, [33], [18], [12]. In Section 9 we suggest a version of the Cauchy-Born rule for deformations of some objective structures.

Following ideas of Caspar and Klug [7], objective structures are ideal candidates for self-assembly, which, intuitively, explains their prevalence as the building blocks of viruses. In particular, if the surface relaxation of a partially grown objective structure is not significant, then a molecule that is about to be added to the structure further completes the environment of each of the molecules already present, as well as its own. It seems that this idea could be developed in general for such structures in a statistical mechanical framework. Guided by some theory of this type, a program of

synthesis of specific objective structures of the type we show in Section 7 could be designed.

In Section 6.1 we give methods that are capable in principle of constructing all objective atomic and molecular structures. First it is noted that the concept of “regular systems of points” in pure geometry corresponds to an objective atomic structure¹. The classification of these is equivalent to the classification of all discrete groups of isometries in 3D (see, e.g., Nikulin and Shafarevich [24] or Vainshtein [36]). These contain the usual 230 space groups, but, more interestingly, the noncrystallographic groups collected in Volume E of the International Tables of Crystallography [17]. These constructions are very useful for some general arguments concerning the equilibrium of such structures, as we explain, but not so useful for actual calculations of the properties of such structures, especially for objective molecular structures. We therefore develop some formulas (Section 6.2) that generalize the formula for T4 tail sheath and that are useful for calculations of properties. These simple formulas are seen to generate an amazing variety of these structures. The relationships involved in some of these structures are quite subtle, often combining reflection or 180° symmetry with other symmetries. Some are essentially helical and others not. Some (both helical and nonhelical) are widely observed in organic and inorganic materials.

We conclude the paper with suggestions for further research on objective structures: the possibility of collective properties like ferromagnetism or ferroelectricity in them, an approach to defects and failure, phase transformations in objective structures, the classification of phonons, ways of interrogating them that are adapted to their particular group structure, molecular dynamics on objective structures, and analogs of the Cauchy-Born rule for them.

Notation: throughout this paper subscripts denote numbering of atoms or molecules, not components of vectors or matrices. Bold lower case letters are vectors in 3 dimensions, while bold upper case letters are 3×3 matrices. Matrix multiplication of \mathbf{A} and \mathbf{B} is denoted \mathbf{AB} while \mathbf{A}^i denotes \mathbf{A} multiplied by itself i times, if i is a positive integer, or \mathbf{A}^{-1} multiplied by itself $|i|$ times if i is a negative integer.

2 Basic definitions

An *objective atomic structure* is one for which each atom sees the same atomic environment, up to translation and orthogonal transformation. In the simplest case, if the atoms are represented by positions $\mathcal{S} = \{\mathbf{x}_1, \dots, \mathbf{x}_N\}$, with N finite or infinite, then this collection is an objective atomic structure if there exists a corresponding set of orthogonal matrices $\{\mathbf{R}_1, \dots, \mathbf{R}_N\}$ such that \mathcal{S} is expressible in the form

$$\mathcal{S} = \{\mathbf{x}_i + \mathbf{R}_i(\mathbf{x}_j - \mathbf{x}_1) : j = 1, \dots, N\} \quad (1)$$

for every fixed choice of $i \in \{1, \dots, N\}$.

By way of explanation, the $(\mathbf{x}_j - \mathbf{x}_1)$ represent the displacements of atoms relative to the position of atom 1. The condition (1) says that we can recover the entire atomic structure by adding to any atom i a suitable orthogonal transformation of these displacements. The key point is that the set on the left hand side of (1) is independent of i . Here and throughout, we assume a sensible numbering system: $\mathbf{x}_i = \mathbf{x}_j \implies i = j$. Notice that, at the level of this definition, there is no assumed group structure of the transformations. However, as we describe in Section 6 a group structure emerges if we augment the set of transformations in a suitable way.

¹However, the concept of “multiregular systems of points” [11] does not correspond to an objective molecular structure. For this reason, and to emphasize the physical origins of this work, we have adopted a different terminology.

An *objective molecular structure* consists of a set of N identical molecules, each of which contains a finite number M of atoms. Thus, the structure is represented by position vectors,

$$\mathbf{x}_{i,j}, \quad i = 1, \dots, N, \quad j = 1, \dots, M. \quad (2)$$

Throughout this paper it will be allowed that N takes the value ∞ but M will be finite. An *objective molecular structure* $\mathcal{S} = \{\mathbf{x}_{i,j} : i = 1, \dots, N, j = 1, \dots, M\}$ by definition has the property that there exists NM orthogonal matrices $\{\mathbf{R}_{1,1}, \dots, \mathbf{R}_{N,M}\}$ such that

$$\mathcal{S} = \{\mathbf{x}_{i,k} + \mathbf{R}_{i,k}(\mathbf{x}_{n,m} - \mathbf{x}_{1,k}) : n = 1, \dots, N, m = 1, \dots, M\} \quad (\text{no sum over } k) \quad (3)$$

for every choice of $i \in \{1, \dots, N\}, k \in \{1, \dots, M\}$. For an objective molecular structure, modulo a rigid transformation, the entire structure looks the same from the perspective of atom k of each molecule. Examples are given below.

A useful way to write the definition of an objective molecular structure is to note that since $\mathbf{x}_{i,k} + \mathbf{R}_{i,k}(\mathbf{x}_{n,m} - \mathbf{x}_{1,k})$ gives back the entire structure, there must be a permutation $(p, q) = \Pi(n, m)$, $n = 1, \dots, N$, $m = 1, \dots, M$ such that

$$\mathbf{x}_{i,k} + \mathbf{R}_{i,k}(\mathbf{x}_{n,m} - \mathbf{x}_{1,k}) = \mathbf{x}_{\Pi(n,m)} \quad (4)$$

In fact, there is such a permutation for each choice of i, k .

If we assign a species to each atom $\mathbf{x}_{i,j}$ of an objective molecular structure, then we would want the definition to preserve the species, but the definition as written above does not necessarily do that. A general way to do that is to assign a mapping $\nu(j)$, $j \in \{1, \dots, M\}$ that gives the atomic number of atom j of any molecule (It is assumed that the numbering of atoms in a molecule is consistent with the species: atom j in molecule k is the same species as atom j of molecule m .) We say that an objective molecular structure *preserves species* if in (4)

$$(p, q) = \Pi(n, m) \implies \nu(q) = \nu(m). \quad (5)$$

In principle, it could be true that if $(j, \ell) = \Pi(n, m)$ and $(j', \ell') = \Pi(n, m')$, that we might have $j' \neq j$. This would have the interpretation that, by rotating the environment of one atom to another, two other atoms from a certain molecule would become members of different molecules. In fact, we have no examples of this possibility, and all our examples satisfy the following stronger condition. We say that an objective molecular structure *preserves molecules* if in basic definition we have

$$\mathbf{x}_{i,k} + \mathbf{R}_{i,k}(\mathbf{x}_{n,m} - \mathbf{x}_{1,k}) = \mathbf{x}_{\Pi_1(n), \Pi_2(m)}, \quad (6)$$

where Π_1 is a permutation of $\{1, \dots, N\}$ and Π_2 is a permutation of $\{1, \dots, M\}$ with $\nu(\Pi_2(m)) = \nu(m)$, and of course both of these permutations depend on the choice of i, k (When we need to emphasize this dependence we will write $\Pi_1^{(i,k)}$ and $\Pi_2^{(i,k)}$). Clearly, an objective molecular structure that preserves molecules will also preserve species. Basic physics (Section 5) favors objective molecular structures that preserve species. Even though we have no examples of objective molecular structures that do not preserve molecules, it is important to maintain maximum generality consistent with basic physics, as there could be new and unexpected structures in the more general classification.

These definitions can be specialized to objective atomic structures. We should also emphasize that, in the definition of an objective molecular structure, a ‘‘molecule’’ could represent several

actual molecules, or it could simply represent a certain convenient collection of atoms that would not ordinarily be considered a molecule, as in Example 3.4 below.

These definitions have been framed to apply to atoms (e.g., ions) but they can be modified in the usual way to apply to a density, such as an electronic density. If $\rho(\mathbf{x})$, $\mathbf{x} \in \mathbb{R}^3$, represents such a density, then we say that it is the density of an objective atomic structure if

$$\rho(\mathbf{x}) = \rho(\mathbf{x}_i + \mathbf{R}_i(\mathbf{x} - \mathbf{x}_1)) \quad (7)$$

for each $i \in \{1, \dots, N\}$ and all $\mathbf{x} \in \mathbb{R}^3$. When $\rho(\mathbf{x}) = \sum_i \delta(\mathbf{x} - \mathbf{x}_i)$ is the sum of Dirac masses at $\mathbf{x}_1, \dots, \mathbf{x}_N$ then (7) implies (1). A density of an objective molecular structure satisfies the invariance condition

$$\rho(\mathbf{x}) = \rho(\mathbf{x}_{i,k} + \mathbf{R}_{i,k}(\mathbf{x} - \mathbf{x}_{1,k})) \quad (8)$$

for all $i \in \{1, \dots, N\}$, $k \in \{1, \dots, M\}$ and all $\mathbf{x} \in \mathbb{R}^3$. When the density is of the form $\rho(\mathbf{x}) = \sum_i \sum_j m_j \delta(\mathbf{x} - \mathbf{x}_{i,j})$, with $m_j > 0$ then (8) implies (3). (For the latter argument to hold it is not required that (8) be satisfied for all such choices of the m_j .) We return to (8) in Section 8 in the context of simplified atomic level calculations.

3 Examples

In this section we show that several interesting structures are objective structures.

3.1 Ordered crystal

A Bravais lattice is a set of the form

$$\mathcal{L} = \{\nu^1 \mathbf{e}_1 + \nu^2 \mathbf{e}_2 + \nu^3 \mathbf{e}_3 : (\nu^1, \nu^2, \nu^3) \in \mathbb{Z}^3\}, \quad (9)$$

where $\mathbf{e}_1, \mathbf{e}_2, \mathbf{e}_3$ are linearly independent vectors and \mathbb{Z}^3 denotes the set of triples of integers. In this case $N = \infty$ and it is convenient to use the indexing set \mathbb{Z}^3 rather than $1, 2, \dots$, as is always possible. Clearly, this is an objective structure because triples of integers form a group under componentwise addition. That is, if $\mathbf{x} \in \mathcal{L}$ then $\mathbf{x} = \mu^i \mathbf{e}_i$ and

$$\mathcal{L} = \{\nu^i \mathbf{e}_i : (\nu^i) \in \mathbb{Z}^3\} = \{(\mu^i + \nu^i) \mathbf{e}_i : (\nu^i) \in \mathbb{Z}^3\} = \{\mathbf{x} + \nu^i \mathbf{e}_i : (\nu^i) \in \mathbb{Z}^3\}. \quad (10)$$

This is of the form (1) with all the orthogonal matrices put equal to the identity matrix.

Let $\{\mathbf{p}_1, \dots, \mathbf{p}_M\}$ be given vectors. A multilattice (i.e., an arbitrary periodic lattice²) is a set of M interpenetrating Bravais lattices of the form

$$\mathcal{L}_M = \{\nu^i \mathbf{e}_i + \mathbf{p}_k : (\nu^i) \in \mathbb{Z}^3, k \in \{1, \dots, M\}\}. \quad (11)$$

This is not in general an objective atomic structure but it is an objective molecular structure. Here, $N = \infty$ and we again use the indexing set \mathbb{Z}^3 . Let $\mathbf{x} \in \mathcal{L}_M$ so that \mathbf{x} is expressible in the form $\mathbf{x} = \mathbf{x}_{\mu,\ell} = \mu^i \mathbf{e}_i + \mathbf{p}_\ell$ for some $\ell \in \{1, \dots, M\}$ and some triple of integers $(\mu^i) \in \mathbb{Z}^3$. Then,

$$\begin{aligned} \mathcal{L}_M &= \{\nu^i \mathbf{e}_i + \mathbf{p}_k : (\nu^i) \in \mathbb{Z}^3, k \in \{1, \dots, M\}\}, \\ &= \{(\mu^i + \nu^i) \mathbf{e}_i + \mathbf{p}_k : (\nu^i) \in \mathbb{Z}^3, k \in \{1, \dots, M\}\}, \\ &= \{\mathbf{x}_{\mu,\ell} + \nu^i \mathbf{e}_i + \mathbf{p}_k - \mathbf{p}_\ell : (\nu^i) \in \mathbb{Z}^3, k \in \{1, \dots, M\}\}. \end{aligned} \quad (12)$$

Since $\mathbf{p}_\ell = 0 \mathbf{e}_i + \mathbf{p}_\ell = \mathbf{x}_{0,\ell}$ we see that this is of the form (3) with $\mathbf{R}_{\nu,k} = \mathbf{I}$.

²This is sometimes called ‘‘a lattice with a basis’’.

3.2 Bacteriophage T4 tail sheath

This is a nonperiodic complex structure consisting of identical globular protein molecules arranged on a kind of cylindrical lattice, Figure 1. There are two forms – extended and contracted sheath – and the phase transition between them plays an important role in the invasion of the bacterial host. Both structures are objective molecular structures. The structures given here are deduced from electron density maps of the molecules and other structural information, [16], [23], [21].

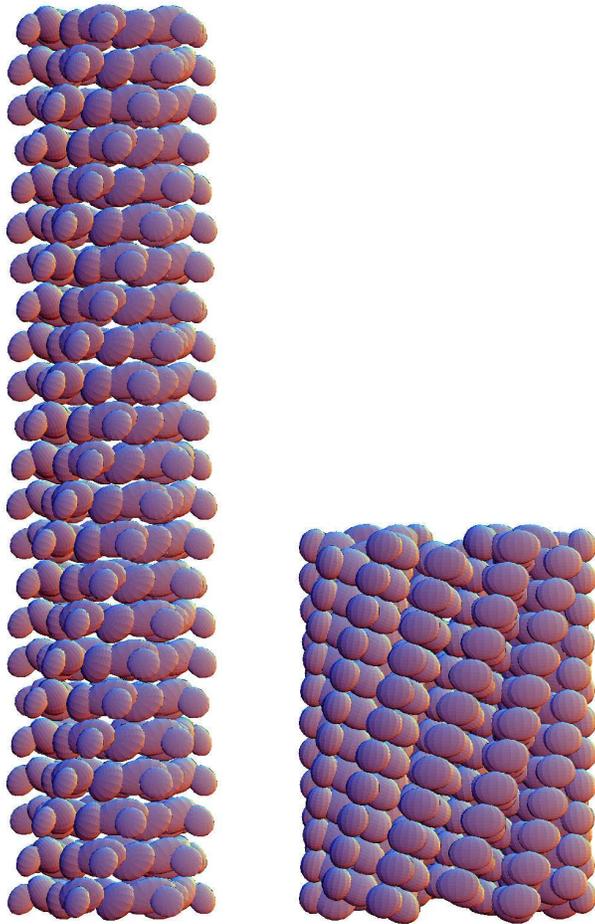


Figure 1: Extended (left) and contracted (right) tail sheath of bacteriophage T4.

To describe this structure consider a reference molecule consisting of M atoms with positions $\{\mathbf{p}_1, \dots, \mathbf{p}_M\}$ relative to its center of mass. The actual values of these vectors are, perhaps rather surprisingly, not important for the present discussion, but they can be obtained from [23], [21]. There are 138 molecules in tail sheath ($N = 138$) and it is again convenient to take the indexing set $\{1, \dots, 138\}$ to be of the form $\{(i, j) : i = 0, \dots, 5, j = 0, \dots, 22\}$. We work in an orthonormal basis $(\mathbf{e}_1, \mathbf{e}_2, \mathbf{e}_3)$ with \mathbf{e}_3 vertical in Figure 1 and introduce two vectors \mathbf{t} , $\hat{\mathbf{t}}$ and two rotation matrices \mathbf{Q} , $\hat{\mathbf{Q}}$ which for tail sheath have the forms

$$\hat{\mathbf{t}} = -\rho\mathbf{e}_1, \quad \mathbf{t} = \lambda\mathbf{e}_3 + (\mathbf{Q} - \mathbf{I})\mathbf{y}_1, \quad \mathbf{Q} = \mathbf{Q}_\gamma, \quad \hat{\mathbf{Q}} = \mathbf{Q}_{\pi/3} \quad (13)$$

with ρ, λ, γ being parameters that define the geometry of the sheath and

$$\mathbf{y}_1 = \rho \left(\frac{1}{2} \mathbf{e}_1 + \frac{\sqrt{3}}{2} \mathbf{e}_2 \right), \quad \mathbf{Q}_\theta = \begin{pmatrix} \cos \theta & -\sin \theta & 0 \\ \sin \theta & \cos \theta & 0 \\ 0 & 0 & 1 \end{pmatrix}. \quad (14)$$

We note the following identities that follow from (13):

$$\hat{\mathbf{t}} + \hat{\mathbf{Q}}\mathbf{t} - \mathbf{Q}\hat{\mathbf{t}} - \mathbf{t} = 0, \quad \hat{\mathbf{Q}}\mathbf{Q} = \mathbf{Q}\hat{\mathbf{Q}}. \quad (15)$$

It's important for the sequel to remark that these identities hold for all values of ρ, λ, γ , not just the experimentally measured ones for T4 tail sheath. The structure of the sheath is then given by the simple formula $\{\mathbf{y}_{i,j} + \mathbf{R}_{i,j}\mathbf{p}_k : i \in \{0, \dots, 5\}, j \in \{0, \dots, 22\}, k \in \{1, \dots, M\}\}^3$, where

$$\begin{aligned} \mathbf{y}_{i,j} &= \mathbf{y}_1 + \sum_{\ell=0}^{i-1} \hat{\mathbf{Q}}^\ell \hat{\mathbf{t}} + \hat{\mathbf{Q}}^i \sum_{\ell=0}^{j-1} \mathbf{Q}^\ell \mathbf{t}, \\ \mathbf{R}_{i,j} &= \hat{\mathbf{Q}}^i \mathbf{Q}^j \mathbf{R}. \end{aligned} \quad (16)$$

Here, we use the convention that $\mathbf{Q}^0 = \mathbf{I}$, the convention for sums to negative upper limits is given in (89), and \mathbf{R} is a certain rotation matrix (the orientation of molecule (0,0)). The resulting sheath is one molecule thick. The pictures in Figure 1 were generated by applying the formula (16) to a 3-domain model of the molecule. This model, for which the molecule is represented by three interpenetrating ellipsoids, was fit to the domains of the molecule using measured electron density maps [16].

