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

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We list all possible point groups for $1, 2, 3, 4$ and n atoms as well as for n-atom molecules with specified formulas. For each point group, we give examples of molecules of each size and formula if they are known, and hence we determine the yet-to-be discovered molecules with under 5 atoms for each point group. We establish a small set of principles that can be used for proofs about the possibility or impossibility for a molecule of a certain size and/or formula to have a point group symmetry.

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] 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. The closest we found was Atkins but it was wrong for minmal S4 (C2, C2v, etc.) and it doesn't include Dnh with extra 2n atoms on axis or extra atom in centre.

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 [37] and by the end of 2020, already more than 100 electronic structure methods/codes were used to calculate energies for all systems in the dataset. It has therefore become a monumental dataset for benchmarking, and efforts were made in [20] and [21] to improve the most accurate calculations that had been done on the system until then (and used to benchmark the other 100+ calculations from various research groups) [22]. But the geometries were wrong and we need to be able to generate them from places like the Landolt-Bornstein volumes [23–35]. Such volumes provide only the point group, a 3D diagram, and a minimal set of bond lengths, angles and dihedrals. For example H_2Si_2 (not in GW100 but good for illustrating this point) gives only two bond lengths and a dihedral, 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 softawre for obtaining either of these from just the limited information given. 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 you might find it surprising that the simplest formulas for the H-Si-H angle in H_2Si_2 are (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):

$$\theta = \arccos\left(\frac{\cos\varphi\left(4r_1^2 - r_2^2\right) + r_2^2}{4r_1^2}\right), \tag{1}$$

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

Determining this bond angle can be accomplished with some high school level trigonometry (applications of the ordinary cosine law), and appliocations 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 formulas as in Eqs. 1-2 would ideally be done by softawre rather than by hand. Unfortunately, not even the most advanced symbolic computation or comptuer algebra software can provide a user with Eqs. 1-2 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 such as GW5000 and OE62 (both from Stuke *et al.* [38]) which involve more than 5000 and 61000 molecules respectively, but they have the same geometry problem (crystal structures vs spectroscopic geometries). This reinforces our motivation for constructing a software that could, for example, convert the ~5000 geometries from Landolt-Bornstein 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 categorieze molecules (e.g. for training neural networks) and the question of which point groups are possibel for molecules of a certain size of formula, will be asked more and more (and those seeking the answers 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 ($r_1 = 2.2079, r_2 =$

$1.6839, \varphi = 103.18°$**) for H_2Si_2 would require specific code blocks for each molecular shape.** It is possible for two molecules with the same point group to have very different shapes (e.g. C_{2v} for H_2Si_2 and C_{2v} planar and maybe another 4-atom C_{2v}, all have 4 atoms but one is pyramidal, one is planar, etc.), so a "z-matrix generator" or "xyz coordinates generator" would need specific code blocks for n-atom molecules not just based on their point group, but also based on other characteristics (perhaps their graph, formula, etc.), but a natural first step towards constructing such a software would be to categorize n-atom molecules based on their point groups (as done in the Landolt Bornstein series, CCCBDB and a lot of other places, check CRC), and to construct code for each case. **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 everyone tell us that it hasn't been done yet. We take this even one step further, by looking at the possible formulas, for example for a 7-atom molecule to have the point group Ci you need its formula to be $A_2B_2C_2D$ (with any of B,C,D being allowed to be a duplicate of one of the previous letters) but a molecule with any other formula cannot have the point group Ci (for example $A_2B_2C_2$ would no work unless B and C are A, which would bring us back to the previously mentioned formula in the case in which A=B=C=D).

In the initial stages of the development of our z-matrix constructor, we found that the Landolt-Bornstein series had all these molecules, but we realized that we missed the tadpole structure because we know that there's 6 connected 4-vertex graphs. Likewise we tried to see if we had representation from all possible point groups, and this required us to first determine the possible point groups for 4-atom molecules (which surprisingly we couldn't find, and we found that experts who wrote books on the topics were also unaware). In doing this, we discovered that D_2 and D_{2d} are possible but not yet found, so this may be an avenue for further experimental research.

Another motivation was geometry optimization. Roland Lindh and others have discovered that you can get fewer cycles, but if point group symemtry is included, then we can have a smaller Wilson-B matrix.

In this paper we provide general principles, 3-atom and 4-atom possible groups, formulas and examples, n-atom groups and formulas for minimal structures, all of which seems to be novel. We skip the polyhedral groups $T, T_d, T_h, O, O_h, I, I_h$ since we discovered something with fewer vertices than the snub cube that has O symmetry.

