

Complete Sets and Redundancies among Small Vibrational Coordinates

J. C. Decius

Citation: *The Journal of Chemical Physics* **17**, 1315 (1949); doi: 10.1063/1.1747158

View online: <http://dx.doi.org/10.1063/1.1747158>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jcp/17/12?ver=pdfcov>

Published by the AIP Publishing

Articles you may be interested in

[Efficient coding of redundancy among formant frequencies in vowels](#)

J. Acoust. Soc. Am. **132**, 1967 (2012); 10.1121/1.4755249

[Unambiguous formalism of molecular vibrations: Use of redundant coordinates and canonical matrices](#)

J. Chem. Phys. **110**, 3302 (1999); 10.1063/1.478195

[A quantum mechanical description of vibrational motion in benzene in terms of a completely symmetrized set of complex vibrational coordinates and wave functions](#)

J. Chem. Phys. **108**, 4797 (1998); 10.1063/1.475890

[Geometry optimization in redundant internal coordinates](#)

J. Chem. Phys. **96**, 2856 (1992); 10.1063/1.462844

[On the Detection and Determination of Redundant Vibrational Coordinates](#)

J. Chem. Phys. **17**, 840 (1949); 10.1063/1.1747412



Complete Sets and Redundancies among Small Vibrational Coordinates*

J. C. DECUS**

Metcalf Chemical Laboratories, Brown University, Providence, Rhode Island

(Received May 6, 1949)

A simple prescription is given for defining internal coordinates of the bond stretching, bending, out-of-plane bending, and torsional types which yields a kinematically complete set of vibrational coordinates with no redundancies in acyclic molecules and with 6μ redundancies in cyclic molecules, where μ is the number of bonds which must be deleted to render the molecule acyclic.

I. INTRODUCTION

THERE are four types of internal coordinates which have been used most extensively in the mathematical formulation of the small vibration problem for polyatomic molecules. All are defined with reference to the valence bonding system assumed for the molecule. They may be described as follows:

(i) Bond stretching: to be designated in general by the symbol r , this coordinate represents the difference of the distance between two directly bonded atoms in a distorted configuration and the distance at equilibrium.

(ii) Bond angle: this class of coordinates is given the general symbol, ϕ , and represents the difference between the angle formed by two adjacent bonds in a distorted configuration and the corresponding angle at equilibrium. In the case of a linear molecule, or of a linear part of a larger molecule (such as the four carbons of dimethyl acetylene) two ϕ 's can be defined at each internal atom, taking the motion to occur in perpendicular planes whose line of intersection is along the molecule. Whenever this case occurs, the second set of angles will be designated by ϕ' .

(iii) Out-of-plane bending: coordinates of this class can be defined at any atom where three or more coplanar bonds are coincident (e.g. formaldehyde, carbonate ion, ethylene). Such a coordinate, for which the class symbol is γ , can be taken as the angle of one bond relative to the plane of any two other bonds.

(iv) Bond torsion: a coordinate of this last class, designated by τ , can be defined wherever the atoms at each end of a bond (or of a linear part of a molecule comprising any number of colinear bonds) each are also bonded to additional atoms by bonds not colinear with the bonds connecting the two atoms in question. These latter two terminal bonds taken respectively with the connecting bond (or bonds) define two planes, and the torsional angle may be defined as the change in the dihedral angle between the two planes. Examples are very common, such as torsion about the carbon-carbon bond in ethane, about a carbon-carbon bond in a benzene or cyclohexane ring, etc.

Once these coordinates have been defined, two rather interesting questions arise. The first is whether coordi-

nates of these four classes are in every case sufficient to describe all vibrational degrees of freedom, i.e., whether sets of them can be chosen so as to be "complete." The second question is concerned with the problem of redundancy, i.e., linear dependency between some of the coordinates chosen when, for reasons of exploiting the symmetry¹ of the molecule, more than the required number of coordinates are selected. It should be remarked at this point that the redundancies may most conveniently be discovered in some cases after passing to symmetry coordinates.²

In the remainder of this paper, it will be shown how to choose coordinates of only the four types described above in such a way as to obtain an exactly complete set for acyclic molecules (no redundancies), or a set which contains redundancies of a purely cyclic nature for cyclic molecules. In other words, we shall show how to distinguish between the only two possible types of redundancies which can occur with our four fundamental coordinate classes, namely *local* and *cyclic* redundancies.

II. CONNECTIVITY OF THE MOLECULE

In our analysis, we shall make use of some of the simplest concepts of *analysis situs*³ in reference to the aggregation of atoms and bonds which constitute the molecule. It will be assumed that all molecules are connected, which means, loosely, that all atoms in the molecule are bonded either directly or indirectly. Put somewhat differently, it is possible to trace a path from any point of the molecule (either an atom or a point along a bond) to any other point, without leaving the bonds or atoms. If the molecule is acyclic, it is not hard to see that

$$a - b = 1 \quad (1)$$

where a is the number of atoms and b is the number of

¹ E. B. Wilson, Jr., J. Chem. Phys. 9, 76 (1941).