To qualify as an objective molecular structure it is clear that the sheath has to be extended to infinity. This is done by keeping all formulas above the same but replacing the interval $\{0, \dots, 22\}$ by the set of all integers (and using the special summation convention (89)). Assuming this has been done, we write a general atomic position in the sheath (atom k in molecule (i, j)) as

$$\begin{aligned} \mathbf{x}_{(i,j),k} &= \mathbf{y}_{i,j} + \mathbf{R}_{i,j}\mathbf{p}_k, \\ &= \mathbf{y}_1 + \sum_{\ell=0}^{i-1} \hat{\mathbf{Q}}^\ell \hat{\mathbf{t}} + \hat{\mathbf{Q}}^i \sum_{\ell=0}^{j-1} \mathbf{Q}^\ell \mathbf{t} + \hat{\mathbf{Q}}^i \mathbf{Q}^j \mathbf{R}\mathbf{p}_k. \end{aligned} \quad (17)$$

The sheath is an objective molecular structure if for every $i, j, m, (i, j) \in \mathbb{Z}^2$, $m \in \{1, \dots, M\}$, there is an orthogonal matrix $\mathbf{R}_{(i,j),m}$ such that

$$\mathbf{x}_{(i,j),m} + \mathbf{R}_{(i,j),m}(\mathbf{x}_{p,q} - \mathbf{x}_{1,m}) \quad (18)$$

completely restores the structure. We show that this is true with the choice $\mathbf{R}_{(i,j),m} = \hat{\mathbf{Q}}^i \mathbf{Q}^j$. With this choice

$$\begin{aligned} \mathbf{x}_{(i,j),m} + \mathbf{R}_{(i,j),m}(\mathbf{x}_{p,q} - \mathbf{x}_{1,m}) &= \mathbf{y}_1 + \sum_{\ell=0}^{i-1} \hat{\mathbf{Q}}^\ell \hat{\mathbf{t}} + \hat{\mathbf{Q}}^i \sum_{\ell=0}^{j-1} \mathbf{Q}^\ell \mathbf{t} + \hat{\mathbf{Q}}^i \mathbf{Q}^j \sum_{\ell=0}^{p-1} \hat{\mathbf{Q}}^\ell \hat{\mathbf{t}} \\ &\quad + \hat{\mathbf{Q}}^i \mathbf{Q}^j \hat{\mathbf{Q}}^p \sum_{\ell=0}^{q-1} \mathbf{Q}^\ell \mathbf{t} + \hat{\mathbf{Q}}^i \mathbf{Q}^j \hat{\mathbf{Q}}^p \mathbf{Q}^q \mathbf{R}\mathbf{p}_m. \end{aligned} \quad (19)$$

³Each molecule Gp18 of tail sheath contains 658 amino acids, so M is of the order of several thousand.

Noting from (15) that \mathbf{Q} and $\hat{\mathbf{Q}}$ commute, we continue

$$\begin{aligned}
&= \mathbf{y}_1 + \sum_{\ell=0}^{i-1} \hat{\mathbf{Q}}^\ell \hat{\mathbf{t}} + \hat{\mathbf{Q}}^i \sum_{\ell=0}^{j-1} \mathbf{Q}^\ell \mathbf{t} + \mathbf{Q}^j \sum_{\ell=0}^{p-1} \hat{\mathbf{Q}}^{i+\ell} \hat{\mathbf{t}} + \hat{\mathbf{Q}}^{i+p} \sum_{\ell=0}^{q-1} \mathbf{Q}^{j+\ell} \mathbf{t} + \hat{\mathbf{Q}}^{i+p} \mathbf{Q}^{j+q} \mathbf{R} \mathbf{p}_m, \\
&= \mathbf{y}_1 + \sum_{\ell=0}^{i-1} \hat{\mathbf{Q}}^\ell \hat{\mathbf{t}} + \hat{\mathbf{Q}}^i \sum_{\ell=0}^{j-1} \mathbf{Q}^\ell \mathbf{t} + \mathbf{Q}^j \sum_{\ell=i}^{i+p-1} \hat{\mathbf{Q}}^\ell \hat{\mathbf{t}} + \hat{\mathbf{Q}}^{i+p} \sum_{\ell=j}^{j+q-1} \mathbf{Q}^\ell \mathbf{t} + \hat{\mathbf{Q}}^{i+p} \mathbf{Q}^{j+q} \mathbf{R} \mathbf{p}_m, \\
&= \mathbf{y}_1 + \sum_{\ell=0}^{i+p-1} \hat{\mathbf{Q}}^\ell \hat{\mathbf{t}} + \hat{\mathbf{Q}}^{i+p} \sum_{\ell=0}^{j+q-1} \mathbf{Q}^\ell \mathbf{t} + \hat{\mathbf{Q}}^{i+p} \mathbf{Q}^{j+q} \mathbf{R} \mathbf{p}_m, \\
&\quad + \left[(\mathbf{Q}^j - \mathbf{I}) \sum_{\ell=i}^{i+p-1} \hat{\mathbf{Q}}^\ell \hat{\mathbf{t}} + (\hat{\mathbf{Q}}^i - \hat{\mathbf{Q}}^{i+p}) \sum_{\ell=0}^{j-1} \mathbf{Q}^\ell \mathbf{t} \right]. \tag{20}
\end{aligned}$$

We will show that the term in square brackets vanishes, from which it is clear by comparison of the next to last line of (20) with (17) that, by choosing p, q, r arbitrarily, we reproduce the entire structure. The term in brackets is, using again the commutability of $\mathbf{Q}, \hat{\mathbf{Q}}$,

$$\begin{aligned}
&(\mathbf{Q}^j - \mathbf{I}) \sum_{\ell=i}^{i+p-1} \hat{\mathbf{Q}}^\ell \hat{\mathbf{t}} + (\hat{\mathbf{Q}}^i - \hat{\mathbf{Q}}^{i+p}) \sum_{\ell=0}^{j-1} \mathbf{Q}^\ell \mathbf{t} \\
&= \hat{\mathbf{Q}}^i \left(\sum_{\ell=0}^{p-1} \hat{\mathbf{Q}}^\ell (\mathbf{Q}^j - \mathbf{I}) \hat{\mathbf{t}} + \sum_{\ell=0}^{j-1} \mathbf{Q}^\ell (\mathbf{I} - \hat{\mathbf{Q}}^p) \mathbf{t} \right), \\
&= \hat{\mathbf{Q}}^i \left(\sum_{\ell'=0}^{j-1} \sum_{\ell=0}^{p-1} \hat{\mathbf{Q}}^\ell (\mathbf{Q}^{\ell'+1} - \mathbf{Q}^{\ell'}) \hat{\mathbf{t}} + \sum_{\ell'=0}^{p-1} \sum_{\ell=0}^{j-1} \mathbf{Q}^\ell (\hat{\mathbf{Q}}^{\ell'} - \hat{\mathbf{Q}}^{\ell'+1}) \mathbf{t} \right), \\
&= \hat{\mathbf{Q}}^i \left(\sum_{\ell'=0}^{j-1} \sum_{\ell=0}^{p-1} \hat{\mathbf{Q}}^\ell \mathbf{Q}^{\ell'} (\mathbf{Q} - \mathbf{I}) \hat{\mathbf{t}} + \sum_{\ell'=0}^{p-1} \sum_{\ell=0}^{j-1} \mathbf{Q}^\ell \hat{\mathbf{Q}}^{\ell'} (\mathbf{I} - \hat{\mathbf{Q}}) \mathbf{t} \right) = 0 \tag{21}
\end{aligned}$$

by virtue of the first of (15). This shows that the tail sheath is an objective molecular structure.

In this argument only the formulas (15), (16) have been used, not the specific forms of $\mathbf{t}, \hat{\mathbf{t}}, \mathbf{Q}, \hat{\mathbf{Q}}$ for T4 tail sheath. In fact this argument with various choices of $\mathbf{t}, \hat{\mathbf{t}}, \mathbf{Q}, \hat{\mathbf{Q}}$ applies to very wide variety of protein sheets including (suitably extended) capsids of the viruses Pf1 and TMV, bacteriophage M13, actin filaments and certain kinds of microtubules. It has been shown in [16] that the equations (15), (16) arise as compatible energy minimizers (called there ‘‘fully relaxed states’’) of quite a general free energy function that accounts for position and orientation of molecules.

There are also many non-protein structures of this type, the carbon nanotube being the most familiar example. The various single-walled carbon nanotubes are objective molecular structures in which each molecule consists of two carbon atoms.

3.3 \mathbf{C}_{60}

The structure of \mathbf{C}_{60} is an objective atomic structure, as can be seen by inspection. What is not quite so obvious is that a suitable placement of an arbitrary complicated molecule on each site of this structure gives an objective molecular structure.

To see this we begin with a representation of the icosahedral rotation group $\{\mathbf{Q}_1, \dots, \mathbf{Q}_{60}\}$. These matrices rotate a specific icosahedron into itself (A differently oriented icosahedron is mapped to itself by the conjugate group $\{\mathbf{R}^T \mathbf{Q}_1 \mathbf{R}, \dots, \mathbf{R}^T \mathbf{Q}_{60} \mathbf{R}\}$, \mathbf{R} being a suitable rotation matrix). The structure of C_{60} is obtained by choosing a single position vector \mathbf{y}_1 , not left invariant by any of the rotations $\{\mathbf{Q}_1, \dots, \mathbf{Q}_{60}\}$, and computing $\{\mathbf{Q}_1 \mathbf{y}_1, \dots, \mathbf{Q}_{60} \mathbf{y}_1\} = \{\mathbf{y}_1, \dots, \mathbf{y}_{60}\}$. To make all the bond lengths equal, one should choose a specific \mathbf{y}_1 , this being of the form $(1/3)\mathbf{a} + (2/3)\mathbf{b}$, where \mathbf{a} and \mathbf{b} are neighboring vertices of the underlying icosahedron. However, the statements below do not depend on this choice, and are valid for the general case where the pentagonal bond lengths are different from the hexagonal ones.

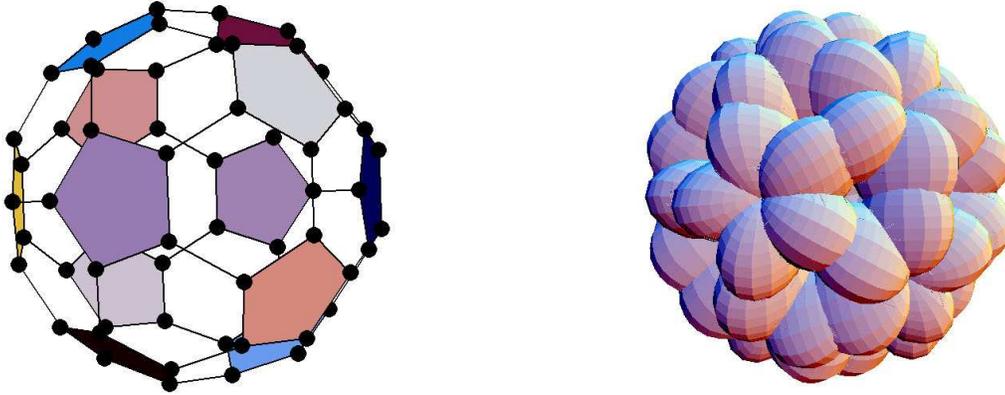


Figure 2: Left: structure of C_{60} with pentagons colored to show the 5-fold axes. Right: an objective molecular structure based on C_{60} .

To see that this is an objective atomic structure, choose the orthogonal transformations \mathbf{R}_i in the definition (1) as simply the group elements above, $\mathbf{R}_i = \mathbf{Q}_i$, $i = 1, \dots, 60$. Then $\mathbf{y}_i + \mathbf{R}_i(\mathbf{y}_j - \mathbf{y}_1) = \mathbf{Q}_i \mathbf{y}_1 + \mathbf{Q}_i(\mathbf{Q}_j \mathbf{y}_1 - \mathbf{y}_1) = \mathbf{Q}_i \mathbf{Q}_j \mathbf{y}_1$. Since $\{\mathbf{Q}_1, \dots, \mathbf{Q}_{60}\}$ is a group, then for any fixed i we have that $\{\mathbf{Q}_i \mathbf{Q}_j : j \in \{1, \dots, 60\}\} = \{\mathbf{Q}_1, \dots, \mathbf{Q}_{60}\}$ and the definition is verified.

Less obviously, it is an objective molecular structure if the molecule placed on each site is oriented suitably. The molecule can have arbitrary structure; in this regard let $\{\mathbf{p}_1, \dots, \mathbf{p}_M\}$ be an arbitrary collection of atoms denoted by position vectors. The full structure is given by

$$\mathbf{x}_{i,j} = \mathbf{Q}_i(\mathbf{y}_1 + \mathbf{p}_j), \quad i = 1, \dots, 60, \quad j = 1, \dots, M. \quad (22)$$

We need to find orthogonal $\mathbf{R}_{1,1}, \dots, \mathbf{R}_{60,M}$ such that (3) holds, and we choose simply $\mathbf{R}_{i,k} = \mathbf{Q}_i$. Then

$$\begin{aligned} \mathbf{x}_{i,k} + \mathbf{R}_{i,k}(\mathbf{x}_{n,m} - \mathbf{x}_{1,k}) &= \mathbf{Q}_i(\mathbf{y}_1 + \mathbf{p}_k) + \mathbf{Q}_i[(\mathbf{Q}_n - \mathbf{I})\mathbf{y}_1 + \mathbf{Q}_n \mathbf{p}_m - \mathbf{p}_k], \\ &= \mathbf{Q}_i \mathbf{Q}_n(\mathbf{y}_1 + \mathbf{p}_m), \quad n = 1, \dots, 60, \quad m = 1, \dots, M, \end{aligned} \quad (23)$$

which restores the full structure. A picture of a structure of this type is shown in Figure 2, right, drawn with a rather unsymmetrical set of \mathbf{p}_k 's that form an ellipsoidal molecule. Because of that choice, the full structure looks somewhat unsymmetrical, but it does have icosahedral symmetry.

There are also a great many examples of this type, also based on different finite orthogonal groups. Two quite different octahedral examples are the DNA octahedron [30] and the capsid of *Streptococcus lactis* [35]. For an interesting perspective on the deformation and mobility of such structures, see Kovács et al. [22].

3.4 Finite bending and torsion of a bar

This example illustrates that sometimes an unusual choice of molecule reveals an objective molecular structure. It also indicates that the term “molecule” should be interpreted broadly. The example is appropriate for large bending and torsional deformations of a bar. There are no assumptions of harmonicity or smallness of strains, or of continuum limits: neighboring molecules could be related by a very large rotation. Below, in Section 8 we suggest how the bending-torsional response of a bar of atomic dimensions can be efficiently calculated from first principles using these ideas.

We consider a molecule consisting of a planar sheet of atoms as pictured in Figure 3A. Although only 25 atoms are pictured there, the number would be more like the $2/3$ power of Avogadro's number in a macroscopic bar, or it could be just two atoms. The atoms within the molecule will be indexed by pairs of integers $(i, j) \subset \Omega$ where Ω is a domain in the two-dimensional plane. The number of points in $(i, j) \subset \Omega$ is M^2 . Each atom occupies the position $\mathbf{p}_{(i,j)}$, $(i, j) \in \mathbb{Z}^2 \cap \Omega$, illustrated in Figure 3A.

Keeping in mind that we index the atoms in an individual molecule by $(i, j) \in \mathbb{Z}^2 \cap \Omega$, we will index the molecules by $k = -N, \dots, 0, \dots, N$, and actually, below, we take $N = \infty$. The structure is defined by

$$\mathbf{x}_{k,(i,j)} = \mathbf{Q}_\gamma^k \mathbf{p}_{(i,j)} + k \lambda \mathbf{e}_3, \quad (24)$$

where λ, γ are real numbers (the former with the dimensions of length) and \mathbf{Q}_γ is defined by (14) relative to the orthonormal basis $\{\mathbf{e}_1, \mathbf{e}_2, \mathbf{e}_3\}$, i.e., \mathbf{Q}_γ has axis \mathbf{e}_3 . To see that (24) defines an objective molecular structure, we make the choice $\mathbf{R}_{k,(i,j)} = \mathbf{Q}_\gamma^k$. Then,

$$\begin{aligned} & \mathbf{x}_{k,(i,j)} + \mathbf{R}_{k,(i,j)}(\mathbf{x}_{m,(r,s)} - \mathbf{x}_{1,(i,j)}) \\ &= \mathbf{Q}_\gamma^k \mathbf{p}_{(i,j)} + k \lambda \mathbf{e}_3 + \mathbf{Q}_\gamma^k (\mathbf{Q}_\gamma^m \mathbf{p}_{(r,s)} + m \lambda \mathbf{e}_3 - \mathbf{p}_{(i,j)}), \\ &= k \lambda \mathbf{e}_3 + \mathbf{Q}_\gamma^k (\mathbf{Q}_\gamma^m \mathbf{p}_{(r,s)} + m \lambda \mathbf{e}_3), \\ &= \mathbf{Q}_\gamma^{k+m} \mathbf{p}_{(r,s)} + (k+m) \lambda \mathbf{e}_3, \end{aligned} \quad (25)$$

which recovers (24).