GENERAL PRINCIPLES FOR POSSIBLE MOLECULES

The following general principles will be used. They might seem obvious, but we don't see them in textbooks (maybe the first one is in textbooks) [1–18, 36].

Ability to orient a molecule according to the valid point group operations on the molecule:

Any molecule with a rotation axis, called a C_n-axis, can be oriented in an xyz (Caterian) coordinate system such that for the largest possible n value in C_n, the z-axis is aligned wtih a C_n axis, and a σ_h plane 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 the molecule contains a subset of atoms that are vertices of an n-sided polygon with equal side-lengths (a regular n-gon). A C_n axis would be in the center of this polygon, and since we can call this axis the z-axis, all atoms that form vertices of the polygon, 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, because of the definition of a C_n rotation, 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 identaical atom in the molecule if the axis is indeed a C_n axis.

Necessary and sufficient conditions for the D_{nh} point group:

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}, and any object with the D_{nh} point group must contain a subset of identical vertices that form a regular n-gon if with $n \geq 3$.

Action of the S_n operation:

An S_n operation is by definition a C_n operation followed by a σ_h reflection operation. If we define the associated C_n-axis to be the z-axis, and the σ_h plane to be the xy-plane, then if an atom originally had coordinates (x, y, z), it will have coordinates (x', y', z) after the C_n rotation, and coordiantes $(x', y', -z)$ after the σ_h reflection. So S_n operation moves atoms from (x, y, z) to $(x', y', -z)$. As described in the section about the existence of a C_n axis, the the new coordinates (x', y') can be different from the old ones (x, y) but will coincide with the original xy-coordinates of another identaical atom in the molecule if the molecule indeed has a C_n axis.

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 $(-x,-y,-z)$.

MINIMUM NUMBER OF ATOMS AND POSSIBLE MOLECULAR FORMULAS FOR EACH POINT GROUP

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

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 invesrion 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 $A_2B_2C_2D_2\cdots$ or $AB_2C_2D_2\cdots$ depenending on if the number of atoms is even or odd.**

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,... 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 one additional atom is not only necessary, but also 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 wtih 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 $A_nBCD\cdots$.**

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 positon $(-x,-y,-z)$ 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 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.**

$\underline{n \geq 3}$

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 concldue 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 $A_nB_2C_2D_2\cdots$, and for an odd number of additional atoms the most general formula would be $A_nBC_2D_2\cdots$.**

$\underline{C_n}$

$\underline{n=2}$

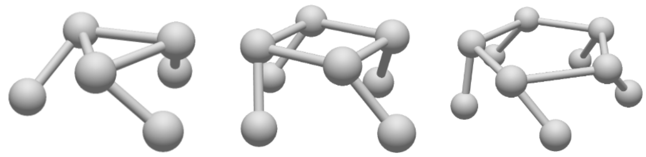
If we have any fewer than three atoms, the point group of the system will be promoted to $K_h, D_{\infty h}$ or $C_{\infty v}$; and if we have only three atoms, they form a plane which will be a mirror plane, meaning that the point group of the system which contains a C_2 axis will be promoted to C_{2v} or D_{3h}. Four atoms would be enough for the point group of the system to be C_2 though, as in the case of H_2O_2. **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 C_2 axis (which we will make the z-axis, as we described in the previous section), these atoms will be at positions $A' = (-x_1 - y_1, z_1)$ and $B' = (-x_2, -y_2, z_2)$ respectively, and for the C_2 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 $A_2B_2CD\cdots$ since the extra atoms C,D,... can be placed on the C_2 axis without any loss of valid symmetry operations, and if their positions are chosen carefully, no new valid symmetry operations would be introduced.**

$\underline{n \geq 3}$

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 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 Fig. 1). 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 $A_nB_nCD\cdots$ since in addition to the A_nB_n structure, extra atoms C,D,... 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.**

Figure 1: Structures with the point group C_n and with the minimum number of atoms, $2n$.

(a) $n = 3$ (b) $n = 4$ (c) $n = 5$



C_{nh}

$n = 2$

d

$n \geq 3$

We can repeat everything that was written in the section about C_n, except that the structure is now allowed for the two regular n-gons to be on the same plane (and therefore concentric since they share the same C_n axis) since having all atoms on the same plane means that the structure lies on a σ_h plane, which is allowed (and needed) for the point group to be C_{nh}. All other elements of the C_{nh} point group can be generated from the C_n and σ_h operations, so the point group of the described structure is indeed C_{nh}. Such a structure with $2n$ atoms is possible, as in the case of...

D_n

$n = 2$

Not explained well.

$n \geq 3$

Not explained well.

D_{nd}

$n = 2$

Not explained well.

