

What are the possible axial point groups for a molecule of a certain size or formula?

Nike Dattani^{1,2,*} and Sichao Xiong^{1,†}

¹HPQC Labs, Waterloo, Canada

²HPQC College, Waterloo, Canada

(Dated: 27th September 2023)

For each axial point group, we determine all possible structures in terms of the number of atoms and the chemical formula. We provide examples of molecules of each size and formula if they are known, and hence we determine the yet-to-be discovered molecules with under five atoms for each point group. We present a set of principles that can be used for proofs about the possibility or impossibility for a certain point group to apply to a molecule of a certain size and/or formula. We also resolve some inconsistencies in a table by P. Atkins, M. Child and C. Phillips, add missing entries to it, and improve it further in a number of ways.

I. INTRODUCTION

One might wonder why, despite group theory being applied to molecules for about 100 years [19], the questions that are being addressed in this paper do not appear to have been answered yet. Indeed we have asked all living authors of [1–18, 36, 40] if they have ever come across a list of all possible point groups for a 4-atom (tetraatomic) system, and in all cases we were explicitly told that they were unaware of such a list, or we received no response at all. We have determined all possible point groups for systems with *any* number of atoms (not just four), and we have gone a step even further by determining all possible point groups for structures with a given chemical formula.

After searching through all of [1–18, 36, 40] thoroughly, the closest work that we found to the results in this paper, is presented in the table of “shapes” found in the 2008 version of the famous “Tables for Group Theory” document by P. Atkins, M. Child and C. Phillips [1]. Nothing similar was found in any of [1–18, 36, 40], and the table of “shapes” in [1] has several shortcomings which we will address and fix in Section III, before we begin presenting the main results of our work in the following sections.

For investigating the novelty of our work, we believe that our thorough examination through all of [1–18, 36, 40] was a fair survey of the known literature on the topic. The 2007 paper [40] reported a thorough survey of known published works that provided character tables for the S_8 and D_{8h} point groups, and our list [1–18, 36, 40] includes all of those works, in addition to [40] itself, the papers that cited [40], and also thoroughly selected work on the topic that did not provide S_8 and D_{8h} character tables.

Our paper focuses on *axial* point groups, which are those belonging to the series C_n , C_{nv} , C_{nh} , $S_{2n}D_n$, D_{nh} , D_{nd} (including C_s which

is equivalent to C_{1h} and C_{1v} , and C_i which is equivalent to S_2). For the *polyhedral* point groups T , T_d , T_h , O , O_h , I , I_h , we will present even more novel results in a forthcoming paper. For example, in all of the literature that we have seen (including [1–18, 36, 40]), the shape with the smallest number of vertices (or the system containing the smallest number of atoms) for which the point group is O , is the snub cube which has 24 vertices (or atoms), but within the last month we have discovered that it is possible to construct an object with only 20 vertices (or for the atoms in a 20-atom system to be arranged) such that the point group is O [44]. Likewise, in all of the literature that we have seen, the shape with the smallest number of vertices for which the point group is I , is the snub dodecahedron which has 60 vertices, but within the last month we have discovered that it is possible to construct an object with only 50 vertices such that the point group is I [44].

The next section of this paper will explain the context which made *us* feel compelled to answer the questions that this paper addresses; for any readers that wish to skip the motivation section, the rest of the paper is self-contained and does not require knowledge of any of the material presented there. The second paragraph of this introduction already described the contents of Section III. The diagrams in Section III will make it easier to follow Section IV, which contains the foundation for obtaining our main results which are provided in Section V and summarized in Section VI. Overall our results are as follows (all results appear to be novel or unusually difficult to find in existing places):

- In Section III: A table that presents visual examples of structures for all aforementioned axial point groups for $2 \geq n \geq 6$ and $n = \infty$,
 - in a more clear way than in [1],
 - with inconsistencies in [1] resolved,
 - with more of the $n = \infty$ shapes presented than in [1],
 - with structures requiring fewer atoms than in [1] for the C_n and D_n series,

* nike@hpqc.org

† sichao@hpqc.org

- with an extra column showing additional structures (in some cases these are more realistic structures than in [1]) for the $n = 2$ cases, and
- with a more logical order, especially for pedagogical reasons, than in [1].

- In Section IV: Properties of some point groups that are very helpful for obtaining or explaining new results, and for pedagogical purposes.
- In Section V: For each axial point group, we determine
 - the minimum number of atoms (cardinality) required;
 - all possible cardinalities allowed (the minimum cardinality is a special case of this); and
 - all possible chemical formulas allowed (the list of all possible cardinalities is a special case of this).
- In Section VI: As a consequence of the results in Section V,

- we were able to list in table ?? all possible point groups allowed for systems with m atoms for $m = 1 - 8$ (and a table with *arbitrary* values of m can be generated with the results from V but would take up too much space to be presented here);
- we also explicitly listed the specific point groups (and diagrams of example structures) that are possible for systems with the specific formulas A_3 , A_2B , and ABC for triatomic systems and A_4 , A_3B , A_2B_2 , A_2BC , and $ABCD$ for tetraatomic systems (analogous lists for *arbitrary* chemical formulas can also be generated with the results from V but would take up too much space to be presented here);
- we attempted to provide examples of known molecules with each possible point group for each formula A_3 , A_2B , ABC , A_4 , A_3B , A_2B_2 , A_2BC , and $ABCD$, and this led us to the discovery of shapes for which no molecule/complex has yet been synthesized or found, despite the existence of such molecules/complexes being proven to be possible (this was not a surprise for larger structures, but we determined that the minimum number of atoms required for the point group D_2 is 4 but we could not find any example of a 4-atom molecule with the D_2 point group despite the apparent simplicity that would come with such a small molecular size).

Section VIA briefly mentions how the results of this work can be used for forthcoming projects.

II. MOTIVATION FOR THIS WORK

Our need for answers to the question in the present paper's title, arose during other work. GW100 is a dataset of 100 systems (95 molecules and 5 atoms)

which was introduced in a 2015 paper [38] and by the end of 2020, already more than 100 electronic structure methods/codes were used to calculate energies for all systems in the GW100 dataset. It has therefore become a monumental dataset for benchmarking, and efforts were made in 2021 [20] and 2023 [21] to improve the most accurate calculations that had been done on the system until then [22], and therefore to create one of the best known sets of benchmark data in existence for electronic structure calculations.