Depending on the choice of $\mathbf{p}_{(i,j)}$ and the parameters γ, λ , this structure can represent either bending or torsion or both, as these terms are usually used. In Figure 3A we show an arbitrarily distorted sheet of 25 atoms (or, they could be molecules) produced by certain choices of $\mathbf{p}_{i,j}$, $i = 1, \dots, 5$, $j = 1, \dots, 5$. In Figure 3B we take \mathbf{e}_3 to be vertical and $\lambda > 0$, in which case we generate a torsional deformation. In Figure 3C we take \mathbf{e}_3 to be directed into the page, we add a suitable constant vector to $\mathbf{p}_{i,j}$, and we take $\lambda = 0$ to get a bending deformation. Figure 3D shows the generic case of combined bending and torsion. These results overlook possible interpenetration of molecules, which does not affect their status as objective structures but may not be reasonable

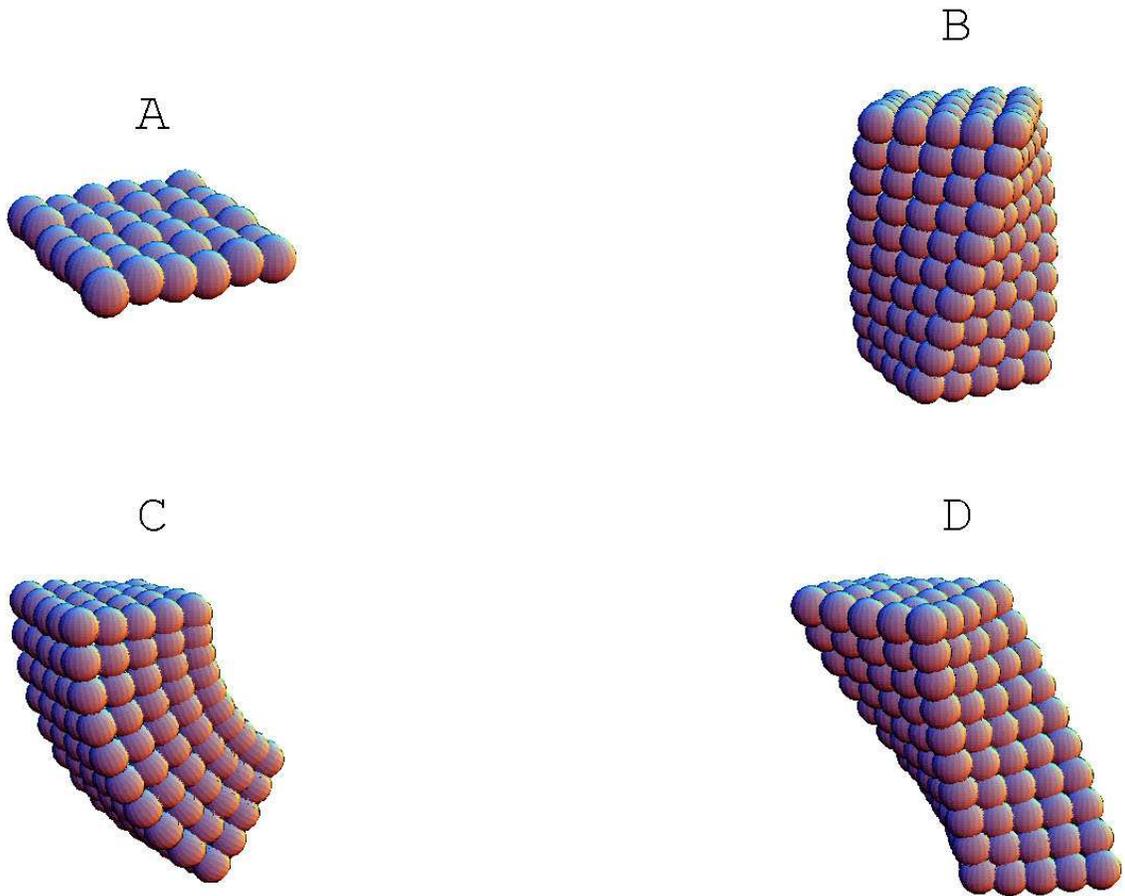


Figure 3: A: the molecule; B: pure torsion; C: pure bending; D: combined torsion-bending-tension. The objective molecular structures B-D were produced by (24) under various conditions: see text.

from a physical viewpoint. For example, in the case of Figure 3C one may want to assume that $2\pi/\gamma = K$ is a positive integer so the circle closes, and then this represents an objective molecular structure with a finite number K of molecules.

The structures given here are objective no matter what are the choices of $\mathbf{p}_{(i,j)}$ and the parameters λ and γ . For an equilibrium structure one expects these to be determined by applied forces and moments. This is discussed in Section 8. We also note that, as is easily seen, the formula (24) for bending/torsion is a special case of that for T4 tail sheath (16).

Although this example illustrates the value of being open minded about the choice of molecule, one should carry this idea too far. For example, any structure with two-fold symmetry is an objective molecular structure having two molecules.

4 Relation between atomic and molecular objective structures

Here, we explore the relation between atomic and molecular objective structures. Consider an objective molecular structure $\mathcal{S} = \{\mathbf{x}_{i,j} : i = 1, \dots, N, j = 1, \dots, M\}$. At first it might seem that if we freeze $j = j_0$, write $\mathbf{x}_i = \mathbf{x}_{i,j_0}$, $\mathbf{R}_i = \mathbf{R}_{i,j_0}$ and $u_i = u_{i,j_0}^{j_0}$, and define $\mathcal{S}_0 = \{\mathbf{x}_i : i = 1, \dots, N\}$, that \mathcal{S}_0 is an objective atomic structure. This is true in some cases, such as multilattices, but it is not true in general. A simple counterexample can be constructed from all permutations of the components of $(\pm 1, 0, \pm \varepsilon)$. This gives six molecules, each with four atoms, where, e.g., molecule 1 consists of the four points $(1, \pm \varepsilon, 0)$, $(1, 0, \pm \varepsilon)$. This is an objective molecular structure, $\{\mathbf{x}_{i,j} : i = 1, \dots, 6, j = 1, \dots, 4\}$ but typically⁴ $\{\mathbf{x}_{i,j} : i = 1, \dots, 6, j = j_0\}$ is not an objective atomic structure.

But there is a relation between atomic and molecular objective structures that can be guessed from the examples above. Consider again an objective molecular structure

$$\begin{aligned} \mathcal{S} &= \{\mathbf{x}_{n,m} : n = 1, \dots, N, m = 1, \dots, M\} \\ &= \{\mathbf{x}_{i,k} + \mathbf{R}_{i,k}(\mathbf{x}_{n,m} - \mathbf{x}_{1,k}) : n = 1, \dots, N, m = 1, \dots, M\}. \end{aligned} \quad (26)$$

We say that the molecule is *generic* if it has a trivial isometry group: that is, if

$$\mathbf{R}\mathbf{x}_{1,\ell} + \mathbf{c} = \mathbf{x}_{1,\Pi(\ell)} \quad (27)$$

holds for $\mathbf{R} \in O(3)$, $\mathbf{c} \in \mathbb{R}^3$ and a permutation Π then

$$\mathbf{R} = \mathbf{I}, \quad \mathbf{c} = 0, \quad \text{and} \quad \Pi(\ell) = \ell, \quad \ell = 1, \dots, M. \quad (28)$$

This definition is written for molecule 1; it is easily seen that molecule 1 is generic if and only if molecule i (i.e., replace 1 by i in (27)) is generic. A further equivalent condition that eliminates the translation is the following: the molecule is generic if and only if

$$\mathbf{R}(\mathbf{x}_{1,\ell} - \mathbf{x}_{1,m}) = \mathbf{x}_{1,\Pi(\ell)} - \mathbf{x}_{1,\Pi(m)} \quad (29)$$

holding for $\mathbf{R} \in O(3)$ and a permutation Π implies that $\mathbf{R} = \mathbf{I}$ and $\Pi(\ell) = \ell$.

Suppose the structure \mathcal{S} preserves molecules (see (6)) and the molecule is generic. First we observe that

$$\Pi_1^{(i,\ell)}(1) = i, \quad \Pi_2^{(i,\ell)}(\ell) = \ell. \quad (30)$$

This follows by putting $n = 1$ and $m = k = \ell$ in (6). We now put $k = n = 1$ and write (6) as

$$\mathbf{R}_{i,1}(\mathbf{x}_{1,m} - \mathbf{x}_{1,1}) = \mathbf{x}_{i,\Pi_2^{(i,1)}(m)} - \mathbf{x}_{i,1}. \quad (31)$$

Subtract (31) at $m = r, s$:

$$\mathbf{R}_{i,1}(\mathbf{x}_{1,r} - \mathbf{x}_{1,s}) = \mathbf{x}_{i,\Pi_2^{(i,1)}(r)} - \mathbf{x}_{i,\Pi_2^{(i,1)}(s)}. \quad (32)$$

⁴There is in fact a very special way to number the atoms of the structure so that $\{\mathbf{x}_{i,j} : i = 1, \dots, 6, j = j_0\}$ is an objective atomic structure. See Section 6.1.

Now evaluate (6) at $n = 1$ and subtract the result at $m = p, q$ to get,

$$\mathbf{R}_{i,k}(\mathbf{x}_{1,p} - \mathbf{x}_{1,q}) = \mathbf{x}_{i,\Pi_2^{(i,k)}(p)} - \mathbf{x}_{i,\Pi_2^{(i,k)}(q)}. \quad (33)$$

Fix i, k and choose a permutation Π to satisfy $\Pi_2^{(i,k)}(\Pi(\ell)) = \Pi_2^{(i,1)}(\ell)$. That is choose $\Pi(\ell) = (\Pi_2^{(i,k)})^{-1}(\Pi_2^{(i,1)}(\ell))$. Substituting $p = \Pi(r)$ and $q = \Pi(s)$ into (33), we get

$$\mathbf{R}_{i,k}(\mathbf{x}_{1,\Pi(r)} - \mathbf{x}_{1,\Pi(s)}) = \mathbf{x}_{i,\Pi_2^{(i,1)}(r)} - \mathbf{x}_{i,\Pi_2^{(i,1)}(s)} = \mathbf{R}_{i,1}(\mathbf{x}_{1,r} - \mathbf{x}_{1,s}), \quad (34)$$

the latter following from (31). Now we can see by comparing (34) and (29) that, because the molecule is generic,

$$\mathbf{R}_{i,k} = \mathbf{R}_{i,1} \quad (35)$$

In summary, for an objective molecular structure that preserves molecules, and has generic molecules, $\mathbf{R}_{i,\ell}$ is independent of ℓ . This explains why $\mathbf{R}_{i,\ell}$ was independent of ℓ in all the examples above.

Now we consider an objective molecular structure that preserves molecules for which (for whatever reason) $\mathbf{R}_{i,\ell}$ is independent of ℓ :

$$\mathbf{x}_{i,k} + \mathbf{R}_i(\mathbf{x}_{n,m} - \mathbf{x}_{1,k}) = \mathbf{x}_{\Pi_1(n),\Pi_2(m)}, \quad (36)$$

Define the simple average position of molecule i by

$$\bar{\mathbf{x}}_i = \frac{1}{M} \sum_{\ell=1}^M \mathbf{x}_{i,\ell}. \quad (37)$$

Now put $n = 1$ in (36), use $\Pi_1(1) = \Pi_1^{(i,k)}(1) = i$, and average over m . We get

$$\mathbf{R}_i(\bar{\mathbf{x}}_1 - \mathbf{x}_{1,k}) = \bar{\mathbf{x}}_i - \mathbf{x}_{i,k}. \quad (38)$$

This shows that \mathbf{R}_i maps molecule 1 rigidly into molecule i . In particular, subtracting (38) at k, k' we get

$$\mathbf{R}_i(\mathbf{x}_{1,k} - \mathbf{x}_{1,k'}) = \mathbf{x}_{i,k} - \mathbf{x}_{i,k'}. \quad (39)$$

Now, without putting $n = 1$, we average (36) over m :

$$\mathbf{x}_{i,k} + \mathbf{R}_i(\bar{\mathbf{x}}_n - \mathbf{x}_{1,k}) = \bar{\mathbf{x}}_{\Pi_1^{(i,k)}(n)}. \quad (40)$$

Here, we have re-emphasized the dependence of Π_1 on i, k . Subtract (40) at k, k' :

$$\bar{\mathbf{x}}_{\Pi_1^{(i,k)}(n)} - \bar{\mathbf{x}}_{\Pi_1^{(i,k')}(n)} = \mathbf{x}_{i,k} - \mathbf{x}_{i,k'} - \mathbf{R}_i(\mathbf{x}_{1,k} - \mathbf{x}_{1,k'}) = 0, \quad (41)$$

the latter following from (39). This shows that $\bar{\mathbf{x}}_{\Pi_1^{(i,k)}(n)}$ is actually independent of k and allows us to average (40) over k . We get

$$\bar{\mathbf{x}}_i + \mathbf{R}_i(\bar{\mathbf{x}}_n - \bar{\mathbf{x}}_1) = \bar{\mathbf{x}}_{\Pi_1^{(i,k)}(n)}. \quad (42)$$

This proves that the set of averages $\bar{\mathbf{x}}_i$, $i = 1, \dots, N$ is an objective atomic structure. It is interesting to note that we deal with simple position averages in this argument. However, we could have also used mass averages, since we have assumed that the permutation Π_2 preserves species and therefore mass.

The question of whether we can reverse these arguments, that is, whether we can begin from an objective atomic structure and construct an objective molecular one, is discussed in Section 6.1.

5 Quantum mechanical significance of objective structures

An important question to consider is why, from the point of view of atomic forces, such structures are rather commonly seen. To begin to explore this question we consider rather general models of atomic forces that could arise from various fundamental theories. For example, consider full quantum mechanics under the Born-Oppenheimer approximation. Given nuclear positions of identical atoms $\mathbf{x}_1, \dots, \mathbf{x}_N$ we write the ground state quantum mechanical energy as $\varphi(\mathbf{x}_1, \dots, \mathbf{x}_N)$. Specifically, this is given by

$$\begin{aligned} \varphi(\mathbf{x}_1, \dots, \mathbf{x}_N) &= \text{KE} + \text{EE} + \text{EN} + \text{NN} = \\ & \min_{\substack{\psi \text{ anti-symmetric} \\ \text{normalized}}} \sum_{\substack{s_1, \dots, s_P \\ = \pm \frac{1}{2}}} \left(\int_{\mathbb{R}^{3P}} |\nabla \psi((\mathbf{r}_1, s_1), \dots, (\mathbf{r}_P, s_P))|^2 d\mathbf{r}_1 \dots d\mathbf{r}_P \right. \\ & + \sum_{\substack{i,j=1 \\ i \neq j}}^P \int_{\mathbb{R}^{3P}} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} |\psi((\mathbf{r}_1, s_1), \dots, (\mathbf{r}_P, s_P))|^2 d\mathbf{r}_1 \dots d\mathbf{r}_P \\ & \left. + \sum_{\ell=1}^P \int_{\mathbb{R}^{3P}} V(\mathbf{r}_\ell; \mathbf{x}_1, \dots, \mathbf{x}_N) |\psi((\mathbf{r}_1, s_1), \dots, (\mathbf{r}_P, s_P))|^2 d\mathbf{r}_1 \dots d\mathbf{r}_P \right) + \frac{1}{2} \sum_{\substack{i,k=1 \\ i \neq k}}^N \frac{Z^2}{|\mathbf{x}_i - \mathbf{x}_k|}, \quad (43) \end{aligned}$$

where Z is the atomic number of the identical atoms and for the assumed Coulomb interactions

$$V(\mathbf{r}; \mathbf{x}_1, \dots, \mathbf{x}_N) = -\frac{1}{2} \sum_{i=1}^N \frac{Z}{|\mathbf{r} - \mathbf{x}_i|}. \quad (44)$$

For overall charge neutrality $P = ZN$. Defined as such, this energy exhibits two fundamental invariances:

$$\varphi(\mathbf{x}_{\Pi(1)}, \dots, \mathbf{x}_{\Pi(N)}) = \varphi(\mathbf{x}_1, \dots, \mathbf{x}_N) = \varphi(\mathbf{Q}\mathbf{x}_1 + \mathbf{c}, \dots, \mathbf{Q}\mathbf{x}_N + \mathbf{c}) \quad (45)$$

for all $\mathbf{Q} \in O(3)$ and $\mathbf{c} \in \mathbb{R}^3$ and all permutations Π of $\{1, \dots, N\}$. The permutation invariance is immediately obvious, and the objectivity is easily seen by changing variables $\mathbf{r}_i \rightarrow \mathbf{Q}\mathbf{r}_i + \mathbf{c}$ in all the terms KE, EE and EN.

For molecular structures we can use the notation we have developed above, $\mathbf{x}_{i,j}$, $i = 1, \dots, N$; $j = 1, \dots, M$ for the position of atom j in molecule i , but we do not assume that this is necessarily an objective molecular structure. Then the energy is given by an expression like (43) except that the electron-nuclear and nuclear-nuclear interaction energies (the last two terms of (43)) are replaced by

$$\begin{aligned} \text{EN} + \text{NN} &= \sum_{\ell=1}^P \sum_{\substack{s_1, \dots, s_P \\ = \pm \frac{1}{2}}} \int_{\mathbb{R}^{3P}} V(\mathbf{r}_\ell; \mathbf{x}_{1,1}, \dots, \mathbf{x}_{N,M}) |\psi((\mathbf{r}_1, s_1), \dots, (\mathbf{r}_P, s_P))|^2 d\mathbf{r}_1 \dots d\mathbf{r}_P \\ &+ \frac{1}{2} \sum_{i,k=1}^N \sum_{\substack{j,m=1 \\ (j,m) \neq (i,k)}}^M \frac{Z^{(j)} Z^{(m)}}{|\mathbf{x}_{i,j} - \mathbf{x}_{k,m}|}. \quad (46) \end{aligned}$$

Here $Z^{(j)}$ is the atomic number of atom j and

$$V(\mathbf{r}; \mathbf{x}_{1,1}, \dots, \mathbf{x}_{N,M}) = -\frac{1}{2} \sum_{i=1}^N \sum_{j=1}^M \frac{Z^{(j)}}{|\mathbf{r} - \mathbf{x}_{i,j}|} \quad (47)$$

The energy is now

$$\varphi(\mathbf{x}_{1,1}, \dots, \mathbf{x}_{1,M}, \dots, \mathbf{x}_{N,1}, \dots, \mathbf{x}_{N,M}) \quad (48)$$

Because of the different atomic numbers associated to the different atoms of the molecule the invariance analogous to (45) that follows from these definitions is

$$\begin{aligned} & \varphi(\mathbf{x}_{\Pi(1,1)}, \dots, \mathbf{x}_{\Pi(1,M)}, \dots, \mathbf{x}_{\Pi(N,1)}, \dots, \mathbf{x}_{\Pi(N,M)}) \\ &= \varphi(\mathbf{x}_{1,1}, \dots, \mathbf{x}_{1,M}, \dots, \mathbf{x}_{N,1}, \dots, \mathbf{x}_{N,M}) \\ &= \varphi(\mathbf{Q}\mathbf{x}_{1,1} + \mathbf{c}, \dots, \mathbf{Q}\mathbf{x}_{1,M} + \mathbf{c}, \dots, \mathbf{Q}\mathbf{x}_{N,1} + \mathbf{c}, \dots, \mathbf{Q}\mathbf{x}_{N,M} + \mathbf{c}), \end{aligned} \quad (49)$$

where Π now is a permutation of $\{(1,1), \dots, (N,M)\}$ that preserves species (cf. (5)) and therefore atomic number: $(k,m) = \Pi(i,j) \implies Z^{(m)} = Z^{(j)}$, and, as above, $\mathbf{Q} \in O(3)$ and $\mathbf{c} \in \mathbb{R}^3$.