$n \geq 3$

We can repeat everything that was written in the section about C_n, except with the second regular n-gon (the one that is added) being rotated by π/n radians (and the two regular n-gons still being on two different planes). Such a structure with $2n$ atoms is possible, as in the case of...

S_{2n}

$n = 2$

If we have any fewer than three atoms,

$n \geq 3$

Since S_{2n} is a generator of the S_{2n} point group, C_n is in the point group because $S_{2n}^2 = C_n$. This means we need a regular n-gon with the C_n axis cutting perpendicularly through its center, but a regular n-gon will not satisfy the S_{2n} operaton unless all atoms are at the origin. You need 2n to have an S2n axis, but then you'd get Dnh, so you need another 2n to break the Dnh. **The minimum number of atoms required is $4n$.**

SUMMARY OF OUR RESULTS

Point groups		Number of atoms								
		Minimum	1	2	3	4	5	6	7	8
K_h		1	✓	✗	✗	✗	✗	✗	✗	✗
$D_{\infty h}$		2	✗	✓	✓	✓	✓	✓	✓	✓
$C_{\infty v}$		2	✗	✓	✓	✓	✓	✓	✓	✓
D_{nh}	$n \geq 3$	n	✗	✗	✓	✓	✓	✓	✓	✓
	$n = 2$	4	✗	✗	✗	✓	✓	✓	✓	✓
D_{nd}	$n \geq 2$	$2n$	✗	✗	✗	✓	✓	✓	✓	✓
D_n	$n \geq 2$	$2n$	✗	✗	✗	✓	✓	✓	✓	✓
S_{2n}	$n \geq 2$	$4n$	✗	✗	✗	✗	✗	✗	✗	✓
C_{nv}	$n \geq 2$	$n+1$	✗	✗	✓	✓	✓	✓	✓	✓
C_{nh}	$n \geq 2$	$2n$	✗	✗	✗	✓	✓	✓	✓	✓
C_n	$n \geq 2$	$2n$	✗	✗	✗	✓	✓	✓	✓	✓
C_s		3	✗	✗	✓	✓	✓	✓	✓	✓
C_i		6	✗	✗	✗	✗	✗	✓	✓	✓
C_1		4	✗	✗	✗	✓	✓	✓	✓	✓

N	Possible groups (not including subgroups)																													
1																														K_h
2																												$D_{\infty h}$	$C_{\infty v}$	
3	C_s									C_{2v}											D_{3h}							$D_{\infty h}$	$C_{\infty v}$	
4	C_s		C_1	C_2			C_{2h}			C_{2v}	C_{3v}					D_2		D_{2d}		D_{2h}	D_{3h}	D_{4h}				T_d		$D_{\infty h}$	$C_{\infty v}$	
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}	D_{5h}			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_3	D_{2d}	D_{3d}	D_{2h}	D_{3h}	D_{4h}	D_{5h}	D_{6h}			O_h	$D_{\infty h}$	$C_{\infty v}$	
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}	D_{7h}		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}	D_2	D_3	D_{2d}	D_{3d}	D_{2h}	D_{3h}	D_{4h}	D_{5h}	D_{6h}	D_{7h}	T_d	O_h	$D_{\infty h}$	$C_{\infty v}$	

Possible point groups for 3-atom (triatomic) molecules

Point group	Chemical formula type		
	A_3	A_2B	ABC
$D_{\infty h}$	C_3	CO_2	✗
$C_{\infty v}$		N_2O	HOS
D_{3h}	H_3^+	✗	✗
C_{2v}	O_3	H_2O	✗
C_s	$H\cdots H_2$	HO_2	HNO

Possible point groups for 4-atom (tetraatomic) molecules

Point group	Chemical formula type				
	A_4	A_3B	A_2B_2	A_2BC	ABCD
T_d	P_4	✗	✗	✗	✗
$D_{\infty h}$	C_4	✗	C_2H_2	✗	✗
$C_{\infty v}$		C_3H	ABAB?	H_2BN	
D_{4h}	S_4^{2+}	✗	✗	✗	✗
D_{3h}	C_4	H_3B	✗	✗	✗
D_{2h}			Br_2Na_2	✗	✗
D_{2d}	S_4	✗	✗	✗	✗
D_2	**Unknown**	✗	✗	✗	✗
C_{3v}		H_3N	✗	✗	✗
C_{2v}		IF_3	H_2Si_2	CH_2O	✗
C_{2h}			H_2N_2	✗	✗
C_2			H_2O_2	✗	✗
C_s		HO_3^+		Cl_2OS	CHFO
C_1				H_2OS	CHBrCl

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