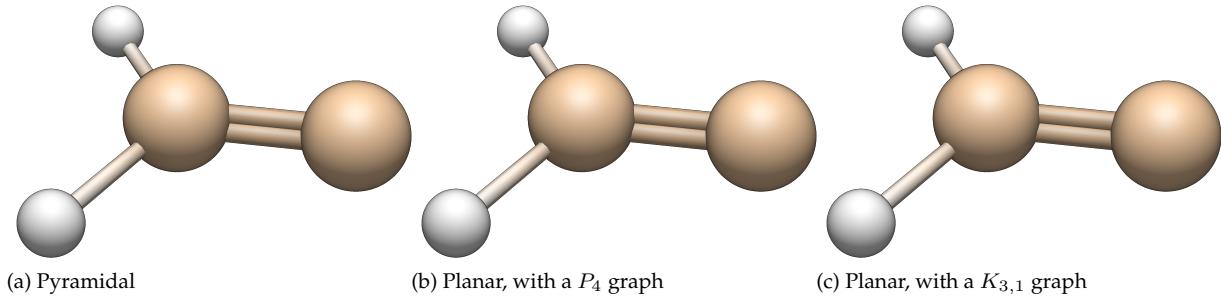
However, for many of the molecules in the GW100 dataset, calculations are done at geometries that were optimized using density functional theory, which means that the results are dependent on the basis set and density functional used; and it also had an effect on the comparisons that have been made between calculations that were done for the GW100 dataset and experimental data on the same dataset. For many of those molecules, very accurate bond lengths and angles that were determined from high-resolution spectroscopic experiments, are available in places such as the Landolt–Bornstein volumes and related books [23–35] and also in the original papers in which the geometric data was determined.

The books [23–35] provide only the *point group*, a 3D diagram, and usually the minimum number of bond lengths, bond angles and dihedrals necessary to generate all XYZ coordinates or a z-matrix. An example is the entry for H_2Si_2 in [26] (this molecule is not in GW100 but it is useful for illustrating this point) which provides the point group (C_{2v}), a 3D shape that is redrawn in Fig. 1 of this paper, and *only* two bond lengths and a dihedral angle: $r_{Si-Si} = (2.2154 \pm 0.0020)\text{\AA}$, $r_{Si-H} = (1.6680 + 0.0030)\text{\AA}$, $\varphi = (104.22 + 0.30)^\circ$ (the original experimental paper from which this data came [42] and the previous paper on the same molecule [41], also provided no additional bond lengths or angles). But to do electronic structure calculations we need either the XYZ coordinates of all atoms, or a z-matrix for the molecule, and there is no software for obtaining either of these from just the limited information given (point group, 3D diagram, two bond lengths and a dihedral angle). A software for generating a z-matrix from this data would be significantly simpler to write than a software for generating XYZ coordinates of all atoms, but the z-matrix for this system would need at least one bond angle, and the reader might find it surprising that the simplest formula for the H-Si-H angle in H_2Si_2 is (in terms of the provided dihedral angle φ , the provided Si-Si bond length r_1 and the provided Si-H bond length r_2):

$$\theta = \arcsin \left(\frac{\sin \left(\frac{\varphi}{2} \right) \sqrt{4r_2^2 - r_1^2}}{r_2} \right). \quad (1)$$

Such a formula is not expected to be found in any compilation of formulas. Determining this formula can be accomplished with some high school level trigonometry (applications of the ordinary cosine law), and ap-

Figure 1: Three molecules that have different geometries despite having the same chemical formula (H_2Si_2) and the same point group (C_{2v}).



plications of the *dihedral cosine law* which is unlikely to be taught in high school or university-level curricula, but can be learned and applied to such small molecules within a day by most researchers; however with the pace of research today, the derivation of such a formula *would ideally be done by software rather than by hand*. Unfortunately, not even the most advanced symbolic computation or computer algebra software can provide a user with Eq. 1 based on the information given.

Furthermore, the interest today in machine learning and big data analysis has lead to the introduction of much larger datasets than GW100, such as GW5000 and OE62 (both from Stuke *et al.* [39]) which involve more than 5000 and 61000 molecules respectively, but the geometries for the molecules in these datasets have issues similar to the ones for the GW100 dataset. This reinforces our motivation for constructing a software that could, for example, convert the thousands of geometries from the Landolt–Börnstein series and related compilations of spectroscopically determined geometry data, into z-matrices or XYZ coordinates.

We believe that as machine learning and big data analysis become more popular over the next century, there will be a rise in interest in being able to categorize molecules (e.g. for training neural networks) and the question of which point groups are possible for molecules of a certain size or formula, will be asked more and more. Anyone seeking the answers to these questions will be able to find them in this paper.

A software to generate z-matrices (or even XYZ coordinates) for molecules with the data presented in experimental papers, such as for H_2Si_2 , would require specific code blocks for each molecular shape. It is possible for two molecules with the same point group and formula to have very different shapes (for example see Fig. X, in which two isomers of H_2Si_2 are shown, both with the C_{2v} point group, but one of them being pyramidal and the other one being planar), so a general-purpose “z-matrix constructor” or “XYZ-coordinates constructor” that uses only a “minimal” set of bond lengths, bond angles and dihedral angles, would need specific code blocks based on their point groups and chemical formulas, in addition to other characteristics. However, a natural first step towards constructing such a software would be to categorize n

atom molecules based on their molecular formulas and point groups (the Landolt–Börnstein volumes and related books [23–35], the CCCBDB [43], and the CRC Handbook of Chemistry and Physics are some examples in which point groups are already used to help describe molecules), and then to write the relevant z-matrix-construction or XYZ-construction code for each case, adding sub-cases when necessary (e.g. to distinguish between the two types of C_{2v} shapes for A_2B_2 molecules as depicted in Fig. 1).

For n atoms, how many cases do we need to consider in order to cover each point group at least once in the software? That is the essence of the question in the present paper’s title, and as mentioned in the opening paragraph of the Introduction section, it appears that this question has not been answered before, or at least the answer is not easily available. We also go even one step further, by determining all possible *chemical formulas* for a particular point group of an n -atom system. For example, in order for a 7-atom molecule to have the point group C_i its formula needs to be $\text{AB}_2\text{C}_2\text{D}_2$ (with any of the variables B, C, or D being allowed to be a duplicate of one of the previous letters) but a 7-atom molecule whose chemical formula does not have that structure cannot have the point group C_i (e.g. for reasons that will be explained in this work, there is no arrangement of the atoms of $\text{C}_3\text{H}_3\text{N}$ such that the point group of the molecule can be C_i).

III. TABLE OF EXAMPLE SHAPES FOR ALL AXIAL POINT GROUP SERIES

The 2008 version of [1] contains a table of “shapes” on Page 37, which appears to be the only table available (in all of the scientific literature) of its kind (see Section I). For the point groups C_n , D_n , C_{nv} , C_{nh} , D_{nh} , D_{nd} , and S_{2n} , with n from 2 to 6, schematic diagrams are presented in attempt to provide an impression of how a molecule with the point group would look. This table has some minor inconsistencies (e.g. one of the lines in the C_4 diagram is black instead of purple, the C_6 diagram has some extra unintended purple lines, and the C_4 , C_5 and C_6 diagrams have lines with inconsistent lengths compared to other lines in the same diagrams

Table I: An improved version of the table presented on Page 37 of [1], depicting example structures for each point group provided in the table. For $n = 2$, two families of structures are presented (one with a rectangular “base” and one with a diatomic “base”). For each point group series and for each value of n , more families of structures also exist, so the examples that are presented are not exhaustive. All objects that are depicted for the $n = \infty$ point groups satisfy the definition of either $D_{\infty h}$ or $C_{\infty v}$, so they are labeled as such. The colors of the atoms are not intended to have any meaning apart from showing that the grey/black atoms have to all be the same element, and the red atoms have to all be the same element (the red atoms in all of these diagrams can also be the same element as the black atoms without affecting the point group, but it is not necessary for them to be the same). No structure is intended to depict a real molecule.