These forms of the energy would not be relevant for biological processes. In that case we wrap statistical mechanics around these energies and consider, e.g., a canonical ensemble parameterized by the mean positions of the atoms. After this transformation, all the invariances given above are preserved and it is only necessary to reinterpret $\mathbf{x}_1, \dots, \mathbf{x}_N$ as mean positions and to keep in mind that φ would also depend on the temperature. Another point to keep in mind is that many objective structures contain an infinite number of atoms so their energy is infinite. In these cases the above has to be modified by considering energy differences of compact perturbations relative to the objective structure but again the invariances are preserved.

Now we show what is nearly obvious by inspection, that the $3N$ equations of equilibrium of the atoms of an objective atomic structure reduce to 3 equations. To see this we consider an objective atomic structure,

$$\mathcal{S} = \{\mathbf{x}_i + \mathbf{R}_i(\mathbf{x}_j - \mathbf{x}_1) : j = 1, \dots, N\}, \quad (50)$$

which we can also write as

$$\mathbf{x}_i + \mathbf{R}_i(\mathbf{x}_j - \mathbf{x}_1) = \mathbf{x}_{\Pi(j)}, \quad (51)$$

where Π is a permutation of $\{1, \dots, N\}$. We solve (51) for \mathbf{x}_j to get

$$\mathbf{x}_j = \mathbf{R}_i^T \mathbf{x}_{\Pi(j)} + \mathbf{x}_1 - \mathbf{R}_i^T \mathbf{x}_i, \quad (52)$$

which can also be expressed (replace $k = \Pi(j)$)

$$\mathbf{R}_i^T \mathbf{x}_k + \mathbf{x}_1 - \mathbf{R}_i^T \mathbf{x}_i = \mathbf{x}_{\bar{\Pi}(k)}, \quad (53)$$

where $\bar{\Pi} = \Pi^{-1}$ is the inverse permutation. Note that from (53) $\bar{\Pi}(i) = 1$. We fix $i \in \{1, \dots, N\}$ and evaluate (45) at the arguments $(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_i + \mathbf{d}, \dots, \mathbf{x}_N)$, and then we make the choice

$$\mathbf{Q} = \mathbf{R}_i^T, \quad \mathbf{c} = \mathbf{x}_1 - \mathbf{R}_i^T \mathbf{x}_i \quad (54)$$

in (45). We get, using (53) and (54),

$$\begin{aligned} \varphi(\mathbf{x}_1, \dots, \mathbf{x}_i + \mathbf{d}, \dots, \mathbf{x}_N) &= \varphi(\mathbf{Q}\mathbf{x}_1 + \mathbf{c}, \dots, \mathbf{Q}(\mathbf{x}_i + \mathbf{d}) + \mathbf{c}, \dots, \mathbf{Q}\mathbf{x}_N + \mathbf{c}), \\ &= \varphi(\mathbf{x}_{\bar{\Pi}(1)}, \dots, \mathbf{x}_1 + \mathbf{Q}\mathbf{d}, \dots, \mathbf{x}_{\bar{\Pi}(N)}), \end{aligned} \quad (55)$$

where we have used that $\bar{\Pi}(i) = 1$. Now use the invariance of φ under arbitrary permutations to rearrange the arguments of the second of (55):

$$\varphi(\mathbf{x}_1, \dots, \mathbf{x}_i + \mathbf{d}, \dots, \mathbf{x}_N) = \varphi(\mathbf{x}_1 + \mathbf{Q}\mathbf{d}, \mathbf{x}_2, \dots, \mathbf{x}_N). \quad (56)$$

Differentiating this with respect to \mathbf{d} at $\mathbf{d} = 0$ and using $\mathbf{Q} = \mathbf{R}_i^T$ we get,

$$-\frac{\partial\varphi}{\partial\mathbf{x}_i} = -\mathbf{R}_i \frac{\partial\varphi}{\partial\mathbf{x}_1} \quad (57)$$

This is the transformation law for forces on atoms of an objective atomic structure. Equilibrium of one atom ($\partial\varphi/\partial\mathbf{x}_k = 0$) implies equilibrium of all atoms.

For an objective molecular structure the $3MN$ equations of equilibrium reduce to $3M$ equations, by a similar argument. In the molecular case the transformation law for forces is,

$$-\frac{\partial\varphi}{\partial\mathbf{x}_{i,j}} = -\mathbf{R}_{i,j} \frac{\partial\varphi}{\partial\mathbf{x}_{1,j}} \quad (\text{no sum over } j). \quad (58)$$

This is the most general result one can obtain without additional assumptions on the atoms that compose the molecules. Note that these results are obtained without the specializing assumptions of preservation of molecules (6). Also, we have tacitly assumed almost nothing (beyond smoothness) about the atomic potential.

The Hessian matrix also is simplified. Its diagonal elements, obtained by taking two derivatives of (56), are vastly simplified. For the off-diagonal elements we need to displace two different atoms simultaneously and only one of these can be transformed to atom 1. The resulting transformation law is easily worked out from (55) and (57) with two atoms displaced. In the atomic case this is

$$\frac{\partial^2\varphi}{\partial\mathbf{x}_i\partial\mathbf{x}_j} = \mathbf{R}_i \frac{\partial^2\varphi}{\partial\mathbf{x}_1\partial\mathbf{x}_j} \mathbf{R}_i^T \quad (\text{no sum over } i), \quad (59)$$

(the right hand side can be symmetrized with respect to i, j). This formula leads to considerable simplification of conditions of (linearized) stability.

Now it is extremely interesting to examine whether these reduced equilibrium equations can be solved for a particular objective structure. We first consider objective atomic structures.

As one can see from the examples above, objective atomic (and molecular) structures have certain free parameters. For bacteriophage T4 tail sheath, for example, these could be chosen as ρ, λ, γ given in (13). In general, let $(\xi_1, \dots, \xi_p) \in \mathcal{D}$ be free parameters for a certain objective atomic structure. Each atomic position is determined by these parameters, so we can write explicitly, $\mathbf{x}_1(\xi_1, \dots, \xi_p), \dots, \mathbf{x}_N(\xi_1, \dots, \xi_p)$. When we substitute this into the energy (or free energy), we get,

$$\bar{\varphi}(\xi_1, \dots, \xi_p) = \varphi(\mathbf{x}_1(\xi_1, \dots, \xi_p), \dots, \mathbf{x}_N(\xi_1, \dots, \xi_p)). \quad (60)$$

As we vary the parameters, we can imagine that there are some cases in which the bond lengths and angles are not far from those typical of the species. As we depart substantially from these, by any changes of the parameters, we expect to encounter stiffness, i.e., higher energies. This suggests that in suitable cases the function $\bar{\varphi}$ may have one or more energy wells.

Let us assume that this is the case: $\bar{\varphi}(\bar{\xi}_1, \dots, \bar{\xi}_p) \leq \bar{\varphi}(\xi_1, \dots, \xi_p)$ for all ξ_1, \dots, ξ_p near $\bar{\xi}_1, \dots, \bar{\xi}_p$. The condition of equilibrium is then,

$$0 = \frac{\partial \bar{\varphi}(\bar{\xi}_1, \dots, \bar{\xi}_p)}{\partial \xi_j} = \sum_{i=1}^N \frac{\partial \varphi}{\partial \mathbf{x}_i} \cdot \frac{\partial \mathbf{x}_i}{\partial \xi_j} = \frac{\partial \varphi}{\partial \mathbf{x}_1} \cdot \left(\sum_{i=1}^N \mathbf{R}_i^T \frac{\partial \mathbf{x}_i}{\partial \xi_j} \right). \quad (61)$$

Here, we have used the transformation law for forces (57). In view of (57) and (61), we have proved the following: If there is an equilibrium state under variations of the parameters, then each atom of the objective atomic structure is in equilibrium if

$$\left(\sum_{i=1}^N \mathbf{R}_i^T \frac{\partial \mathbf{x}_i}{\partial \xi_j} \right) \Big|_{j=1, \dots, p} \quad \text{contains three linearly independent vectors.} \quad (62)$$

Described compactly, we can say that structural equilibrium implies atomic equilibrium for objective structures satisfying (62). In Section 6.1 we will show that for every objective atomic structure $p = 3$ and the condition (62) is satisfied, with a certain particular choice of structural parameters⁵. This will then show that for every objective atomic structure structural equilibrium implies equilibrium of all the atoms.

In Section 8 we will explain that there is substantial simplification of first principles calculations of the energy of an objective structure. Thus, the process of actually finding a stable equilibrium of an objective structure among structures of the same type (structural equilibrium) is expected to be quite easy.

The analogous condition for objective molecular structures is different but quite interesting. In the molecular case we can think of varying both the atoms in molecule 1 and also the parameters that describe the overall shape of the structure. For the purposes of this paragraph we include in “structural parameters” both of these. In the objective molecular case the condition analogous to (62) is that

$$\left(\sum_{i=1}^N \mathbf{R}_{i,k}^T \frac{\partial \mathbf{x}_{i,k}}{\partial \xi_j} \right) \Big|_{j=1, \dots, p} \quad (\text{no sum over } k) \quad (63)$$

contains 3 linearly independent vectors for each $k = 1, \dots, M$ and these M different sets can be independently chosen (More precisely: these pM vectors span the M -fold Cartesian product $\mathbb{R}^3 \times \dots \times \mathbb{R}^3$). If (63) holds for an objective molecular structure, then structural equilibrium implies equilibrium of every atom.

This ease of satisfying equilibrium is illustrated in a physical way by carbon: the structures C_{60} , a single graphite sheet, a carbon nanotube and diamond are all objective molecular structures of carbon, each case having two carbon atoms per molecule, but these structures all have different lattice parameters.

⁵For T4 tail sheath these turn out not to be ρ, λ, γ .

6 Group structure, classification and formulas for objective structures

6.1 Group structure

Consider an objective atomic structure $\mathcal{S} = \{\mathbf{x}_i : i = 1, \dots, N\}$. We can define the *isometry group* \mathcal{G} of this structure as the set of all (\mathbf{Q}, \mathbf{c}) , $\mathbf{Q} \in \text{O}(3)$, $\mathbf{c} \in \mathbb{R}^3$ that restore the structure, i.e.,

$$\mathbf{Q}\mathbf{x}_n + \mathbf{c} = \mathbf{x}_{\Pi(n)}, \quad n = 1, \dots, N, \quad (64)$$

where Π is a permutation of $\{1, \dots, N\}$. These form a group with the usual operations, $(\mathbf{Q}_1, \mathbf{c}_1) \circ (\mathbf{Q}_2, \mathbf{c}_2) = (\mathbf{Q}_1\mathbf{Q}_2, \mathbf{Q}_1\mathbf{c}_2 + \mathbf{c}_1)$. If we add the physically natural assumption that there is a minimum distance between any two atoms of the structure then these groups are discrete groups of isometries in 3-D. These groups are more numerous than the 230 groups associated with crystal lattices, as can be seen from the fact that cyclic groups and icosahedral groups are included.

By the definition of an objective atomic structure, there are orthogonal transformations $\{\mathbf{R}_i : i = 1, \dots, N\}$ such that $\mathcal{S} = \{\mathbf{x}_i + \mathbf{R}_i(\mathbf{x}_n - \mathbf{x}_1) : n = 1, \dots, N\}$ for each i . We collect the set of N orthogonal transformations and translations that appear in this definition, $\mathcal{H} = \{(\mathbf{R}_i, \mathbf{c}_i), i = 1, \dots, N\}$, where we make the obvious choice $\mathbf{c}_i = \mathbf{x}_i - \mathbf{R}_i\mathbf{x}_1$. The set \mathcal{H} defined in this way is not generally a group, but it is clear by the definitions that $\mathcal{H} \subset \mathcal{G}$. However, we note that if $(\mathbf{Q}, \mathbf{c}) \in \mathcal{G}$ and Π is associated to $(\mathbf{Q}, \mathbf{c}) \in \mathcal{G}$ via (64), then (\mathbf{Q}, \mathbf{c}) does satisfy the definition of an objective atomic structure for $i = \Pi(1)$, where Π is defined in (64). That is, evaluating (64) at $n = 1$ we have $\mathbf{c} = \mathbf{x}_{\Pi(1)} - \mathbf{Q}\mathbf{x}_1$, and substituting this value of \mathbf{c} back in (64) we have

$$\mathbf{x}_{\Pi(1)} + \mathbf{Q}(\mathbf{x}_n - \mathbf{x}_1) = \mathbf{x}_{\Pi(n)} \quad (65)$$

That is, (\mathbf{Q}, \mathbf{c}) satisfies the definition of an objective atomic structure with $i = \Pi(1)$.

At first this seems to say that $\mathcal{H} \subset \mathcal{G}$ and therefore $\mathcal{H} = \mathcal{G}$ but this is not true. The point is that for a given \mathbf{x}_i the definition of an objective atomic structure only requires that we select one $(\mathbf{R}_i, \mathbf{c}_i)$, whereas the isometry group of the structure will include all of them that satisfy the definition of an objective structure. Thus, if we simply enlarge \mathcal{H} to include all such transformations, then we get the nice group structure. This can be stated in an analytical way:

$$\mathcal{G} = \{(\mathbf{Q}, \mathbf{c}) : \text{there is an } i \in \{1, \dots, N\} \text{ and a permutation } \Pi \text{ such that } \mathbf{x}_i + \mathbf{Q}(\mathbf{x}_j - \mathbf{x}_1) = \mathbf{x}_{\Pi(j)}, j = 1, \dots, N, \text{ and } \mathbf{c} = \mathbf{x}_i - \mathbf{Q}\mathbf{x}_1\}. \quad (66)$$

From this characterization a method of construction of all objective atomic structures is possible. That is, given an objective atomic structure $\mathbf{x}_i + \mathbf{R}_i(\mathbf{x}_n - \mathbf{x}_1) = \mathbf{x}_{\Pi(n)}$, we put $n = 1$, note that $\Pi(1) = i$, and solve for \mathbf{x}_i :

$$\mathbf{x}_i = \mathbf{R}_i\mathbf{x}_1 + \mathbf{x}_i - \mathbf{R}_i\mathbf{x}_1 = \mathbf{R}_i\mathbf{x}_1 + \mathbf{c}_i, \quad (67)$$

that is, using (66), $\mathcal{S} = \{\mathbf{Q}\mathbf{x}_1 + \mathbf{c} : (\mathbf{Q}, \mathbf{c}) \in \mathcal{G}\}$, the orbit of the point \mathbf{x}_1 . We get the full set \mathcal{S} by using either \mathcal{G} , in which case some of the points might be given multiple times, or by using the subset \mathcal{H} .

This characterization immediately suggests using the components $\xi_i = \mathbf{e}_i \cdot \mathbf{x}_1$, $i = 1, 2, 3$ as the parameters described at the end of the preceding section. Thus there are three of them, and

with this choice (62) becomes $N\mathbf{e}_i$, showing that for every objective atomic structure structural equilibrium (in this sense) implies atomic equilibrium.

All discrete groups of isometries in 3-D are evidently known. An enumeration of generators is given in volumes A (crystallographic groups) and, of greater interest here, volume E (non-crystallographic groups, called “sub-periodic” there). This is not a useful way to generate these structures for the purpose of studying their properties; formulas like (16) are much more useful. We return to this point in the following section.

The degeneracy associated with the gap between \mathcal{H} and \mathcal{G} can be easily quantified. Define

$$\mathcal{P}_1 = \{\mathbf{Q} \in O(3) : \mathbf{x}_1 + \mathbf{Q}(\mathbf{x}_j - \mathbf{x}_1) = \mathbf{x}_{\Pi(j)} \text{ for some permutation } \Pi\} \quad (68)$$

This is a group (The product $\mathbf{Q}_1\mathbf{Q}_2$ corresponds to the permutation $\Pi_1(\Pi_2(j))$), *the point group of atom 1*. Now let (\mathbf{Q}, \mathbf{c}) and $(\hat{\mathbf{Q}}, \hat{\mathbf{c}})$ belong to \mathcal{G} and suppose these correspond to the same value of i in the definition of an objective atomic structure:

$$\mathbf{x}_i + \hat{\mathbf{Q}}(\mathbf{x}_j - \mathbf{x}_1) = \mathbf{x}_{\hat{\Pi}(j)}, \quad \mathbf{x}_i + \mathbf{Q}(\mathbf{x}_j - \mathbf{x}_1) = \mathbf{x}_{\Pi(j)}. \quad (69)$$

Putting $\ell = \hat{\Pi}(j)$, the first of these yields

$$\hat{\mathbf{Q}}^T(\mathbf{x}_\ell - \mathbf{x}_i) = \mathbf{x}_{\hat{\Pi}^{-1}(\ell)} - \mathbf{x}_1. \quad (70)$$

Hence, using the second of (69) we have,

$$\hat{\mathbf{Q}}^T\mathbf{Q}(\mathbf{x}_j - \mathbf{x}_1) = \hat{\mathbf{Q}}^T(\mathbf{x}_{\Pi(j)} - \mathbf{x}_i) = \mathbf{x}_{\hat{\Pi}^{-1}(\Pi(j))} - \mathbf{x}_1, \quad (71)$$

which implies that $\hat{\mathbf{Q}}^T\mathbf{Q} \in \mathcal{P}_1$. Thus, the orthogonal transformations in an objective atomic structure foliate the orthogonal part of \mathcal{G} into cosets, each conjugate to \mathcal{P}_1 .

Now we turn to the case of objective molecular structures. This case is somewhat different from the atomic case. Consider such a structure $\mathcal{S} = \{\mathbf{x}_{i,k} : i = 1, \dots, N, k = 1, \dots, M\}$. We can again define the isometry group \mathcal{G} of this structure as the set of all (\mathbf{Q}, \mathbf{c}) , $\mathbf{Q} \in O(3)$, $\mathbf{c} \in \mathbb{R}^3$ that restore the structure, i.e.,

$$\mathbf{Q}\mathbf{x}_{n,m} + \mathbf{c} = \mathbf{x}_{\Pi(n,m)}, \quad n = 1, \dots, N, \quad m = 1, \dots, M, \quad (72)$$

where Π is a permutation of $\{1, \dots, N\} \times \{1, \dots, M\}$ that preserves species (cf., (5)). By the definition of an objective molecular structure, there are orthogonal transformations $\{\mathbf{R}_{i,k} : i = 1, \dots, N, k = 1, \dots, M\}$ such that $\mathcal{S} = \{\mathbf{x}_{i,k} + \mathbf{R}_{i,k}(\mathbf{x}_{n,m} - \mathbf{x}_{1,k}) : n = 1, \dots, N, m = 1, \dots, M\}$ for each i, k . We collect the set of MN orthogonal transformations and translations that appear in this definition, $\mathcal{H} = \{(\mathbf{R}_{i,k}, \mathbf{c}_{i,k}), i = 1, \dots, N, k = 1, \dots, M\}$, where we make the choice $\mathbf{c}_{i,k} = \mathbf{x}_{i,k} - \mathbf{R}_{i,k}\mathbf{x}_{1,k}$, and it is again clear by the definitions that $\mathcal{H} \subset \mathcal{G}$. Evaluating (72) at $n = 1$ and $m = \ell$, we have $\mathbf{c} = \mathbf{x}_{\Pi(1,\ell)} - \mathbf{Q}\mathbf{x}_{1,\ell}$, and substituting this value of \mathbf{c} back in (72) we find that

$$\mathbf{x}_{\Pi(1,\ell)} + \mathbf{Q}(\mathbf{x}_{n,m} - \mathbf{x}_{1,\ell}) = \mathbf{x}_{\Pi(n,m)}. \quad (73)$$

However, now one can see that this is similar to, but not the same as the definition of an objective molecular structure. That is, it can happen that $\Pi(1, \ell)$ is not of the form (k, ℓ) for any $\ell = 1, \dots, M$. Hence, to obtain the subset of elements of \mathcal{H} one has to do a careful sorting procedure to find

transformations in \mathcal{G} for which $\Pi(1, \ell)$ is of the form (k, ℓ) for some ℓ . Once \mathcal{H} is found by a sorting procedure, it then follows that

$$\mathbf{x}_{i,k} = \mathbf{R}_{i,k}\mathbf{x}_{1,k} + \mathbf{c}_{i,k}. \quad (74)$$

Then, the choice of one molecule $\mathbf{x}_{1,k}$, $k = 1, \dots, M$, together with the knowledge of \mathcal{H} gives the structure. Unfortunately, this argument is circular, and so a further sorting of the groups would be necessary. That is, the isometry group of the structure depends on the symmetry of the molecule, so the group cannot be chosen independently of the molecule. Equivalently, if we want to give the isometry group, then there are restrictions on the choices of $\mathbf{x}_{1,k}$ in (74).

That being the situation, we then have to understand why the examples of multilattices, T4 tail sheath, and objective molecular structures based on C_{60} do allow a simple mapping of an arbitrary set of atoms to form the structure. The point is that for the underlying objective atomic structures in all these cases \mathcal{H} as defined above is already a group. To explain further, consider an objective molecular structure that preserves molecules for which $\mathbf{R}_{i,\ell}$ is independent of ℓ . Suppose that $\bar{\mathbf{x}}_i + \mathbf{R}_i(\bar{\mathbf{x}}_k - \bar{\mathbf{x}}_1) = \bar{\mathbf{x}}_{\Pi^{(i)}(k)}$, is the underlying objective atomic structure, related to the given structure by averaging as described in Section 4. Finally, suppose that for this objective atomic structure $\{\bar{\mathbf{x}}_i, i = 1, \dots, N\}$ we have $\mathcal{H} = \mathcal{G}$. We then assign arbitrary positions \mathbf{p}_k , $k = 1, \dots, M$, and define the $\mathbf{x}_{i,k} = \bar{\mathbf{x}}_i + \mathbf{R}_i\mathbf{p}_k$. Then

$$\begin{aligned} \mathbf{x}_{i,k} + \mathbf{R}_i(\mathbf{x}_{n,m} - \mathbf{x}_{1,k}) &= \bar{\mathbf{x}}_i + \mathbf{R}_i\mathbf{p}_k + \mathbf{R}_i(\bar{\mathbf{x}}_n + \mathbf{R}_n\mathbf{p}_m - \bar{\mathbf{x}}_1 - \mathbf{p}_k) \\ &= \bar{\mathbf{x}}_i + \mathbf{R}_i(\bar{\mathbf{x}}_n + \bar{\mathbf{x}}_1) + \mathbf{R}_i\mathbf{R}_n\mathbf{p}_m \\ &= \bar{\mathbf{x}}_{\Pi^{(i)}(n)} + \mathbf{R}_i\mathbf{R}_n\mathbf{p}_m. \end{aligned} \quad (75)$$

So, it is sufficient to show that $\mathbf{R}_{\Pi^{(i)}(n)} = \mathbf{R}_i\mathbf{R}_n$ in this case. But, by the definition of an objective atomic structure applied twice,

$$\begin{aligned} \bar{\mathbf{x}}_{\Pi^{(i)}(n)} + \mathbf{R}_i\mathbf{R}_n(\bar{\mathbf{x}}_k - \bar{\mathbf{x}}_1) &= \bar{\mathbf{x}}_i + \mathbf{R}_i(\bar{\mathbf{x}}_n - \bar{\mathbf{x}}_1) + \mathbf{R}_i\mathbf{R}_n(\bar{\mathbf{x}}_k - \bar{\mathbf{x}}_1) \\ &= \bar{\mathbf{x}}_i + \mathbf{R}_i(\bar{\mathbf{x}}_{\Pi^{(i)}(n)} - \mathbf{R}_n(\bar{\mathbf{x}}_k - \bar{\mathbf{x}}_1) - \bar{\mathbf{x}}_1) + \mathbf{R}_i\mathbf{R}_n(\bar{\mathbf{x}}_k - \bar{\mathbf{x}}_1) \\ &= \bar{\mathbf{x}}_i + \mathbf{R}_i(\bar{\mathbf{x}}_{\Pi^{(i)}(n)} - \bar{\mathbf{x}}_1) \\ &= \bar{\mathbf{x}}_{\Pi^{(i)}(\Pi^{(n)}(k))}. \end{aligned} \quad (76)$$

When $\mathcal{H} = \mathcal{G}$ there is one and only one orthogonal transformation associated to $\bar{\mathbf{x}}_{\Pi^{(i)}(n)}$. Thus, $\mathbf{R}_{\Pi^{(i)}(n)} = \mathbf{R}_i\mathbf{R}_n$. In summary, if $\mathcal{H} = \mathcal{G}$ for an objective atomic structure, then the associated transformations generate an objective molecular structure that preserves molecules via the formula $\mathbf{x}_{i,k} = \bar{\mathbf{x}}_i + \mathbf{R}_i\mathbf{p}_k$.

Now we return to (63), the condition (structural equilibrium \implies atomic equilibrium). In general, this is evidently not true in the molecular case because, as noted above in the context of (74), there are symmetry restrictions on the choice of molecule. It can be seen, however, from (74) and (63) that the condition (structural equilibrium \implies atomic equilibrium) holds for every objective molecular structure in which the underlying atomic structure satisfies $\mathcal{H} = \mathcal{G}$. These are necessarily objective molecular structures that preserve molecules.

6.2 Formulas for objective structures

The results of the preceding section are useful for identifying structural parameters, but do not seem to be useful for analysis of the properties of objective structures. For that, it would be extremely

useful to have formulas that generate objective atomic and molecular structures like the ones given in the examples above.

To explain what we mean, we note that regardless of which of the 230 space groups applies to it, we can generate any multilattice by assigning any vectors $\{\mathbf{p}_1, \dots, \mathbf{p}_M\}$ and a basis $\{\mathbf{e}_1, \mathbf{e}_2, \mathbf{e}_3\}$ and then writing the simple formula $\{\nu^i \mathbf{e}_i + \mathbf{p}_k : (\nu^i) \in \mathbb{Z}^3, k \in \{1, \dots, M\}\}$. This assignment immediately tells us how to generate the objective molecular structure that preserves species, how to find a unit cell and then how to set periodic boundary conditions for a first principles calculation, or to do other property calculations as described below in Sections 8 and 9. We would like formulas like this that generate objective structures in the noncrystallographic case.

We first consider objective atomic structures. The case of N finite is simple. That is, consider an objective atomic structure $\mathcal{S} = \{\mathbf{x}_i + \mathbf{R}_i(\mathbf{x}_j - \mathbf{x}_1) = \mathbf{x}_{\Pi(i)(j)}\}$ with N finite. Let

$$\bar{\mathbf{x}} = \frac{1}{N} \sum_{j=1}^N \mathbf{x}_j \quad (77)$$

and average the equation $\mathbf{x}_i + \mathbf{R}_i(\mathbf{x}_j - \mathbf{x}_1) = \mathbf{x}_{\Pi(i)(j)}$ over j . We get

$$\mathbf{x}_i = \bar{\mathbf{x}} + \mathbf{R}_i(\mathbf{x}_1 - \bar{\mathbf{x}}). \quad (78)$$

According to the results of the preceding section, we can without loss of generality assume that the \mathbf{R}_i belong to a subgroup \mathcal{G} of $O(3)$. Then the argument of Section 3.3 (which does not use the finiteness of the group nor the fact that the group is icosahedral) shows that (78) generates an objective atomic structure. This method generates objective structures (like C_{60}) associated with the Platonic solids. Thus, for N finite, since there are only a few finite orthogonal groups, this method is effective.

Now we discuss $N = \infty$. Consider an objective atomic structure $\mathcal{S} = \{\mathbf{x}_i + \mathbf{R}_i(\mathbf{x}_j - \mathbf{x}_1) = \mathbf{x}_{\Pi(i)(j)}\}$, where now we emphasize the dependence of Π on i . The set of permutations generates a finite or infinite matrix

$$\begin{array}{c|cccc} & j = 1 & 2 & \dots & N \\ \hline i = 1 & \Pi^{(1)}(1) & \Pi^{(1)}(2) & \dots & \Pi^{(1)}(N) \\ 2 & \Pi^{(2)}(1) & \Pi^{(2)}(2) & \dots & \Pi^{(2)}(N) \\ 3 & \Pi^{(3)}(1) & \Pi^{(3)}(2) & \dots & \Pi^{(3)}(N) \\ \vdots & \vdots & \vdots & & \vdots \\ N & \Pi^{(N)}(1) & \Pi^{(N)}(2) & \dots & \Pi^{(N)}(N) \end{array} \quad (79)$$

Each row is a permutation of $\{1, \dots, N\}$ and the first row can be taken to be $1, 2, \dots, N$ (Without loss of generality, we choose $\mathbf{R}_1 = \mathbf{I}$). The first column is also $1, 2, \dots, N$. However, the columns need not in general be permutations of $1, \dots, N$. We focus on the second row. We consider successive applications of $\Pi^{(2)}$ to 1, i.e.,

$$[\Pi^{(2)}(1)]^P := \underbrace{\Pi^{(2)}(\Pi^{(2)}(\dots \Pi^{(2)}(1) \dots))}_{P \text{ times}} \quad (80)$$

Suppose that $[\Pi^{(2)}(1)]^L = 1$ for $L \leq N$ and that L is the smallest integer for which this is true (We allow $L = \infty$). Now define a new permutation $\hat{\Pi}$ by

$$\hat{\Pi}(1) = 1,$$

$$\begin{aligned}
\hat{\Pi}(2) &= \Pi^{(2)}(1) = 2, \\
\hat{\Pi}(3) &= \Pi^{(2)}(2) = \Pi^{(2)}(\Pi^{(2)}(1)), \\
&\vdots \\
\hat{\Pi}(L) &= [\Pi^{(2)}(1)]^{L-1}.
\end{aligned} \tag{81}$$

We claim that $\hat{\Pi}(1), \dots, \hat{\Pi}(L)$ are distinct numbers. If not – say we were to have $\hat{\Pi}(K) = \hat{\Pi}(M)$ for $K < M \leq L$ – then by applying successively the inverse of $\Pi^{(2)}$ to the equation $\hat{\Pi}(K) = \hat{\Pi}(M)$, we would get $[\Pi^{(2)}]^K = 1$ for $K < L$ which contradicts the assumption that L is the smallest such number.

Extend the definition of $\hat{\Pi}$ to the remaining numbers $L+1, \dots, N$ in any way as a permutation. Now define

$$\hat{\mathbf{x}}_j = \mathbf{x}_{\hat{\Pi}(j)} \tag{82}$$

and note that $\hat{\mathbf{x}}_1 = \mathbf{x}_1$ and $\hat{\mathbf{x}}_2 = \mathbf{x}_2$. Effectively we have renumbered the atoms of the given objective structure in a convenient way from the perspective of the second row of the matrix (79). That is, if we replace j by $\hat{\Pi}(\ell)$ in the formula $\mathbf{x}_2 + \mathbf{R}_2(\mathbf{x}_j - \mathbf{x}_1) = \mathbf{x}_{\Pi^{(2)}(j)}$ and use (82), we get

$$\hat{\mathbf{x}}_2 + \mathbf{R}_2(\hat{\mathbf{x}}_\ell - \mathbf{x}_1) = \hat{\mathbf{x}}_{\ell+1}, \quad \ell = 1, \dots, L-1. \tag{83}$$

But now we can develop a simple formula for $\hat{\mathbf{x}}_\ell$ by iterating (83):

$$\begin{aligned}
\hat{\mathbf{x}}_2 &= \hat{\mathbf{x}}_2 + \mathbf{R}_2(\hat{\mathbf{x}}_1 - \mathbf{x}_1) = \mathbf{I}(\hat{\mathbf{x}}_2 - \hat{\mathbf{x}}_1) + \hat{\mathbf{x}}_1, \\
\hat{\mathbf{x}}_3 &= \hat{\mathbf{x}}_2 + \mathbf{R}_2(\hat{\mathbf{x}}_2 - \mathbf{x}_1) = (\mathbf{R}_2 + \mathbf{I})(\hat{\mathbf{x}}_2 - \hat{\mathbf{x}}_1) + \hat{\mathbf{x}}_1, \\
&\vdots \\
\hat{\mathbf{x}}_L &= \hat{\mathbf{x}}_2 + \mathbf{R}_2(\hat{\mathbf{x}}_{L-1} - \mathbf{x}_1) = (\mathbf{R}_2^{L-2} + \mathbf{R}_2^{L-3} + \dots + \mathbf{R}_2 + \mathbf{I})(\hat{\mathbf{x}}_2 - \hat{\mathbf{x}}_1) + \hat{\mathbf{x}}_1.
\end{aligned} \tag{84}$$

But the latter, i.e.,

$$\hat{\mathbf{x}}_P = (\mathbf{R}_2^{P-2} + \mathbf{R}_2^{P-3} + \dots + \mathbf{R}_2 + \mathbf{I})(\hat{\mathbf{x}}_2 - \hat{\mathbf{x}}_1) + \hat{\mathbf{x}}_1, \tag{85}$$

is the equation for a helix in the case⁶ $\mathbf{R}_2 \in \text{SO}(3)$, [16, Section 5]. We can immediately make a classification of structures produced by (85) and draw several conclusions:

1. Infinite case. This is the generic case in which the formula (85) produces an infinite number of distinct atomic positions. There are various ways this can happen, enumerated below (Recall that by assumption $\hat{\mathbf{x}}_2 \neq \hat{\mathbf{x}}_1$).
 - (a) $\mathbf{R}_2(\hat{\mathbf{x}}_2 - \hat{\mathbf{x}}_1) = (\hat{\mathbf{x}}_2 - \hat{\mathbf{x}}_1)$. This produces an infinite line of atoms.
 - (b) $\det \mathbf{R}_2 = 1, \mathbf{R}_2 \neq \mathbf{I}$ and $(\hat{\mathbf{x}}_2 - \hat{\mathbf{x}}_1)$ not parallel or perpendicular to the axis of \mathbf{R}_2 . These are nondegenerate helices of atoms.
 - (c) $\det \mathbf{R}_2 = 1, \mathbf{R}_2 \neq \mathbf{I}$ and $(\hat{\mathbf{x}}_2 - \hat{\mathbf{x}}_1)$ perpendicular to the axis of \mathbf{R}_2 and there is no integer $K > 0$ such that $\mathbf{R}_2^K = \mathbf{I}$. This case is not interesting physically, as it corresponds to a circle of infinitely closely spaced points.

⁶Some interesting nonhelical configurations produced by this equation when $\mathbf{R}_2 \in \text{O}(3) \setminus \text{SO}(3)$ are seen in the enumeration and in the following section.

- (d) $\det \mathbf{R}_2 = -1$. In this case, letting $|\mathbf{e}| = 1$ be an axis of $-\mathbf{R}_2$, we have that $\mathbf{x}_2 - \mathbf{x}_1$ is not parallel to \mathbf{e} and that either $\mathbf{R}_2 = \mathbf{I} - 2\mathbf{e} \otimes \mathbf{e}$ (two parallel lines of points) or that $\mathbf{R}_2^K = \mathbf{I}$ has no integer solution $K > 0$. The latter case is not interesting physically, as it produces two rings of infinitely closely spaced points.

2. Finite cases.

- (a) $\det \mathbf{R}_2 = 1, \mathbf{R}_2 \neq \mathbf{I}$, $\mathbf{x}_2 - \mathbf{x}_1$ is perpendicular to the axis of \mathbf{R}_2 and there is an integer $K > 0$ such that $\mathbf{R}_2^K = \mathbf{I}$ (a ring of atoms).
- (b) $\det \mathbf{R}_2 = -1$ and $\mathbf{x}_2 - \mathbf{x}_1$ is parallel to the axis of $-\mathbf{R}_2$ (two atoms).
- (c) $\det \mathbf{R}_2 = -1$ and $\mathbf{x}_2 - \mathbf{x}_1$ is not parallel to the axis of $-\mathbf{R}_2$ and $\mathbf{R}_2^K = \mathbf{I}$ for some integer $K > 2$ (two rings of atoms).