	$n = 2$	$n = 2$	$n = 3$	$n = 4$	$n = 5$	$n = 6$	$n = \infty$
D_{nh}							
D_{nd}							
D_n							
S_{2n}							
C_{nv}							
C_{nh}							
C_n							

and compared to analogous lines in the C_{4h}, C_{5h} and C_{6h} diagrams). Although any inconsistency in such a table can hamper the experience of its readers, and although in these cases some readers are likely to lose a bit of time wondering why some lines aren't the same size and why there's some extra lines, most readers will be comfortable to ignore these ones and to simply attribute them to human error.

However, the aforementioned table in [1] has more major consistencies which we would like to address in this section of the paper. For example, the table in in [1] shows the C_{nv} series converging to a cone in the $n = \infty$ case, but does not show the D_{nh} series converging to a circle in the $n = \infty$ case (the reader may compare with our Table I for context). The table in [1] showed the D_{nd} series converging to what appears to be a single circle in the $n = \infty$ case, but it would be more logical for the D_{nd} series to converge to two equivalent and co-axial circles on different parallel planes (as shown in our Table I) and to label the $n = \infty$ object as having the point group $D_{\infty h}$ since whether we have one circle (as in their table) or two parallel co-axial circles (as in our table), the point group is in fact $D_{\infty h}$ if we are dealing with physical objects (the distinction between $D_{\infty d}$ and $D_{\infty h}$ arises only when considering vector fields rather than physical objects). The table in [1] also does not show the objects to which the point group series D_n, S_{2n}, C_{nh} , and C_n converge in the $n = \infty$ case, so we have shown these objects (and whether the point group series converges to $C_{\infty v}$ or $D_{\infty h}$) in our Table I.

The next issue with the table in [1] that we addressed was the readability and interprability of their figures. This problem is perhaps most severe in their figures for S_{2n} , in which the atoms in the first and third planes are of one elemental type (depicted in a beige color in their figure), and the atoms in the second and fourth planes are of another elemental type (depicted in a purple or maroon color in their figure); whereas for reasons that will be explained in Section IV, it would be more correct to show the atoms in the first and fourth planes being one elemental, and the atoms in the second and third planes being one elemental type (as depicted in our Table III). This issue is also a problem for the D_n and D_{nd} series in their table: the figures for the D_{nd} series have two different colors, even though all atoms actually need to be the *same* type, and the figures in the D_{nd} series do not make it clear that the two polygons shown for each value of n , are on different planes. For the D_n series, again the colors appear to be incorrect. The chemical formulas and object shapes are made much more clear in our Table III and are explained in detail in subsequent sections of this paper.

On a more fundamental level, the table in [1] does not make it clear what precisely is being shown: most readers will likely assume that each polygon vertex represents an atom (although this is not made obvious), but what about the thin lines and small triangles that appear at some vertices? Do the thin lines represent one additional atom each, while the triangles de-

pict more than one additional atom each? In fact, both the straight lines and the small triangles represent just one additional atom in each case, but the triangles depict atoms that are outside of the plane of the shown polygon, and the straight lines depict atoms that are in the same plane as the shown polygon (but many readers, like us, may at first think that the use of straight lines versus small triangles was just a "typo" akin to the various "minor inconsistencies" that we mentioned earlier).

We also note that the "appendages" in the $C_{3h}, C_{4h}, C_{5h}, C_{6h}, C_4, C_5, C_6$ figures in [1] are parallel (in fact co-linear) with the edges of the triangle, but for C_3 they are *not*. This is likely another "typo" but we will note that the "appendages" do not need to be parallel, as long as they do not bisect the exterior angles at the polygons' vertices, and as long as the atoms are not in the center of the polygons' edges, since if either of these situations were to occur, the point group of the system would be promoted to D_{nh} . In our Table I, we kept the angles of the "appendages" consistent throughout the table, and chose to make them all non-parallel with the "bonds" in the structures.

We also attempted to resolve a confusion associated with the $n = 2$ column in the table in [1]. The example structure shown for C_2 , for example is obscure and a far less common example for the C_2 point group than the structure of H_2O_2 for example. Likewise, H_2O is the first system that usually comes to mind when we consider the point group C_{2v} , but the structure shown in the table for C_{2v} is very different. Also to add to the confusion, the table in [1] uses a rectangular "base" for the example systems for the $D_2, C_{2h}, D_{2h}, D_{2d}$ and S_4 point groups, but an ambiguous or uninterpretable "base" for C_2 and C_{2v} . We have resolved this confusion by including two $n = 2$ columns in our Table I: one with a diatomic "base" and one with a rectangular "base". so that readers can see example shapes for both cases.

For the C_n and D_n series, perhaps the authors of [1] had specific molecules in mind, but one of the early questions that arose for us before we began writing this paper, was "what is the minimum number of atoms required for the point group so a system to be G [with G being the point group]", and after answering that question we found that the table in [1] correctly depicts the minimum number of atoms required for all point groups except for the $n = 2$ ones (all of them!) and for C_n and D_n . In our Table I, we have shown the "minimal" structures that we found for C_n and D_n as well as for the $n = 2$ cases for all other point group series. It is important to note that for each point group, multiple structures can be valid, even when the number of atoms and the chemical formula are the same (we already mentioned this in the previous section and illustrated it in Figure 1), so the figures that we presented in I and that the authors of [1] presented in their original table, are not the only correct examples that can be provided for each point group; but ours were at least

chosen based on a non-arbitrary criterium, which was to only include for each point group, the structure that require the minimum number of atoms (except for the first $n = 2$ column for each point group series, in which we decided that it would be interesting to show a structure requiring the minimum number of atoms that uses a “rectangular base”).

The final difference that we will note between the table in [1] and our Table I is the order in which the point group series are presented. The order in which we present them is far better from a pedagogical standpoint, because with the D_{nh} series presented first (these are the simplest shapes in the entire table), all other shapes in the table are built on top of these D_{nh} shapes and contain the D_{nh} shapes as a subsystem of a larger shape. The order that we presented the point group series in Table I is the same as the order in which we present the arguments for the minimum numbers of atoms and the possible chemical formulas for each point group in Section V.

IV. GENERAL PRINCIPLES FOR POSSIBLE MOLECULES

In this section we will state some general principles that we will use in the following section when formulating proofs for the required numbers of atoms and required chemical formulas for each point group. Some of the statements made in this section may already be familiar or intuitive to the reader, but we have not seen most of them stated in textbooks about group theory for chemistry [1–18, 36, 40], although parts of the first statement are mentioned in other places, such as [37].

Ability to orient the coordinate system according to a C_n axis and σ_h plane:

Any molecule with a rotation axis, called a C_n -axis, can be oriented in an xyz (Cartesian) coordinate system such that for the largest possible n value in C_n , the z -axis is aligned with a C_n axis, and a σ_h plane (if one exists) is a mirror plane coinciding with the xy -plane in the coordinate system.

Existence of a C_n axis:

The existence of a C_n axis is only possible if all atoms are on the C_n axis or if the system contains a subset of identical atoms that are vertices of an n -sided polygon with equal side-lengths (a regular n -gon), or if $n < 3$ we simply need to have n identical atoms in the molecule. A C_n axis would go through the center of this polygon (or in the case of $n = 2$, it would go through the centre of the line joining the two identical atoms), and since we can call this axis the z -axis, all atoms that form vertices of the polygon (or the two identical atoms in the case of $n = 2$), would have to have the same z -coordinates. Therefore, a minimum of n atoms is needed in order to have a C_n axis.

If a C_n axis is the z -axis, then after a C_n rotation, an atom that originally had coordinates (x, y, z) , will have

coordinates (x', y', z) in which the z -coordinate does not change, and the new coordinates (x', y') can be different from the old ones (x, y) but will coincide with the original (x, y) coordinates of another identical atom in the molecule.

Necessary and sufficient conditions for the D_{nh} point group when $n \geq 3$:

A regular n -gon with uniform vertices (in a molecule, this would mean the presence of identical atoms at the vertices) has a point group of D_{nh} (this was already depicted visually in Table I), and any non-linear object with the D_{nh} point group must contain a subset of identical vertices that form a regular n -gon if $n \geq 3$.

Necessary and sufficient conditions for the S_{2n} operation to be valid when $n \geq 3$:

The S_{2n} operation is valid on a regular $2n$ -gon with uniform vertices, because the S_{2n} operation is the combination of a C_{2n} operation (which is valid on such a system) followed by a σ_h operation (which is also valid on such a system, since it is planar); and any non-linear object in which the S_{2n} operation is valid, must contain a subset of identical vertices that form a regular n -gon if $n \geq 3$.

However, for the S_{2n} operation to be valid in a system in which the σ_h operation is not valid (as in the D_{nd} , S_{2n} , and T_d point groups), we can not just have a $2n$ -gon since the $2n$ -gon itself forms a plane that can act as a σ_h plane. It turns out that instead of one regular $2n$ -gon, two regular n -gons with one of them rotated by an angle of π/n from the other one, and both of them being on different parallel planes with a C_n axis going through the center of each of the n -gons, is a sufficient property and a necessary part of any system for there to be a valid S_{2n} operation and no valid σ_h operations (when $n \geq 3$). Each D_{nd} point group contains S_{2n} elements and no σ_h elements, and the examples for D_{nd} that we presented for $n \geq 3$ in Table I have exactly the form described in the previous sentence.

The σ_h plane that is part of the S_{2n} operation, cannot contain all atoms of the system, because then this plane would not only be the σ_h part of the S_{2n} operation, but it would also be a valid σ_h operation for the entire system. At least one atom needs to not be on the σ_h plane of the S_{2n} operation, and if it is on the C_{2n} axis, then since a C_{2n} operation does nothing to atoms that are on the C_{2n} axis, a valid S_{2n} operation would require the σ_h plane of the S_{2n} operation to be a valid σ_h plane for the atom too; so at least one atom needs to be neither on the S_{2n} operation's C_{2n} axis nor on its σ_h plane. Since we can make the C_{2n} axis of the S_{2n} operation the z -axis, and the σ_h plane of the S_{2n} operation the xy -plane, we can summarize the previous sentence by saying that one point exists at a point (x_1, y_1, z_1) in which $(x_1, y_1) \neq (0, 0)$ and $z_1 \neq 0$. One S_{2n} operation will rotate the (x, y) coordinates of the point by an angle of $\frac{2\pi}{2n} = \pi/n$ and the z -coordinate of

that point to $-z_1$, and an identical atom needs to be at this new point: $(x_2, y_2, -z_1)$. The S_{2n} operation on the atom at $(x_2, y_2, -z_1)$ will rotate the (x, y) coordinates of the point by an angle of π/n and the z -coordinate of that point to $+z_1$, and an identical atom needs to be at this new point. By repeating this procedure, we will be forced to have a regular n -gon with uniform vertices on the plane $z = +z_1$ and another one on the plane $z = -z_1$ but with all vertices rotated by π/n with respect to corresponding vertices on the other n -gon, and the C_{2n} axis of the S_{2n} operation (also called the S_{2n} axis) going through the centers of each n -gon. So not only is this shape sufficient for the existence of a valid S_{2n} operation in a system that does not have a valid σ_h operation on its own, but it is a necessary subunit of any system whose point group has an S_{2n} element and no σ_h elements.

When $z_1 = 0$ in the shape described in the previous paragraph, both n -gons will be on the same plane, and rotated by an angle of π/n from each other, so we will again have a $2n$ -gon, as described earlier.

Action of the inversion operation, i :

We can always choose center of inversion to be at the origin $(0, 0, 0)$, so if an atom is located at (x, y, z) , the inversion operator will move it to $(-x, -y, -z)$.

V. POSSIBLE NUMBER OF ATOMS AND CHEMICAL FORMULAS FOR EACH AXIAL POINT GROUP

As usual, we only consider the maximum point group. All in order of number of atoms (except C_i is before others).

A. Point groups without axial rotational symmetry

C_s

Any two atoms form a line, and if all atoms of a molecule are on the same line, then the point group will be promoted to either $C_{\infty v}$ or $D_{\infty h}$. Likewise, a single atom has the point group K_h , so it is not possible for a molecule with fewer than three atoms to have the point group C_s . Three atoms is enough for the point group of a molecule to be C_s though, as in the example ABC. The minimum number of atoms required is three, and any formula is allowed.

C_1

Any three atoms form a plane or a line, and if all atoms of a molecule are on the same plane, then that plane is a reflection/mirror plane. Therefore if a molecule has three or fewer atoms, it will at least have one reflection plane, and would be promoted from C_1 to at least C_s . Four atoms is enough for the point group of a molecule to be C_1 though, as in the example ABCD.

The minimum number of atoms required is four, and any formula is allowed.

C_i

Any five atoms with an inversion center will lie on the same plane (or same line) and will therefore have a reflection/mirror plane. Since the C_i point group does not have any reflection elements, for any five atom molecule with an inversion center the maximal point group must be larger than C_i .

If we have three or fewer atoms, then there does not even need to be an inversion center for the atoms to be confined to a plane (or line).