The construction given above could exhaust all of row 2 of the permutation matrix (79). In fact, we are then done, as it can be shown that all of the structures produced so far are objective atomic structures. More than that, with a suitable choice of the molecular orientation, they are all objective molecular structures. We do not explain the reasons for that here, as these structures will emerge as special cases of the more general ones described below. Alternatively, the construction leading to (85) could exhaust a finite or infinite proper subset of indices in row 2. (Even if it exhausts an infinite subset, this could simply be a subsequence of row 2 so there could be an infinite set of elements left over.) In such cases there is some point \mathbf{x}_r in the assumed objective atomic structure that is not produced by the formula (85).

Let us suppose without loss of generality that this point is \mathbf{x}_3 . We can now describe a new permutation $\tilde{\Pi}$ in the same way as above but beginning with \mathbf{x}_3 . That is, we define

$$\begin{aligned}\tilde{\Pi}(1) &= 3, \\ \tilde{\Pi}(2) &= \Pi^{(2)}(3), \\ \tilde{\Pi}(3) &= \Pi^{(2)}(\Pi^{(2)}(3)), \\ &\vdots \\ \tilde{\Pi}(L) &= [\Pi^{(2)}(3)]^{L-1}.\end{aligned}\tag{86}$$

This does not lead to a formula that is strictly analogous to (85) because in the previous case we made use of the fact that \mathbf{x}_2 appeared as the first term on the right of (84), that is, we based the derivation on using row 2 and \mathbf{x}_2 . However, now we get points $\tilde{\mathbf{x}}_1 = \mathbf{x}_3, \tilde{\mathbf{x}}_2, \tilde{\mathbf{x}}_3, \dots$ given by the different formula,

$$\tilde{\mathbf{x}}_P = \hat{\mathbf{x}}_P + \mathbf{R}_2^{P-1}(\mathbf{x}_3 - \mathbf{x}_1),\tag{87}$$

where $\hat{\mathbf{x}}_P$ is given by (85). Now we can see an interesting pattern develop, when we compare this formula to that formula for T4 tail sheath. In particular we can see if, instead of having begun with \mathbf{x}_3 , we had begun with a “different helix”, then we would get an interesting generalization of (87). We can get a possibly different helix by looking to row 3 of the permutation matrix and using $\mathbf{x}_3 - \mathbf{x}_1$ as the generator. This gives immediately a formula analogous to (85) but with $\mathbf{x}_2, \mathbf{R}_2$ replaced by $\mathbf{x}_3, \mathbf{R}_3$. Using this new helix in place of \mathbf{x}_3 in (87), we get the formula

$$\mathbf{x}_{p,q} = \sum_{i=0}^{p-1} \mathbf{R}_2^i(\mathbf{x}_2 - \mathbf{x}_1) + \mathbf{R}_2^p \sum_{j=0}^{q-1} \mathbf{R}_3^j(\mathbf{x}_3 - \mathbf{x}_1) + \mathbf{x}_1.\tag{88}$$

This formula is essentially the same as (16) which generates T4 tail sheath.

The formula (88) has been derived for $p > 1, q > 1$. One can revisit the derivation for negative values of the upper limit of the sum and one finds that the same formula still emerges if the sum is interpreted properly. This interpretation is

$$\sum_{i=0}^r a_i = \begin{cases} 0, & r = -1, \\ -a_{-1} - a_{-2} - \cdots - a_{r+1}, & r < -1. \end{cases} \quad (89)$$

All sums in this paper should be interpreted in this way.

We now do a calculation that suggests that the formula (88) might be more general than it appears. First we recognize that we have only exploited necessary conditions: the formula (88) does not in general give an objective structure. To see that, consider $\mathbf{x}_{1,1} = \mathbf{x}_2 + \mathbf{R}_2(\mathbf{x}_3 - \mathbf{x}_1)$, and note that, by the basic definition of an objective atomic structure, this point must be expressible in the form,

$$\mathbf{x}_{1,1} = \mathbf{x}_2 + \mathbf{R}_2(\mathbf{x}_3 - \mathbf{x}_1) = \mathbf{x}_3 + \mathbf{R}_3(\mathbf{x}_{p,q} - \mathbf{x}_1) \quad (90)$$

for some p, q . Whatever choice we make, it is clear that we get further restrictions on $\mathbf{x}_2 - \mathbf{x}_1, \mathbf{x}_3 - \mathbf{x}_1, \mathbf{R}_2, \mathbf{R}_3$ that the structure be objective. The most obvious choice is $(p, q) = (1, 0)$, which gives the restriction,

$$\mathbf{x}_2 - \mathbf{x}_1 + \mathbf{R}_2(\mathbf{x}_3 - \mathbf{x}_1) = \mathbf{x}_3 - \mathbf{x}_1 + \mathbf{R}_3(\mathbf{x}_2 - \mathbf{x}_1), \quad (91)$$

or, in compact notation,

$$\hat{\mathbf{t}} + \hat{\mathbf{R}}\mathbf{t} = \mathbf{t} + \mathbf{R}\hat{\mathbf{t}}, \quad (92)$$

where $\hat{\mathbf{t}} = \mathbf{x}_2 - \mathbf{x}_1$, $\mathbf{t} = \mathbf{x}_3 - \mathbf{x}_1$, $\hat{\mathbf{R}} = \mathbf{R}_2, \mathbf{R} = \mathbf{R}_3$. This can immediately be recognized as the first of (15). Now we look at \mathbf{x}_2 from the perspective of \mathbf{x}_3 , that is, following the basic definition of an objective atomic structure, we seek (p, q) such that

$$\mathbf{x}_{1,0} = \mathbf{x}_2 = \mathbf{x}_3 + \mathbf{R}_3(\mathbf{x}_{p,q} - \mathbf{x}_1). \quad (93)$$

Now the obvious choice is $(p, q) = (1, -1)$, from which, after a little calculation that makes use of (91), we get the restriction

$$\hat{\mathbf{R}}\mathbf{t} = \mathbf{R}\hat{\mathbf{R}}^T\mathbf{t}. \quad (94)$$

Finally, we look at $\mathbf{x}_{2,1}$ from the perspective of \mathbf{x}_3 , that is, we seek $\mathbf{x}_{p,q}$ satisfying

$$\mathbf{x}_{2,1} = \mathbf{x}_3 + \mathbf{R}_3(\mathbf{x}_{p,q} - \mathbf{x}_1). \quad (95)$$

Again, the choice $(p, q) = (2, 0)$ seems compelling, from which we get that

$$\hat{\mathbf{R}}\hat{\mathbf{t}} = \mathbf{R}\hat{\mathbf{R}}\hat{\mathbf{t}}. \quad (96)$$

Combining (94) and (96) under the hypothesis that \mathbf{t} is not parallel to $\mathbf{R}\hat{\mathbf{t}}$ we get the second of (15):

$$\hat{\mathbf{R}}\mathbf{R} = \mathbf{R}\hat{\mathbf{R}}. \quad (97)$$

Of course, we made some arbitrary choices along the way to these restrictions. Different choices might have given new objective structures. However, if we satisfy (91) and (97) we are assured that the formula (88) gives an objective atomic structure, the proof being exactly the same as for T4

tail sheath (recall that we only used (15) in that proof, not the particular parameters of T4 tail sheath). Not only that, but with a suitable definition of the orientation of the molecule, given by the second of (16), objective molecular structures are obtained. In the following section we will see that this formula delivers some rather unexpected structures, that are quite different from T4 tail sheath.

In summary we have obtained the formula $\{\mathbf{x}_{i,j} + \mathbf{R}_{i,j}\mathbf{p}_k\}$

$$\begin{aligned}\mathbf{x}_{p,q} &= \sum_{i=0}^{p-1} \hat{\mathbf{R}}^i \hat{\mathbf{t}} + \hat{\mathbf{R}}^p \sum_{j=0}^{q-1} \mathbf{R}^j \mathbf{t} + \mathbf{x}_1, \\ \mathbf{R}_{p,q} &= \hat{\mathbf{R}}^p \mathbf{R}^q.\end{aligned}\tag{98}$$

together with the restrictions

$$\hat{\mathbf{t}} + \hat{\mathbf{R}}\mathbf{t} = \mathbf{t} + \mathbf{R}\hat{\mathbf{t}}, \quad \hat{\mathbf{R}}\mathbf{R} = \mathbf{R}\hat{\mathbf{R}}\tag{99}$$

with $\hat{\mathbf{t}} \neq 0, \mathbf{t} \neq 0, \hat{\mathbf{R}}, \mathbf{R} \in O(3)$. As explained in the preceding section, equations (98), (99) always deliver an objective molecular structure. To complete the analysis, we solve the conditions (99). This is not at all difficult using standard facts about rotation matrices but it is tedious. All solutions of (99) are given in the Appendix.

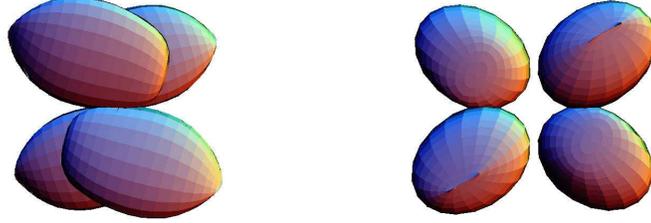


Figure 4: A four molecule objective molecular structure. Left: front view. Right: side view.

In the argument above, we reconciled the possibility of two different (generalized) helices through a point. By extending the reasoning, we can add a third helix through the same point. The pattern of argument is the same as above so we do not give the details. The result is the more general formula for objective molecular structures $\{\mathbf{x}_{p,q,r} + \mathbf{R}_{p,q,r}\mathbf{p}_k\}$:

$$\begin{aligned}\mathbf{x}_{p,q,r} &= \sum_{i=0}^{p-1} \hat{\mathbf{R}}^i \hat{\mathbf{t}} + \hat{\mathbf{R}}^p \sum_{j=0}^{q-1} \bar{\mathbf{R}}^j \bar{\mathbf{t}} + \hat{\mathbf{R}}^p \bar{\mathbf{R}}^q \sum_{k=0}^{r-1} \mathbf{R}^k \mathbf{t} + \mathbf{x}_1, \\ \mathbf{R}_{p,q,r} &= \hat{\mathbf{R}}^p \bar{\mathbf{R}}^q \mathbf{R}^r.\end{aligned}\tag{100}$$

together with the restrictions

$$\begin{aligned}\hat{\mathbf{t}} + \hat{\mathbf{R}}\bar{\mathbf{t}} &= \bar{\mathbf{t}} + \bar{\mathbf{R}}\hat{\mathbf{t}}, & \hat{\mathbf{R}}\bar{\mathbf{R}} &= \bar{\mathbf{R}}\hat{\mathbf{R}}, \\ \hat{\mathbf{t}} + \hat{\mathbf{R}}\mathbf{t} &= \mathbf{t} + \mathbf{R}\hat{\mathbf{t}}, & \hat{\mathbf{R}}\mathbf{R} &= \mathbf{R}\hat{\mathbf{R}}, \\ \bar{\mathbf{t}} + \bar{\mathbf{R}}\mathbf{t} &= \mathbf{t} + \mathbf{R}\bar{\mathbf{t}}, & \bar{\mathbf{R}}\mathbf{R} &= \mathbf{R}\bar{\mathbf{R}},\end{aligned}\tag{101}$$

with $\hat{\mathbf{t}} \neq 0, \bar{\mathbf{t}} \neq 0, \mathbf{t} \neq 0, \hat{\mathbf{R}}, \mathbf{R}, \bar{\mathbf{R}} \in O(3)$. The proof that (100)-(101) always delivers an objective molecular structure is a long version of the argument presented in Section 3.2 (and is available from the author). Of course, the formulas (98), (99) are limiting cases of (100), (101), obtained by putting $\mathbf{R} = \mathbf{I}$ and passing to the limit $\mathbf{t} \rightarrow 0$. Based on exploratory calculations, there is a basis for believing that (100)₁, (101) deliver all infinite objective atomic structures, and we conjecture that that is true. In any case, in the next section we show that the formulas (100), (101) generate an amazing variety of objective molecular structures.

7 Objective molecular structures given by (100), (101)

In Section 3 we gave some examples of objective structures that either motivated this study (as in T4 tail sheath) or were obvious after some thought. The methods of the preceding section gave formulas for generating objective structures. It is clear from the forms of these formulas how to recover the examples of Section 3, but it is more interesting to generate new structures with these formulas, at least structures that were not anticipated by this author. We collect some of these examples in this section. All of them are objective molecular structures. Some of the most interesting of these arise from the use of orthogonal transformations not in $SO(3)$.



Figure 5: An eight molecule objective molecular structure. Left: front view. Right: side view.

The simple helix (as in one of the helices of T4 tail sheath) the ring of molecules (e.g., as pictured on the cover of the classic, *Introduction to Protein Structure*, by Branden and Tooze [5]), structures based on the Platonic solids or simple 1, 2 or 3 dimensional periodic structures are not pictured here, as they are regarded as obviously objective.

We illustrate the structures using a particular molecule. The shape of this molecule is irrelevant, as is the touching or nontouching of molecules, because all these structures are objective molecular structures regardless of the choice of the molecule; it is the *relationship* between molecules that is being illustrated. The molecule shown in the pictures is chosen to be simple and rather unsymmetrical, so these relationships can be seen (Note that it has a blunt and a pointed end). Still, it is sometimes difficult (but important) to distinguish two configurations that are related by 180° rotation vs. reflection. To make this clear, we give in each case the orthogonal transformations used to construct each figure and the corresponding values of $\hat{\mathbf{t}}, \bar{\mathbf{t}}, \mathbf{t}$. It should also be mentioned that what is called “molecule” here could represent a collection of several actual molecules in a real structure.

Certain systems of four or eight molecules are objective molecular structures. Figure 4 shows two views such a system of four molecules. This is produced by formula (100) with $\bar{\mathbf{R}} = \mathbf{R} = -\mathbf{I} +$

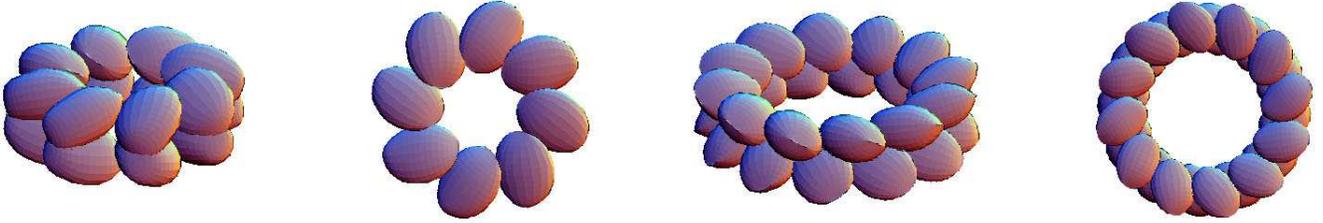


Figure 6: Double rings. Left pair: unstaggrered with 8 molecules per ring. Right pair: staggrered with 12 molecules per ring.

$2\mathbf{e} \otimes \mathbf{e}$, $\hat{\mathbf{R}} = -\mathbf{I} + 2\hat{\mathbf{e}} \otimes \hat{\mathbf{e}}$, $\mathbf{t} = \mathbf{t}_1$, $\bar{\mathbf{t}} = \mathbf{t}_1$, $\hat{\mathbf{t}} = \tau\mathbf{e} + \hat{\mathbf{t}}_1$, $|\hat{\mathbf{e}}| = |\mathbf{e}| = 1$, $\hat{\mathbf{e}} \cdot \mathbf{e} = 0$, $\mathbf{t}_1 \cdot \mathbf{e} = 0$, $\hat{\mathbf{t}}_1 = \mathbf{t}_1 - (\hat{\mathbf{e}} \cdot \mathbf{t}_1)\hat{\mathbf{e}}$. Many choices of combinations of two-fold orthogonal transformations in formula (100) produce eight molecule structures, with typically more reflection symmetry than the four molecule systems. Figure 5 was produced using formula (100) with the choices $\mathbf{R} = -\mathbf{I} + 2\mathbf{e} \otimes \mathbf{e}$, $\bar{\mathbf{R}} = -\mathbf{I} + 2\bar{\mathbf{e}} \otimes \bar{\mathbf{e}}$, $\hat{\mathbf{R}} = \mathbf{I} - 2\hat{\mathbf{e}} \otimes \hat{\mathbf{e}}$, with \mathbf{e} , $\bar{\mathbf{e}}$, $\hat{\mathbf{e}}$ orthonormal, and with $\mathbf{t} = \tau_2\bar{\mathbf{e}} + \tau_3\hat{\mathbf{e}}$, $\bar{\mathbf{t}} = \sigma_1\bar{\mathbf{e}} + \sigma_3\hat{\mathbf{e}}$, $\hat{\mathbf{t}} = \sigma_3\hat{\mathbf{e}}$. Evidently these structures can also be produced by certain finite orthorhombic groups, but it is interesting that they also emerge from (100), (101).

A common type of structure delivered by either (98) or (100) is the pair of rings. There are both staggrered and unstaggrered rings, Figure 6. They can have any number of molecules per ring, but the two rings have the same number. The staggrering is not arbitrary. Of course, one could not have an objective structure consisting of three rings because then the middle ring would be distinguished. The pairs of rings shown were produced by (98) evaluated at Case 2c of the Appendix. A natural example of an unstaggrered double ring (or a structure close to that) is the GroEL protein, an important chaperone protein that assists protein folding [4], [5, p. 101].

Certain kinds of bilayers are also objective structures, Figure 7. These are produced from formula (100) using either the choice $\hat{\mathbf{R}} = \bar{\mathbf{R}} = \mathbf{R} = \mathbf{I} - 2\mathbf{e} \otimes \mathbf{e}$, $|\mathbf{e}| = 1$, $\mathbf{e} \cdot \mathbf{t} = \mathbf{e} \cdot \bar{\mathbf{t}} = \mathbf{e} \cdot \hat{\mathbf{t}}$ or the choice $\hat{\mathbf{R}} = \bar{\mathbf{R}} = \mathbf{I} - 2\mathbf{e} \otimes \mathbf{e}$, $|\mathbf{e}| = 1$, $\mathbf{R} = \mathbf{I}$, $\mathbf{e} \cdot \mathbf{t} = 0$, $\mathbf{e} \cdot \bar{\mathbf{t}} = \mathbf{e} \cdot \hat{\mathbf{t}}$. A bilayer with staggrered molecules (not pictured) is given by the formula (98) evaluated either at Case 2a or Case 4d of the Appendix. It should be noted that the values of $\hat{\mathbf{t}}$, $\bar{\mathbf{t}}$, \mathbf{t} chosen should be rationally related, i.e., their components in the same fixed basis should be rational numbers. If not, then the formulas typically give an infinite bilayer of infinitely densely packed molecules.