If we have four atoms, and we make the inversion center the origin, the atoms must come in pairs according to the inversion operation i that was described earlier: $A = (x_1, y_1, z_1)$ will be paired with $-A = (-x_1, -y_1, -z_1)$ and $B = (x_2, y_2, z_2)$ will be paired with $-B = (-x_2, -y_2, -z_2)$. Assuming that no two atoms will have the same xyz -coordinates, none of these four atoms can be on the origin. A and $-A$ form a line, and B and $-B$ form another line, and that these two lines both intersect at the origin, and two lines that cross are always co-planar.

If we have five atoms, the fifth one must be at the origin, because atoms need to either be paired or at the origin in order for the inversion operation to be valid on the system of atoms. However, the other four atoms form a plane that contains the origin (because the plane is formed by two lines that intersect at the origin). Therefore the fifth atom will also be on the same plane as the other four atoms, and the point group will be promoted beyond C_i .

Six atoms is enough for a molecule's maximal point group to be C_i , for example $C_2H_2Br_2Cl_2$ with the two carbons removed. The minimum number of atoms required is six, and the formula must be of the form $A_2B_2C_2D_2 \dots$ or $AB_2C_2D_2 \dots$ depending on if the number of atoms is even or odd.

B. Point groups with axial rotational symmetry

D_{nh}

$$\underline{n = 2}$$

If we have any fewer than three atoms, the point group of the system will be promoted to K_h , $D_{\infty h}$ or $C_{\infty v}$, however all D_{nh} point groups with even values of n (including D_{2h}) have an inversion element i , and the only way for a three atom system to have an inversion element is for it to be linear, which would promote it either to $D_{\infty h}$ or $C_{\infty v}$. If we choose the origin $(0, 0, 0)$ to be the center of inversion, and one atom is at the position (x, y, z) , then an identical atom would need to be at the position $(-x, -y, -z)$ and the third atom would need to be at the origin. We therefore would have two identical atoms on a line going through the origin, and

Table II: Possible point groups for systems with $m = 1$ to $m = 8$ atoms.

m	Possible groups (not including subgroups)	
1		K_h
2		$D_{\infty h} C_{\infty v}$
3	C_s	C_{2v}
4	C_s — C_1 C_2 — C_{2h} — $C_{2v}C_{3v}$ —	D_{3h}
5	C_s — C_1 C_2 — C_{2h} — $C_{2v}C_{3v}$ C_{4v} —	D_2 — D_{2d} — $D_{2h} D_{3h} D_{4h}$ — T_d — $D_{\infty h} C_{\infty v}$
6	C_s C_i C_1 C_2 C_3 — $C_{2h} C_{3h}$ — $C_{2v}C_{3v}$ C_{4v} C_{5v} —	D_2 — D_{2d} — $D_{2h} D_{3h} D_{4h} D_{5h}$ — T_d — $D_{\infty h} C_{\infty v}$
7	C_s C_i C_1 C_2 C_3 — $C_{2h} C_{3h}$ — $C_{2v}C_{3v}$ C_{4v} C_{5v} C_{6v} —	D_2 D_3 $D_{2d} D_{3d} D_{2h} D_{3h} D_{4h} D_{5h} D_{6h}$ — O_h $D_{\infty h} C_{\infty v}$
8	C_s C_i C_1 C_2 C_3 C_4 $C_{2h} C_{3h} C_{4h} C_{2v} C_{3v}$ C_{4v} C_{5v} C_{6v} C_{7v} S_4	D_2 D_3 $D_{2d} D_{3d} D_{2h} D_{3h} D_{4h} D_{5h} D_{6h} D_{7h} T_d$ O_h $D_{\infty h} C_{\infty v}$

a third atom in the center of that line. We therefore would need a minimum of four atoms for the D_{2h} point group, and indeed four atoms is enough as in the case of Br_2Na_2 . **The minimum number of atoms required is four, and the most general formula for the minimal structure is A2B2.**

$n \geq 3$

Since a regular n -gon with identical atoms at each vertex is both necessary and sufficient for the point group of a system of atoms to be D_{nh} for $n \geq 3$, we can conclude the **the minimum number of atoms required is n , and the formula for this minimal structure would be A_n .** An even number of additional atoms can be added along the C_n axis in such a way that no new valid symmetry operations are made possible, and such that none of the existing valid symmetry operations are invalidated, provided that these atoms are added in pairs on each side of the plane formed by the n -gon. One additional atom can also be added at the center of the n -gon. Therefore **the most general formula for a structure with n atoms plus an even number of additional atoms would be $A_n B_2 C_2 D_2 \dots$, and for an odd number of additional atoms the most general formula would be $A_n B C_2 D_2 \dots$**

D_{nd}

$n = 2$

The D_{2d} group does not include any horizontal mirror planes, and since any three atoms can form a plane which can serve as a horizontal mirror plane, we need more than four atoms for the point group of the system to be D_{2d} . Four atoms is indeed enough for the point group of the system to be D_{2d} as depicted in the second $n = 2$ column in Table III, in which **we have two diatomic molecules that are perpendicular to each other, but on different planes.**

$n \geq 3$

Each D_{nd} point group contains an S_{2n} operation and no σ_h operation on its own, and in Section IV we ex-

plained that any system with a valid S_{2n} but no σ_h operation on its own, must at least have a subset of atoms that form the shape shown for each $D_{nd}, n \geq 3$ case in Table III, so we need at least this shape. Since all other elements in D_{nd} are valid symmetry operations on this structure, and no other symmetry operations that are not in D_{nd} are valid on this structure, the point group of the structure is D_{nd} , and since it is not possible to have the S_{2n} operation without the σ_h operation with fewer atoms, we know that **the minimum number of atoms required is $2n$, and the most general formula would be $A_{2n} B_{2n} C_2 D_2 \dots$**

D_n

$n = 2$

The D_2 group does not include any horizontal mirror planes, and since any three atoms can form a plane which can serve as a horizontal mirror plane, we need more than four atoms for the point group of the system to be D_{2d} . Four atoms is indeed enough for the point group of the system to be D_2 as depicted in the second $n = 2$ column in Table III, in which **we have two diatomic molecules that are not perpendicular to each other, and are also on different planes.**

$n \geq 3$

The D_n point groups can be generated by a C_n operation and a perpendicular C'_2 operation, whereas the D_{nd} point groups can be generated by an S_n operation and a perpendicular C'_2 operation (the only difference being the S_{2n} generator for D_{nd} instead of the C_n generator for D_n). If we start with the structure that we described in the previous subsection for D_{nd} , one way that we can denote the S_{2n} axis to a C_n axis without changing any of the other valid symmetry operations and without introducing any new ones, would be to rotate one of the two n -gons in the D_{nd} shape so that the two n -gons are no longer perfectly rotated by an angle of π/n (as required by the logic that was presented in Section IV). The resulting structures are depicted in Table III, and the minimum number of atoms required for

Table III: Possible number of atoms and possible chemical formulas for each point group or point group series.

Point groups		Number of atoms															Possible chemical formula				
		Minimum	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	Even # of atoms	Odd # of atoms	
K_h	—	1	✓	✗	✗	✗	✗	✗	✗	✗	✗	✗	✗	✗	✗	✗	✗	✗	✗	A	
$D_{\infty h}$	—	2	✗	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	$A_2B_2C_2D_2\dots$	$AB_2C_2D_2\dots$	
$C_{\infty v}$	—	2	✗	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	$ABCD\dots$	
D_{nh}	$n \geq 3$	n	✗	✗	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	$A_nB_2C_2D_2\dots$	$AB_nC_2D_2\dots$	
D_{nd}	$n = 2$	4	✗	✗	✗	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	A_2n	AB_{2n}	
D_n	$n \geq 2$	$2n$	✗	✗	✗	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	A_2n	AB_{2n}	
S_{2n}	$n \geq 2$	$4n$	✗	✗	✗	✗	✗	✗	✗	✓	✓	✓	✓	✓	✓	✓	✓	✓	$A_{2n}B_{2n}C_2D_2\dots$	$AB_{2n}C_{2n}D_2E_2\dots$	
C_{nv}	$n \geq 2$	$n + 1$	✗	✗	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	AB_n		
C_{nh}	$n \geq 2$	$2n$	✗	✗	✗	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	A_nB_n	AB_nC_n	
C_n	$n \geq 2$	$2n$	✗	✗	✗	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	A_nB_n	AB_nC_n	
C_s	—	3	✗	✗	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	$ABCD\dots$		
C_i	—	6	✗	✗	✗	✗	✗	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	$(ABCD\dots)_2$	$A(BCD\dots)_2$	
C_1	—	4	✗	✗	✗	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	$ABCD\dots$		

each D_n point group are the same as for D_{nd} , as are the possible chemical formulas.

S_{2n}

$$\underline{n = 2}$$

From Section IV we know that a C_n axis can be chosen to be along the z -axis and a σ_h plane can be chosen to be the xy -plane in the same coordinate system. With that convention, a C_4 operation will transform the point (x, y, z) to $(-y, x, z)$ and the σ_h operation will transform the point $(-y, x, z)$ to $(-y, x, -z)$; so the S_4 operation which is the C_4 operation followed by the σ_h operation, will transform (x, y, z) to $(-y, x, -z)$. If our first atom is at the position (x_1, y_1, z_1) then the S_4 transformation will move it to the position $(-y_1, x_1, -z_1)$, and an identical atom must be there for the S_4 operation to be valid. Also after the same S_4 transformation, the atom at the position $(-y_1, x_1, -z_1)$ will move to the position $(-x_1, -y_1, z_1)$ and an identical atom must be there too. Since no atom has replaced our first atom which was at the position (x_1, y_1, z_1) , we need to keep applying S_4 transformations and keeping track of the atoms that are necessary to include in our system, until we do successfully replace the first atom. We show below that $m = 4$ identical atoms are required in order for an m -atom system to undergo an S_4 transformation and recover the same system:

$$(x_1, y_1, z_1) \rightarrow (-y_1, x_1, -z_1) \rightarrow (-x_1, -y_1, z_1) \rightarrow (y_1, -x_1, -z_1) \rightarrow (x_1, y_1, z_1). \quad (2)$$

Unfortunately the coordinates in 2 form the shape that we presented in the second $n = 2$ column in

our D_{nd} examples in Table III, because (x_1, y_1, z_1) and $(-x_1, -y_1, z_1)$ form a line on the $z = z_1$ plane, whereas $(-y_1, x_1, -z_1)$ and $(y_1, -x_1, -z_1)$ form a perpendicular line of the same size but on the $z = -z_1$ plane. We can add at least one more atom (it does not necessarily need to be homonuclear in comparison to the first set of four atoms) in order to break the σ_d planes that are in D_{2d} , but adding any number of atoms on the C_4 axis, or on the σ_h plane, or on the $z = \pm z_1$ planes will not break the σ_d planes. Since we have chosen the convention in which the C_4 axis is the z -axis, adding atoms on this axis would mean adding atoms with $(x, y) = 0$; since we have chosen the convention in which the σ_h plane associated with the S_4 operation is the xy -plane, adding atoms on this plane would mean adding atoms with $z = 0$; and regardless of those conventions, any atom on one of the $\pm z$ planes will have a z -coordinate of z or $-z$. To break the σ_d planes, we therefore need an atom at a different z -value such as z_2 and with non-zero x - and y -values. Regardless of the x - and y -values of this new atom (the fifth atom), the pattern in 2 shows that we will not recover the new atom's position by applying S_4 operations unless we have another three atoms that are identical to the fifth atom.

The example that we have provided in the second $n = 2$ column for S_{2n} in Table III is able to satisfy the above relationships among the coordinates of the atoms; since the S_4 group is generated by the S_4 operation only, and an S_4 operation can successfully be applied to this example, and there are no other symmetry operations valid on this structure which are not in the S_4 point group, so the point group of the 8-atom structure is S_4 . **The minimum number of atoms required is 8 with the formula A_4B_4 .**

$$\underline{n \geq 3}$$

In section IV we described structures that have the minimum number of atoms required for an S_{2n} operation to be valid and for no σ_h operations to be valid on their own. We also described earlier that the point group of such structures is D_{nd} : in order to make a minimal structure in which the point group is S_{2n} , we can start with the D_{nd} structure and add atoms to break the extra symmetry elements that are present in D_{nd} but not in S_{2n} . If we add any number of atoms to the S_{2n} axis or the σ_h plane that forms part of the S_{2n} operation, it will not break the σ_d planes that elements of D_{nd} , so we need to add at least one atom to a location that is neither on the S_{2n} axis nor on the σ_h plane associated with it. This atom does not need to be homonuclear with the existing atoms in the structure, but as we described in Section IV, we would have no choice but to add not just this one atom but two entire regular n -gons which are identical to each other and parallel to each other but not on the same planes as the two previously existing n -gons in the structure, and the S_{2n} axis must pass through the centre of all four n -gons.