Certain staggrered and unstaggrered molecular fibers with four molecules in the ‘‘cross-section’’ are objective molecular structures, via the formula (100). A staggrered case follows from the choice $\hat{\mathbf{R}} = \bar{\mathbf{R}} = \mathbf{I} - 2\hat{\mathbf{e}} \otimes \hat{\mathbf{e}}$, $\mathbf{R} = -\mathbf{I} + 2\mathbf{e} \otimes \mathbf{e}$, $\bar{\mathbf{t}} = \bar{\tau}\mathbf{e} + (\hat{\mathbf{e}} \cdot \mathbf{t})\hat{\mathbf{e}}$, $\hat{\mathbf{t}} = \hat{\tau}\mathbf{e} + (\hat{\mathbf{e}} \cdot \mathbf{t})\hat{\mathbf{e}}$, $|\hat{\mathbf{e}}| = |\mathbf{e}| = 1$, $\hat{\mathbf{e}} \cdot \mathbf{e} = 0$ (\mathbf{t} arbitrary), while an unstaggrered case is given by $\hat{\mathbf{R}} = \bar{\mathbf{R}} = \mathbf{I} - 2\hat{\mathbf{e}} \otimes \hat{\mathbf{e}}$, $\mathbf{R} = \mathbf{I} - 2\mathbf{e} \otimes \mathbf{e}$, $\mathbf{t} = \tau_1\mathbf{e} + \tau_3(\mathbf{e} \times \hat{\mathbf{e}})$, $\bar{\mathbf{t}} = \tau_2\hat{\mathbf{e}} + \bar{\tau}_3(\mathbf{e} \times \hat{\mathbf{e}})$, $\hat{\mathbf{t}} = \tau_2\hat{\mathbf{e}} + \hat{\tau}_3(\mathbf{e} \times \hat{\mathbf{e}})$, $|\hat{\mathbf{e}}| = |\mathbf{e}| = 1$, $\hat{\mathbf{e}} \cdot \mathbf{e} = 0$. There is also different kind of staggrered case (not pictured) having again a four molecule cross-section, in which the opposing pair of molecules in the cross-section are at the same height; this is produced from formula (98) evaluated at Case 2b of the Appendix. As for the bilayers, here it is also important to choose rationally related $\hat{\mathbf{t}}$, $\bar{\mathbf{t}}$, \mathbf{t} ; otherwise the formula produces an infinite fiber with infinitely densely packed molecules. It can be seen that these structures are quite different from helical structures as represented by T4 tail sheath. In addition to being objective molecular structures, these are also 1-D periodic structures; we only found fibrous structures like this with four molecule unit cells.

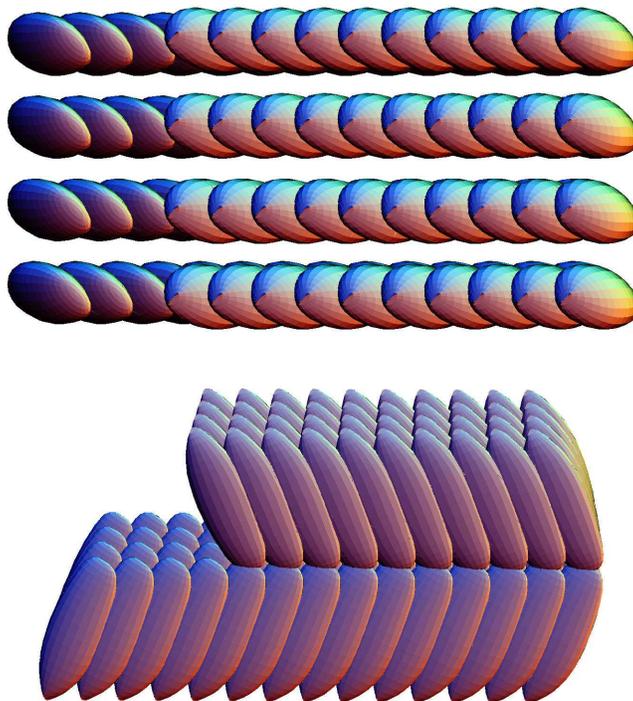


Figure 7: An objective molecular structure consisting of a bilayer of molecules. Top: view perpendicular to layer. Bottom, side view. On the left of both pictures, a few rows of the top layer have been removed to reveal the relationship between the layers.

In hindsight, some of the structures illustrated here have examples in Nature. In other cases it is not so clear, and it could be interesting to revisit various structures, particularly protein structures, to see if the special relationships given here are indeed satisfied.

8 Bending and torsional response of nanoscale beams

In this section we present a rather different application of objective structures: the calculation of bending and torsional response of nanoscale beams. The formulas given here, together with an efficient implementation of density functional theory, allow one to compute such a response for beams of elemental materials, say, as a function of atomic number and cross-sectional dimensions. The simplifications afforded by the observation of Example 3.4, that configurations produced by bending and torsion of a beam can be described as objective structures, make these kinds of computations possible.

The rapid expansion of first principles calculations for crystalline materials in recent years is owing to two factors: (1) the development and efficient implementation of density functional theory (profound) and (2) the use of periodic boundary conditions on a small unit cell (trivial). A recurring theme of this paper is that the interesting properties of crystals do not fundamentally arise from periodicity but rather from their status as objective structures. For other objective structures, such as a bent and twisted beam, a first principles' approach is also possible, also on a small domain

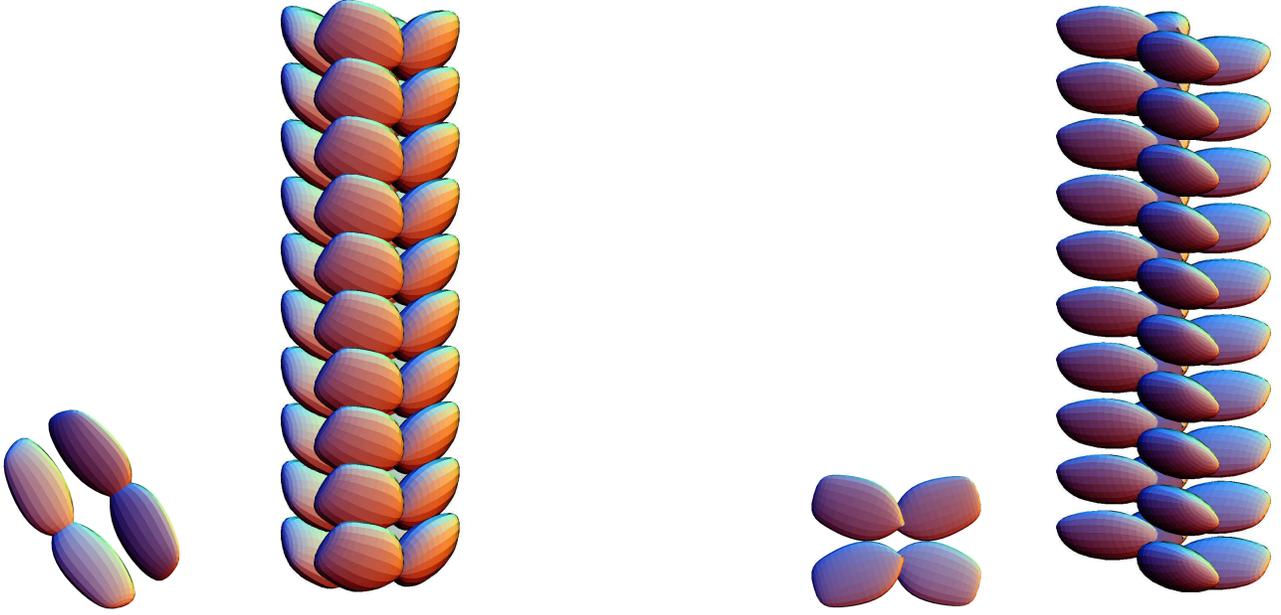


Figure 8: Some objective molecular fibers. Left pair: unstaggered. Right pair: staggered.

containing relatively few atoms. It is only necessary to clarify what is this domain and to explain what kind of boundary conditions should replace periodic boundary conditions. In computations on crystals, the assumption behind (2) is that the electronic density inherits the periodicity of the lattice. For objective structures, the analogous assumption is that the electronic density inherits the group structure of the objective structure. Both assumptions, to the extent that they are justified, have equal status with regard to the frame-indifference of quantum mechanics.

We consider the objective molecular structure described in Example 3.4 given by

$$\mathbf{x}_{k,(i,j)} = \mathbf{Q}_\gamma^{k-1} \mathbf{p}_{(i,j)} + (k-1)\lambda \mathbf{e}_3, \quad (102)$$

As described there, the “molecule” is indexed by $(i, j) \in \mathbb{Z}^2 \cap \Omega$. For simplicity let us suppose that $\mathbb{Z}^2 \cap \Omega = \{(i, j) : i = 1, \dots, M, j = 1, \dots, M\}$ is the $M \times M$ square and so there are M^2 atoms per molecule.

A simple way to define the fundamental domain and “objective boundary conditions” is the following. Define the average position of molecule 1 by $\bar{\mathbf{p}} = (1/M^2) \sum_{(i,j)} \mathbf{p}_{i,j}$. Let $|\mathbf{e}| = 1$ and consider the two planes $\mathcal{P}_1 = \{\mathbf{x} : \mathbf{x} \cdot \mathbf{e} = \bar{\mathbf{p}} \cdot \mathbf{e} - (\lambda/2)\mathbf{e} \cdot \mathbf{e}_3\}$ and $\mathcal{P}_2 = \mathbf{Q}_\gamma \mathcal{P}_1 + \lambda \mathbf{e}_3 = \{\mathbf{x} : \mathbf{x} \cdot \mathbf{Q}_\gamma \mathbf{e} = \bar{\mathbf{p}} \cdot \mathbf{e} + (\lambda/2)\mathbf{e} \cdot \mathbf{e}_3\}$. Assuming $\lambda \mathbf{e} \cdot \mathbf{e}_3 > 0$ (otherwise, exchange the inequalities in (103)), let \mathcal{D} be given by the region between the planes

$$\mathcal{D} = \{\mathbf{x} : \mathbf{x} \cdot \mathbf{e} \geq \bar{\mathbf{p}} \cdot \mathbf{e} - (\lambda/2)\mathbf{e} \cdot \mathbf{e}_3 \text{ and } \mathbf{x} \cdot \mathbf{Q}_\gamma \mathbf{e} < \bar{\mathbf{p}} \cdot \mathbf{e} + (\lambda/2)\mathbf{e} \cdot \mathbf{e}_3\} \quad (103)$$

With a good choice of \mathbf{e} and the molecule, typically we will have that $\mathbf{p}_{(i,j)} \in \mathcal{D}$, $i, j = 1, \dots, M$, which we assume. There is quite a bit of freedom here about the choice of \mathbf{e} and $\mathbf{p}_{(i,j)}$. We could also choose \mathcal{P}_1 to be more a general surface than a plane (\mathcal{P}_2 must still satisfy $\mathcal{P}_2 = \mathbf{Q}_\gamma \mathcal{P}_1 + \lambda \mathbf{e}_3$). For example, \mathcal{P}_1 could be a surface that triangulates the atomic positions $\mathbf{p}_{(i,j)}$. This freedom

could be quite useful if a major surface reconstruction⁷ would take place as we increase the applied forces and moments (see below). Also, we may want to introduce a cut-off to avoid calculating the electronic density far from the atoms; a sensible boundary condition based on the decay properties of the electronic density could then be imposed on this cut-off surface, or else the density could be matched to an implicit model of a solvent in the case of a submerged beam. The cut-off would also have to respect the following condition (cf., (105) below): if \mathcal{A}_1 and \mathcal{A}_2 are the subsets of \mathcal{P}_1 and \mathcal{P}_2 determined by the cut-off condition, then $\mathcal{A}_2 = \mathbf{Q}_\gamma \mathcal{A}_1 + \lambda \mathbf{e}_3$.

We define $\mathcal{D}^k = \mathbf{Q}_{(\gamma)}^{k-1} \mathcal{D} + (k-1)\lambda \mathbf{e}_3$ for all integers k and then

$$\mathcal{S} = \cup_k \mathcal{D}^k. \quad (104)$$

\mathcal{S} contains all the atoms of the objective structure.

The density functional theory calculation of the electronic density $\rho(\mathbf{x})$ is then carried out on the domain \mathcal{D} with the *objective boundary condition*:

$$\rho(\mathbf{x}) = \rho(\mathbf{Q}_\gamma \mathbf{x} + \lambda \mathbf{e}_3), \quad \mathbf{x} \in \mathcal{P}_1. \quad (105)$$

If a lateral boundary has been introduced by having a cut-off, we expect that no additional boundary condition needs to be imposed there, beyond what is expected to make the solution behave as if these boundary had not been imposed. Then ρ is extended to the whole structure by noting that if $\mathbf{x} \in \mathcal{S}$ then there is an integer k and a point $\mathbf{z} \in \mathcal{D}$ such that $\mathbf{x} = \mathbf{Q}_\gamma^{k-1} \mathbf{z} + (k-1)\lambda \mathbf{e}_3$. Then we define

$$\rho(\mathbf{x}) = \rho(\mathbf{z}). \quad (106)$$

A simple argument shows that if ρ is defined in this way, then it satisfies the basic invariance condition (8) on all of \mathcal{S} .

If \mathbf{e} is not parallel to \mathbf{e}_3 then the two planes \mathcal{P}_1 and \mathcal{P}_2 intersect. This may or may not lead to a problem for implementation but should not affect the invariance of ρ , which is expected to satisfy (8) on all of space.

The density functional calculation described above just gives one value of the energy per unit length $\hat{\varphi}$ which depends on the parameters that define the structure: $\mathbf{p}_{(i,j)}$, γ , λ . We have noted in (58) that the equations of equilibrium for this objective molecular structure reduce to the M^2 equations,

$$\frac{\partial \hat{\varphi}}{\partial \mathbf{x}_{1,(i,j)}} = 0, \quad i = 1, \dots, M, \quad j = 1, \dots, M. \quad (107)$$

It would be natural to try to solve these by relaxing the M^2 values $\mathbf{p}_{(i,j)}$. But there remain two additional parameters γ and λ . These additional parameters provide freedom to prescribe applied forces and moments. Working out formulas for these is nontrivial in the present general context and we do not confront this problem here. If $\hat{\varphi}$ satisfies rather strong conditions of locality (which might exclude phenomena of ferroelectricity or ferromagnetism) then it is expected that these solutions are consistent with an applied force $\mathbf{f} = f \mathbf{e}_3$ and moment $\mathbf{m} = m \mathbf{e}_3$ necessarily parallel to the axis \mathbf{e}_3 and with

$$f = \frac{\partial \hat{\varphi}}{\partial \lambda}, \quad m = \frac{\partial \hat{\varphi}}{\partial \gamma}, \quad (108)$$

⁷Surface reconstruction by itself does not invalidate the objective-structure ansatz. However, as in crystals, one should always be aware of the possible necessity of having to double or triple, etc., the size of the molecule (unit cell, in crystals) in order to achieve the lowest energy state.

cf. Ericksen [14]. Here, to be precise, $\hat{\varphi}$ is the energy per unit length measured in the direction \mathbf{e}_3

Following this pattern of thought, simplified atomic level simulations on a fundamental domain with objective boundary conditions are possible with a variety of objective molecular structures, including structures like the four and eight molecule systems illustrated above. For a general objective molecular structure defined by $\mathcal{S} = \{\mathbf{x}_{i,k} + \mathbf{R}_{i,k}(\mathbf{x}_{n,m} - \mathbf{x}_{1,k}) : n = 1, \dots, N, m = 1, \dots, M\}$ one finds a fundamental domain \mathcal{D} such that the sets $\mathbf{x}_{i,1} + \mathbf{R}_{i,k}(\mathcal{D} - \mathbf{x}_{1,1})$ are pairwise disjoint and cover all of space (or at least an enlarged neighborhood of the structure). Then, objective boundary conditions are that if $\mathbf{x} \in \partial\mathcal{D}$ and $\mathbf{x}_{i,k} + \mathbf{R}_{i,k}(\mathbf{x} - \mathbf{x}_{1,k}) \in \partial\mathcal{D}$ for some (i, k) then $\rho(\mathbf{x}) = \rho(\mathbf{x}_{i,k} + \mathbf{R}_{i,k}(\mathbf{x} - \mathbf{x}_{1,k}))$.

Returning to the case of the bent and twisted beams, it is interesting to speculate about St. Venant's principle. That is the principle that, for a long beam with free sides loaded at its ends, all solutions of the equations of elasticity corresponding to a given force and moment tend to each other and, among these, there is one which is particularly simple, the appropriate St. Venant solution of linear elasticity. The point about this condition is that there are a great many diverse boundary conditions, very far from each other in any of the usual norms, that correspond to a given force and moment, so the fact that solutions corresponding only to a given force and moment all should approach one solution is rather amazing. The only rigorous proof of this classic version of St. Venant's principle is in linear elasticity (Toupin [34]). In nonlinear elasticity, Ericksen [14] also speculates about its validity, and despite the big difference in the theories (nonlinear elasticity vs. atomic) – except the invariance groups which of course are the same – his arguments are not so far from those in this section. Thus, we conjecture here that under suitable conditions on the energy there is also a St. Venant's principle at atomic level, even with just a few atoms in the cross-section. In fact, from the present viewpoint, one could say that it is the invariance group that is the crucial point, together with the definition of an objective structure. One could even think that a single molecule chain subject to a resultant force and moment consistent with (108) would be close to the present solution away from the ends, even when the relative rotation between molecules is a large fraction of 2π .

A counterpoint to this speculation is the flexure solution of linear elasticity, which has no counterpart among objective structures (In the flexural deformation, corresponding atoms in different cross-sections, however these are defined, do not see the same environment). The flexure solution is important to the general statement of St. Venant's principle in linear elasticity because it corresponds to an applied transverse force, and this, together with the other St. Venant solutions, is used to build up a solution corresponding to an arbitrary force and moment via superposition. In nonlinear theory there is anyway no superposition. Our feeling is that it is the underlying invariance group that is critical to a general version of St. Venant's principle and that the inclusion of the flexure solution is an artifact of linear elasticity.