We have shown examples of such structures in Table I (our choice of chemical “bonds” shown in these examples was made to resemble some known real S_{2n} structure, but we could also have chosen them differently, for example we could have had four polygons rather than two polygons with appendages). **The minimum number of atoms required is $4n$, and the formula for this minimal structure would be $A_{2n}B_{2n}$.** An even number of additional atoms can be added along the S_{2n} axis in such a way that no new valid symmetry operations are made possible, and such that none of the existing valid symmetry operations are invalidated, provided that these atoms are added in pairs on each side of the σ_h plane associated with the S_{2n} operation. One additional atom can also be added at the center of the overall system. Therefore **the most general formula for a structure with $4n$ atoms plus an even number of additional atoms would be $A_{2n}B_{2n}C_2D_2\cdots$, and for an odd number of additional atoms the most general formula would be $AB_{2n}C_{2n}D_2E_2\cdots$.**

C_{nv}

$n = 2$

If we have any fewer than three atoms, the point group of the system will be promoted to K_h , $D_{\infty h}$ or $C_{\infty v}$, however three atoms is indeed enough for the point group of a molecule to be C_{2v} , as in the case of H_2O . **The minimum number of atoms required is three, and the most general formula is $A_2BCD\cdots$ since the extra atoms C,D, \dots can be placed on the C_2 axis without any loss of valid symmetry operations, and without allowing any new valid symmetry operations.**

$n \geq 3$

Since the point group of a regular n -gon with identical atoms at each vertex is required in order to have the C_n axis that forms part of the point group C_{nv} and we have already mentioned in the previous section that the point group of such a structure would be D_{nh} , we would need at least one additional atom to break any symmetries in D_{nh} that are not present in C_{nv} . It turns out that at least one additional atom is not only necessary, but only one atom is sufficient, since if this atom is placed on a C_n axis that goes through the center of the n -gon, but the atom is not placed on the plane of the n -gon, it will break the horizontal mirror plane and any S_n axes, while maintaining the n vertical mirror planes that are in C_{nv} . The only point group with a C_n axis and n vertical mirror planes, without having any horizontal mirror planes or S_n axes, is C_{nv} , so the pyramid that we have formed must have the point group C_{nv} . **The minimum number of atoms required is $n+1$, and the most general formula is $A_nBCD\cdots$.**

C_{nh}

$n = 2$

We need a minimum of four atoms for the C_{2h} point group, for the same reason that we gave when we made this statement for the D_{2h} point group (because the C_{2h} point group has an inversion element i). Indeed four atoms is enough for the point group of a molecule to be C_{2h} , as in the case of trans- H_2N_2 . **The minimum number of atoms required is four, and the most general formula for the minimal structure is A_2B2 .**

$n \geq 3$

From Section IV we know that the system needs to contain a subset of atoms that form a regular n -gon, in order to have a C_n axis, but if we only have one regular n -gon, the point group would be D_{nh} , so we need to add at least one more atom in order to break the additional symmetries that D_{nh} compared to C_{nh} . Adding any number of atoms to the C_n axis (which we will make our z -axis) will not break the σ_v planes, so we are forced to add another regular n -gon. We can add this second regular n -gon on the same plane as the first one, as long as its vertices do not bisect the exterior angles at the first n -gon’s vertices, and as long as the second n -gon’s vertices are not on the edges of the first n -gon (both of these placements of the vertices would result in a failure to break the σ_v planes and would not successfully demote the point group from D_{nh} to C_{nh}).

Table IV: Possible point groups and example systems for all possible chemical formulas of triatomic systems.

Point group	Chemical formula type		
	A ₃	A ₂ B	ABC
D _{∞h}	C ₃	CO ₂	✗
C _{∞v}		N ₂ O	HOS
D _{3h}	H ₃ ⁺	✗	✗
C _{2v}	O ₃	H ₂ O	✗
C _s	H _· ···H ₂	HO ₂	HNO

C_n
n = 2

If we have any fewer than three atoms, the point group of the system will be promoted to K_h, D_{∞h} or C_{∞v}; and if we have only three atoms, they form a plane which will be a mirror plane, meaning that the point group of the system which contains a C₂ axis will be promoted to C_{2v} or D_{3h}. Four atoms would be enough for the point group of the system to be C₂ though, as in the case of H₂O₂. **The minimum number of atoms required is four.** In terms of the possible formulas, if we have two atoms at positions A and B, then after rotation around the C₂ axis (which we will make the z-axis, as we described in the previous section), these atoms will be at positions A' = (-x₁ - y₁, z₁) and B' = (-x₂ - y₂, z₂) respectively, and for the C₂ operation to be valid, the atoms that were originally at positions A and A' need to be identical, and likewise for the atoms that were originally at B and B'. **The most general formula is therefore A₂B₂CD··· since the extra atoms C,D,··· can be placed on the C₂ axis without any loss of valid symmetry operations, and if their positions are chosen carefully, no new valid symmetry operations would be introduced.**

n ≥ 3

Since the point group of a regular n-gon with identical atoms at each vertex is required in order to have a C_n axis, and we have already mentioned in the previous section that the point group of such a structure would be D_{nh}, we would need at least one additional atom to break any symmetries in D_{nh} that are not present in C_n. In order for the C_n operation to remain valid, we can either add any number of atoms (including just one) on the C_n axis, or a full set of n more atoms that form a regular n-gon with the C_n axis going through its center and perpendicular to the plane

Table V: Possible point groups and example systems for all possible chemical formulas of tetratomic systems.

Group	Chemical formula type				
	A ₄	A ₃ B	A ₂ B ₂	A ₂ BC	ABCD
T _d		✗	✗	✗	✗
P ₄					
D _{∞h}		✗		✗	✗
C ₄					
C _{∞v}		Unlikely			
D _{4h}		✗	✗	✗	✗
S ₄ ²⁺					
D _{3h}			✗	✗	✗
S ₄					
D _{2h}		✗		✗	✗
D _{2d}		✗	✗	✗	✗
S ₄					
D ₂		✗	✗	✗	✗
C _{3v}			✗	✗	✗
C _{2v}					✗
S ₄					
C _{2h}		✗		✗	✗
C ₂		✗		✗	✗
S ₄ ²⁻					
C _s					
C ₁					

formed by the n -gon. However, adding any number of atoms to the C_n axis will not break the σ_v planes, so by adding one or more atoms to the C_n axis that goes through the center of a regular n -gon, would form a structure with a C_{nv} point group, so instead of adding any number of atoms to the C_n axis, we must add at least one set of n more atoms forming a regular n -gon (and we know that this one set is enough for us to form a structure in which C_n is the point group, as in Table I). The two parallel n -gons, A_n and B_n , must lie on different planes so that the molecular is not planar, and therefore would not get promoted to C_{nh} . **The minimum number of atoms required is $2n$, and the most general formula would be $A_nB_nCD\dots$** since in addition to the A_nB_n structure, extra atoms C,D,\dots can be placed on the C_n axis without any loss of valid symmetry operations, and if their positions are chosen carefully, no new valid symmetry operations would be introduced.

VI. SUMMARY OF OUR RESULTS AND OUTLOOK

The results of the previous section are summarized in Tables II and III. Table II only shows the possible

point groups for system with up to 8 atoms because a smaller font or a change in other aspects of the formatting would be needed to extend the table to include systems with 9 atoms, and such an extension would not be particularly enriching, especially since the general chemical formulas presented in the previous section and summarized in Table III can be used to generate a table that includes systems with any *arbitrary* number of atoms. Likewise the reason for Table III having columns up to 16 atoms is similar, but such a table can be constructed with up to an arbitrary number of atoms, with each column after 8 atoms containing indicating that the point group of such a system cannot be K_h and it can be any of the other point groups that are listed in the table.

A. Outlook

Apart from finding molecules to fill in the tables, z-matrix generator in OpenMolcas.

- [1] P. W. Atkins, *Tables for Group Theory* (London, Oxford University Press, 1970).
- [2] D. M. Bishop, *Group Theory and Chemistry* (Clarendon Press, Oxford, 1973).
- [3] R. L. Carter, *Molecular Symmetry and Group Theory* (J. Wiley, New York, 1998).
- [4] F. A. Cotton, *Chemical Applications of Group Theory* (Interscience, New York, 1963).
- [5] G. Davidson, *Group Theory for Chemists*, Macmillan physical science (Macmillan, Basingstoke, 1991).
- [6] M. Diem, *Introduction to Modern Vibrational Spectroscopy* (Wiley, New York, 1993).
- [7] R. S. Drago, *Physical Methods in Chemistry*, Saunders golden sunburst series (Saunders, Philadelphia, 1977).
- [8] J. Ferraro and J. Ziomek, *Introduction to Group Theory and Its Application to Molecular Structure* (Plenum Press, 1969).
- [9] L. Hall, *Group Theory and Symmetry in Chemistry* (McGraw-Hill, 1969).
- [10] D. Harris and M. Bertolucci, *Symmetry and Spectroscopy: An Introduction to Vibrational and Electronic Spectroscopy* (Oxford University Press, 1978).
- [11] R. M. Hochstrasser, *Molecular Aspects of Symmetry* (W. A. Benjamin, New York, 1966).
- [12] J. M. Hollas, *Symmetry in Molecules*, Chapman and Hall chemistry textbook series (Chapman and Hall, London, 1972).
- [13] P. W. M. Jacobs, *Group Theory with Applications in Chemical Physics* (Cambridge University Press, Cambridge, 2005).
- [14] Y. Ohrn, *Elements of Molecular Symmetry* (Wiley Interscience, New York, 2000).
- [15] D. S. Urch, *Orbitals and Symmetry*, Penguin library of physical sciences. Chemistry. (Penguin Books, Harmondsworth, 1970).
- [16] J. P. Lowe, *Quantum Chemistry* (Academic Press, New York, 1978).
- [17] J. P. Lowe, *Quantum Chemistry*, 2nd ed. (Academic Press, Boston, 1993).
- [18] A. Vincent, *Molecular Symmetry and Group Theory : a Programmed Introduction to Chemical Applications* (Wiley, Chichester, 1977).
- [19] H. Bethe, *Annalen der Physik* **395**, 133 (1929).
- [20] F. Bruneval, N. Dattani, and M. Setten, *Frontiers in Chemistry* **9** (2021), 10.3389/fchem.2021.749779.
- [21] L. Monzel, C. Holzer, and W. Klopper, *The Journal of Chemical Physics* **158**, 144102 (2023).
- [22] K. Krause, M. E. Harding, and W. Klopper, *Molecular Physics* **113**, 1952 (2015).
- [23] L. E. Sutton and H. J. M. Bowen, *Tables of Interatomic Distances and Configuration in Molecules and Ions* (Chemical Society London, London, 1958).
- [24] L. E. Sutton, *Tables of Interatomic Distances and Configuration in Molecules and Ions* (Chemical Society London, London, 1965).
- [25] N. Vogt, *Structure Data of Free Polyatomic Molecules* (Springer, Cham, Switzerland, 2019).
- [26] K. Kuchitsu, *Structure Data of Free Polyatomic Molecules . Inorganic Molecules* (Springer, 1998).
- [27] K. Kuchitsu, *Structure Data of Free Polyatomic Molecules . Molecules containing One or Two Carbon Atoms* (Springer, 1999).
- [28] K. Kuchitsu, *Structure Data of Free Polyatomic Molecules . Molecules containing Three or Four Carbon Atoms* (Springer, 2001).
- [29] K. Kuchitsu, *Structure Data of Free Polyatomic Molecules . Molecules Containing Five or More Carbon Atoms* (Springer, 2003).

- [30] N. V. K. Kuchitsu, M. Tanimoto, *Structure Data of Free Polyatomic Molecules · Inorganic Molecules Supplement to Volume II/25* (Springer, 2006).
- [31] N. V. K. Kuchitsu, M. Tanimoto, *Structure Data of Free Polyatomic Molecules · Molecules containing One or Two Carbon Atoms Supplement to Volume II/25* (Springer, 2006).
- [32] N. V. K. Kuchitsu, M. Tanimoto, *Structure Data of Free Polyatomic Molecules · Molecules containing Three or Four Carbon Atoms Supplement to Volume II/25* (Springer, 2007).
- [33] N. V. K. Kuchitsu, M. Tanimoto, *Structure Data of Free Polyatomic Molecules · Molecules containing Five or More Carbon Atoms Supplement to Volume II/25* (Springer, 2007).
- [34] M. T. K. Kuchitsu, N. Vogt, *Structure Data of Free Polyatomic Molecules · Molecules Containing No Carbon Atoms and Molecules Containing One or Two Carbon Atoms* (Springer, 2014).
- [35] M. T. K. Kuchitsu, N. Vogt, *Structure Data of Free Polyatomic Molecules · Molecules Containing Three or Four Carbon Atoms and Molecules Containing Five or More Carbon Atoms* (Springer, 2014).
- [36] E. B. Wilson, *Molecular vibrations : the theory of infrared and Raman vibrational spectra* (McGraw-Hill, New York ;, 1955).
- [37] V. Bakken and T. Helgaker, *The Journal of Chemical Physics* **117**, 9160 (2002).
- [38] M. J. van Setten, F. Caruso, S. Sharifzadeh, X. Ren, M. Scheffler, F. Liu, J. Lischner, L. Lin, J. R. Deslippe, S. G. Louie, C. Yang, F. Weigend, J. B. Neaton, F. Evers, and P. Rinke, *Journal of Chemical Theory and Computation* **11**, 5665 (2015), pMID: 26642984.
- [39] A. Stuke, C. Kunkel, D. Golze, M. Todorović, J. T. Margraf, K. Reuter, P. Rinke, and H. Oberhofer, *Scientific Data* **7**, 58 (2020).
- [40] R. B. Shirts, *Journal of Chemical Education* **84**, 1882 (2007).
- [41] M. Bogey, H. Bolvin, C. Demuynck, and J. L. Destombes, *Phys. Rev. Lett.* **66**, 413 (1991).
- [42] M. Bogey, H. Bolvin, M. Cordonnier, C. Demuynck, J. L. Destombes, and A. G. Császár, *The Journal of Chemical Physics* **100**, 8614 (1994).
- [43] R. D. Johnson, “*NIST Computational Chemistry Comparison and Benchmark Database*,” (2022), NIST Standard Reference Database Number 101.
- [44] Private conversation between Nike Dattani and Gabe Cunningham (2023).