9 Discussion

There are numerous interesting directions of research suggested by the relation between objective structures and crystal lattices. Some of these are already being studied for C nanotubes and C_{60} but other objective structures may present new opportunities for interesting properties, arising from the variety of possible relationships between molecules. There are also opportunities for unified treatment of properties of all objective structures.

1. Collective properties, like ferromagnetism, ferroelectricity or superconductivity. Since each atom in an objective structure sees the same environment, then each atom can have the same unpaired spins, for example. More generally, each atom may have the same local band structure. Similarly, the molecules of an objective structure could undergo a simultaneous ferroelectric transition. If the macroscopic effect of these identical electronic structures are enhanced by the overall structure, then one can get a strong macroscopic effect. Such collective effects are particularly interesting in objective structures when enhancement occurs due to the relative rotations between molecules (interpreted broadly) of the structure, since such effects cannot occur in crystal lattices. Optical properties may be of greatest interest.
2. Defects and failure. To understand the failure of crystal lattices, one calculates all “lattice invariant deformations”, the deformations in a certain class that restore the structure. Under severe stress, such deformations are effected by the passage of dislocations. One can take a similar approach to objective structures: find the deformations that restore the structure and then study what kinds of “dislocations” produce these deformations along a low energy pathway, i.e., without simultaneously breaking a large number of bonds. An interesting starting point for these thoughts is the study of dislocations in structures like T4 tail sheath by Harris and Scriven [19].
3. Phase transitions in objective structures. As quantified above in several cases, objective structures have free parameters. The energy or free energy as a function of these parameters may have energy wells. As one varies the temperature, pressure, field, etc., one may be able to induce a passage from one energy well to another, leading to a transition from one objective structure to another of the same type. Structural transitions of this type are expected to be common in objective structures, and the tail sheath of bacteriophage T4 is a nice example.
4. Phonons and statistical mechanics. Because of the underlying group properties discussed in Section 6 (cf. (59)) one should be able to organize the phonon calculation for an objective structure along the lines already done for crystal lattices. The appropriate mathematical subject is Fourier analysis on groups. A concrete study could begin with simple formulas like (98) and (100) and this would be both interesting and applicable to a broad collection of interesting structures. In crystals such calculations lay the groundwork for simplified calculations of free energy via the method of Effective Hamiltonians [28], [29], which introduces a lattice Wannier basis that conveniently parameterizes the low energy phonon modes. The symmetry properties of crystal lattices play an important role for the derivation of this basis. One can expect a similar kind of theory for other objective structures that specifically makes use of the objective property.
5. The measurement of structure. As noted in the introduction, much of what we know from experiment on the structure of matter comes from x-ray analysis of crystallized structures. However, many objective structures are not periodic. Could it be that, by forcing them into a periodic structure via crystallization, one perturbs the special relations between molecules that make it an objective structure, leading to a misinterpretation of the structure? Are there new ways of interrogating objective structures from uncrystallized samples? For crystalline solids, due to the fact that $e^{i\mathbf{k}\cdot\mathbf{x}}$ is an eigenfunction of the Laplacian with the translation invariance of a 3-D periodic crystal, the Fourier transform has a special relationship to both

periodicity and the wave equation. In practical terms these properties relate to the Bragg law and the procedures of x-ray analysis. In objective structures one would seek other kind of polarized solution of the wave equation invariant under the isometry group of an objective structure. This is expected to lead to a transform, a theory of scattering, and, ultimately, the design of an x-ray machine for the analysis of objective structures. These procedures are likely to involve a particular way of preparing the incoming radiation. Current work on fiber diffraction (Stubbs [31]) from viruses does not seem to take this point of view, but may contain important information for the development of these ideas. A good starting point for this line of reasoning is formula (98) which in fact produces most of the structures discussed by Stubbs.

6. Dynamics. Above we have noted the possibility of substantial simplification of first principles calculations of energy and equilibrium in an objective structure resulting from two features: 1) structural equilibrium implies atomic equilibrium (Sections 5 and 6.1) and 2) the use of objective boundary conditions on a fundamental domain (Section 8). There is also the possibility of a simplification of molecular dynamics (MD) calculations. This is a generalization of the standard idea ([1], [26], [32]) for crystal lattices of assuming periodicity of atomic positions with a large supercell. This allows MD on the supercell to represent exact MD on the infinite crystal lattice, but corresponding to the special initial conditions that are precisely periodic with the supercell periodicity. In objective structures one could do a completely analogous thing with a superfundamental domain, using the objectivity group of the objective structure to relate atomic positions in domains related to the superfundamental domain by the appropriate group transformations. In the objective case the reason that this procedure gives an exact solution to the equations of MD (for appropriate objective initial conditions) is because the right hand side of those equations is equivariant under the full set of objectivity transformations. Some of these ideas are worked out in [20].
7. The Cauchy-Born rule for objective structures. In recent years, the Cauchy-Born rule [15], [37], [18] has played an important role in the development of multiscale methods for crystalline materials involving the passage from atomic to larger scales. The rule begins with the multilattice description of crystals, the \mathcal{L}_M of (11) using the minimum number M of vectors \mathbf{p}_k to describe the multilattice of the reference structure. Strictly speaking, that rule is that, to arrive at a macroscopic theory with a local deformation gradient \mathbf{F} one computes at atomic level energies or stresses from a lattice defined by

$$\{\nu^i \mathbf{F} \mathbf{e}_i + \tilde{\mathbf{p}}_k : (\nu^i) \in \mathbb{Z}^3, k \in \{1, \dots, M\}\} \quad (109)$$

with the $\tilde{\mathbf{p}}_k$ chosen to secure equilibrium of the lattice. Zanzotto [37] generalizes this notion by allowing the number M not to be determined by the reference lattice. Essentially, the rule permits calculations on homogeneous configurations to be extended to inhomogeneous ones. This idea is also at the heart of the quasicontinuum method [33]. In the author's view, the physical idea behind the rule is that crystalline materials prefer nearly crystalline configurations even if they are inhomogeneously stressed. Then the fact that the periodicity of the deformed crystal is determined by the macroscopic deformation gradient acting on local lattice vectors is inescapable based on any reasonable multiscale idea. The same physical idea can be extended to objective structures: a macroscopic deformation should preserve locally the

objective structure. Our suggestion for a Cauchy-Born rule for an inhomogeneously deformed objective atomic structure is strictly analogous to the crystalline case: it would always be based on calculations on structures defined by, e.g., (98), (99) to extract an energy per unit area. The values of $\mathbf{t}, \hat{\mathbf{t}}, \mathbf{R}, \hat{\mathbf{R}}$ that would go into each such calculation would be determined by the local values of stretch and curvature in the underlying shell theory that is being used to describe the inhomogeneous structure.

This idea seems to be slightly different than the exponential Cauchy-Born rule successfully used by Arroyo and Belytschko [2]. That is, their rule relates atomic positions in a geometrically accurate way to the kinematics of the shell theory they choose, but they do not use an underlying objective structure to do the calculation of energy. Since, as we show above in Section 8, first principles calculations on objective structures can be drastically simplified, then this observation seems to suggest an efficient way to do first principles calculations for an inhomogeneously deformed C nanotube.

Alternatively, one could try to develop a “shell theory” in which the basic kinematics uses exactly the variables $\mathbf{t}, \hat{\mathbf{t}}, \mathbf{R}, \hat{\mathbf{R}}$. This is done in [16].

A Appendix: solution of (99)

The following is an enumeration of all solutions of (99).

1. $\mathbf{R}, \hat{\mathbf{R}} \in \text{SO}(3)$. Let $|\mathbf{e}| = 1$ be on an axis of \mathbf{R} , $\mathbf{R}\mathbf{e} = \mathbf{e}$. Then the second of (99) implies that $\hat{\mathbf{R}}\mathbf{R}\mathbf{e} = \mathbf{R}\hat{\mathbf{R}}\mathbf{e} \implies \mathbf{R}\hat{\mathbf{R}}\mathbf{e} = \hat{\mathbf{R}}\mathbf{e}$. Thus, $\mathbf{R} = \mathbf{I}$ or $\hat{\mathbf{R}} = \mathbf{I}$, or $[\mathbf{R} \neq \mathbf{I} \text{ and } \hat{\mathbf{R}}\mathbf{e} = \pm\mathbf{e}]$.
 - (a) $\mathbf{R} = \hat{\mathbf{R}} = \mathbf{I}$. In this case $\hat{\mathbf{t}}$ and \mathbf{t} are arbitrary (The structure is a 2-D crystal).
 - (b) $\mathbf{R} = \mathbf{I}, \hat{\mathbf{R}} \neq \mathbf{I}$. Here, $\hat{\mathbf{t}}$ is arbitrary but \mathbf{t} is on the axis of $\hat{\mathbf{R}}$, $\hat{\mathbf{R}}\mathbf{t} = \mathbf{t}$.
 - (c) $\hat{\mathbf{R}} = \mathbf{I}, \mathbf{R} \neq \mathbf{I}$. Here, \mathbf{t} is arbitrary but $\hat{\mathbf{t}}$ is on the axis of \mathbf{R} , $\mathbf{R}\hat{\mathbf{t}} = \hat{\mathbf{t}}$.
 - (d) $\hat{\mathbf{R}} \neq \mathbf{I}, \mathbf{R} \neq \mathbf{I}$.
 - i. $\hat{\mathbf{R}}\mathbf{e} = \mathbf{R}\mathbf{e} = \mathbf{e}$. In this case we write

$$\hat{\mathbf{t}} = \hat{\mathbf{t}}_1 + \hat{\tau}\mathbf{e}, \quad \mathbf{t} = \mathbf{t}_1 + \tau\mathbf{e} \quad (110)$$

where $\mathbf{t}_1 \cdot \mathbf{e} = \hat{\mathbf{t}}_1 \cdot \mathbf{e} = 0$. Then $\hat{\tau}, \tau$ are unrestricted but

$$\mathbf{t}_1 = (\hat{\mathbf{R}} - \mathbf{I})^{-1}(\mathbf{R} - \mathbf{I})\mathbf{t}_1, \quad (111)$$

where the inverse is taken on the plane perpendicular to \mathbf{e} (Note that since $\hat{\mathbf{R}} \neq \mathbf{I}$ then $\hat{\mathbf{R}} - \mathbf{I}$ is invertible on this plane).

- ii. $\hat{\mathbf{R}}\mathbf{e} = -\mathbf{e}$. Here, $\hat{\mathbf{R}} = -\mathbf{I} + 2\hat{\mathbf{e}} \otimes \mathbf{e}$ for some $|\hat{\mathbf{e}}| = 1, \hat{\mathbf{e}} \cdot \mathbf{e} = 0$. The corresponding $\mathbf{t}, \hat{\mathbf{t}}$ are

$$\hat{\mathbf{t}} = \tau_1\mathbf{e} + \tau\mathbf{e} \times \hat{\mathbf{e}}, \quad \mathbf{t} = \tau_2\hat{\mathbf{e}} + \tau\mathbf{e} \times \hat{\mathbf{e}} \quad (112)$$

for some τ_1, τ_2, τ .

2. $\mathbf{R} \in \text{SO}(3), \hat{\mathbf{R}} \in \text{O}(3) \setminus \text{SO}(3)$. In this case either $\mathbf{R} = \mathbf{I}$ or $[\mathbf{R} \neq \mathbf{I}, \mathbf{R}\mathbf{e} = \mathbf{e}, |\mathbf{e}| = 1 \text{ and } \hat{\mathbf{R}}\mathbf{e} = \pm\mathbf{e}]$.

- (a) $\mathbf{R} = \mathbf{I}$. In this case $\hat{\mathbf{R}} = \mathbf{I} - 2\hat{\mathbf{e}} \otimes \hat{\mathbf{e}}$, $|\hat{\mathbf{e}}| = 1$, $\mathbf{t} = \tau\mathbf{e}$, $\mathbf{e} \cdot \hat{\mathbf{e}} = 0$ and $\tau, \hat{\mathbf{t}} \neq 0$ are arbitrary.
(b) $\mathbf{R} \neq \mathbf{I}$ and $\hat{\mathbf{R}}\mathbf{e} = \mathbf{e}$. In this case $\mathbf{R} = -\mathbf{I} + 2\mathbf{e} \otimes \mathbf{e}$, $\hat{\mathbf{R}} = \mathbf{I} - 2\hat{\mathbf{e}} \otimes \hat{\mathbf{e}}$, $|\hat{\mathbf{e}}| = 1$, $\hat{\mathbf{e}} \cdot \mathbf{e} = 0$, and

$$\mathbf{t} = \tau_1\mathbf{e} + \tau_2\hat{\mathbf{e}} + \tau_3\mathbf{e} \times \hat{\mathbf{e}} \quad \hat{\mathbf{t}} = \hat{\tau}_1\mathbf{e} + \tau_2\hat{\mathbf{e}} \quad (113)$$

for arbitrary $\tau_1, \tau_2, \tau_3, \hat{\tau}_1$.

- (c) $\mathbf{R} \neq \mathbf{I}$ and $\hat{\mathbf{R}}\mathbf{e} = -\mathbf{e}$. In this case $\mathbf{R}\mathbf{e} = -\hat{\mathbf{R}}\mathbf{e} = \mathbf{e}$ (\mathbf{R} and $-\hat{\mathbf{R}}$ are coaxial rotations) and

$$\mathbf{t} = \mathbf{t}_1, \quad \hat{\mathbf{t}} = \tau_1\mathbf{e} + \hat{\mathbf{t}}_1, \quad (114)$$

where $\mathbf{t}_1 \cdot \mathbf{e} = \hat{\mathbf{t}}_1 \cdot \mathbf{e} = 0$ and $\hat{\mathbf{t}}_1 = (\mathbf{R} - \mathbf{I})^{-1}(\hat{\mathbf{R}} - \mathbf{I})\mathbf{t}_1$, the inverse taken on the plane perpendicular to \mathbf{e} .

3. $\mathbf{R} \in O(3) \setminus SO(3)$, $\hat{\mathbf{R}} \in SO(3)$. This can be read off of Case 2 because the equations are invariant under the change $(\hat{\mathbf{R}}, \hat{\mathbf{t}}) \leftrightarrow (\mathbf{R}, \mathbf{t})$.
4. $\mathbf{R} \in O(3) \setminus SO(3)$, $\hat{\mathbf{R}} \in O(3) \setminus SO(3)$. In this case either $\mathbf{R} = -\mathbf{I}$ or $[\mathbf{R} \neq -\mathbf{I}, \mathbf{R}\mathbf{e} = -\mathbf{e}, |\mathbf{e}| = 1$, and $\hat{\mathbf{R}}\mathbf{e} = \pm\mathbf{e}]$

- (a) $\mathbf{R} = -\mathbf{I}$. In this case \mathbf{t} and $\hat{\mathbf{R}} \in O(3) \setminus SO(3)$ are arbitrary but $\hat{\mathbf{t}} = (1/2)(\mathbf{I} - \hat{\mathbf{R}})\mathbf{t}$.

- (b) $\mathbf{R} \neq -\mathbf{I}, \hat{\mathbf{R}}\mathbf{e} = \mathbf{e}$. In this case $\mathbf{R} = \mathbf{I} - 2\mathbf{e} \otimes \mathbf{e}$, $\hat{\mathbf{R}} = \mathbf{I} - 2\hat{\mathbf{e}} \otimes \hat{\mathbf{e}}$, $|\hat{\mathbf{e}}| = 1$, $\hat{\mathbf{e}} \cdot \mathbf{e} = 0$ and

$$\mathbf{t} = \tau_1\mathbf{e} + \tau_2(\mathbf{e} \times \hat{\mathbf{e}}), \quad \hat{\mathbf{t}} = \hat{\tau}_1\hat{\mathbf{e}} + \hat{\tau}_2(\mathbf{e} \times \hat{\mathbf{e}}), \quad (115)$$

where $\tau_1, \tau_2, \hat{\tau}_1, \hat{\tau}_2$ are arbitrary.

- (c) $\mathbf{R} \neq -\mathbf{I}, \hat{\mathbf{R}}\mathbf{e} = -\mathbf{e}, \mathbf{R} - \mathbf{I}$ invertible. In this case $\hat{\mathbf{R}} = \mathbf{I} - 2\mathbf{e} \otimes \mathbf{e}$ and

$$\mathbf{t} = \tau\mathbf{e} + \mathbf{t}_1, \quad \hat{\mathbf{t}} = \tau\mathbf{e}, \quad (116)$$

where $\mathbf{t}_1 \cdot \mathbf{e} = 0$.

- (d) $\mathbf{R} \neq -\mathbf{I}, \hat{\mathbf{R}}\mathbf{e} = -\mathbf{e}, \mathbf{R} - \mathbf{I}$ not invertible. In this case $\mathbf{R} = \hat{\mathbf{R}} = \mathbf{I} - 2\mathbf{e} \otimes \mathbf{e}$ and

$$\mathbf{t} = \tau\mathbf{e} + \mathbf{t}_1, \quad \hat{\mathbf{t}} = \tau\mathbf{e} + \hat{\mathbf{t}}_1, \quad \mathbf{t}_1 \cdot \mathbf{e} = \hat{\mathbf{t}}_1 \cdot \mathbf{e} = 0. \quad (117)$$

- (e) $\mathbf{R} \neq -\mathbf{I}, \hat{\mathbf{R}}\mathbf{e} = -\mathbf{e}, \hat{\mathbf{R}} \neq \mathbf{I} - 2\mathbf{e} \otimes \mathbf{e}$. In this case $\hat{\mathbf{R}} - \mathbf{I}$ is invertible, $-\mathbf{R}$ and $-\hat{\mathbf{R}}$ are coaxial (with axis \mathbf{e}), and

$$\mathbf{t} = \tau\mathbf{e} + \mathbf{t}_1, \quad \hat{\mathbf{t}} = \tau\mathbf{e} + \hat{\mathbf{t}}_1, \quad (118)$$

where $\mathbf{t}_1 = (\hat{\mathbf{R}} - \mathbf{I})^{-1}(\mathbf{R} - \mathbf{I})\hat{\mathbf{t}}_1$.

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