² C. E. Sun, R. G. Parr, and B. L. Crawford, Jr., J. Chem. Phys. 17, 840 (1949).

³ The following correspondence exists between the notation in this paper and that employed by O. Veblen, "Analysis Situs" (American Mathematical Society, New York, 1931):

Present paper	Veblen
μ	μ
a	α_0
b	α_1

* This work was supported by the Office of Naval Research under Contract N6ori-88, Task Order No. 1.

** Present address: Department of Chemistry, Oregon State College, Corvallis, Oregon.

bonds.⁴ For cyclic molecules, the quantity, μ , defined by

$$\mu = b - a + 1 \quad (2)$$

is greater than zero, and is, in fact, equal to the number of bonds which must be deleted in order to render the molecule acyclic. As an example, naphthalene has 19 bonds and 18 atoms, hence $\mu = 2$.

It will prove useful to classify atoms in terms of their *multiplicity*, that is the number of bonds which meet at the atom in question. If the number of atoms of multiplicity m be designated by the symbol a_m , then it is obvious that

$$a = \sum_{m \geq 1} a_m \quad (3)$$

moreover

$$b = \frac{1}{2} \sum_{m \geq 1} m a_m \quad (4)$$

since $\sum m a_m$ counts every bond twice.

III. LINEAR MOLECULES

Although the case of the linear molecule is very simple, it is carried through by way of introduction. The number of vibrational degrees of freedom is

$$f = 3a - 5. \quad (5)$$

Obviously there are $n_r = b = a - 1$ independent stretching coordinates. Moreover, the numbers of bending coordinates are clearly $n_\phi = a - 2$ and $n_{\phi'} = a - 2$. Thus there are in all

$$n_r + n_\phi + n_{\phi'} = (a - 1) + 2(a - 2) = 3a - 5 \quad (6)$$

independent internal coordinates, which is precisely the required number.

IV. PLANAR MOLECULES

Here the in-plane and out-of-plane degrees of freedom can be distinguished, with

$$f_i = 2a - 3, \quad (7)$$

$$f_o = a - 3 \quad (8)$$

respectively. The numbers of coordinates of the four basic types may therefore be considered separately for the two types of motions.

In-plane modes. Only two of the types can contribute to the description of in-plane motions, namely r and ϕ . For the first type, the maximum number of coordinates which can be defined is clearly

$$n_r = b.$$

On the other hand, it is possible to define a maximum of $m(m-1)/2$ ϕ 's at each atom of multiplicity m , but this would lead to certain *local* redundancies which we prefer

⁴ It should be clear that in the present analysis the chemical nature of the bond is irrelevant, i.e., the carbon-carbon bond counts as one bond only, whether in ethane, ethylene, or acetylene.

to eliminate at the outset. From elementary geometry it is apparent that the number of locally independent angles at an atom of multiplicity m is $m-1$. Therefore, this number of angles will be taken at each such atom, giving rise to the following total number of ϕ :

$$\begin{aligned} n_\phi &= a_2 + 2a_3 + 3a_4 + \cdots \\ &= \sum (m-1)a_m \\ &= 2b - a \end{aligned} \quad (9)$$

where the final form makes use of (3) and (4). Therefore, the sum of the stretching and bending coordinates is

$$\begin{aligned} n_r + n_\phi &= 3b - a \\ &= f_i + 3\mu \end{aligned} \quad (10)$$

using the definition of μ given in (2). We conclude that the above prescription of the choice of coordinates leads to at least 3μ redundancies. But it is proved in an Appendix that the coordinates left after deleting μ -bonds (so as to make the molecule acyclic) are linearly independent (the proof is conveniently given for linear, planar, or general molecules, simultaneously), hence the sets of internal coordinates prescribed are complete.

Out-of-plane modes. To simplify the discussion, it will be assumed initially that the molecule contains no linear submolecule, that is, no set of two or more adjacent colinear bonds. Later it will be shown how to modify the result when such submolecules do occur.

The prescription of coordinates is as follows:

(i) Choose one τ to correspond to each non-terminal bond (e.g., one for each of the six C-C bonds in benzene, but none for the C-H bonds).

(ii) Choose $m-2$ γ 's at each atom of multiplicity m . The numbers of out-of-plane coordinates are then:

$$n_\tau = \sum_{m \geq 2} (m-2)a_m = 2(b-a) + a_1 \quad (11)$$

and

$$n_r = b - a_1 \quad (12)$$

so that the sum is:

$$n_\gamma + n_\tau = 3b - 2a = f_o + 3\mu. \quad (13)$$

This result makes it clear that if the molecule has been rendered acyclic by deleting μ -bonds, the number of coordinates defined will be exactly the number required. An examination of the elementary geometry of any one of the polygons constituting a cycle shows that the redundancies consist of exactly three relations per polygon between the τ 's only. In the symmetrical case, one relation is the simple sum of the τ 's (in a given polygon), while the other two relations are slightly more complicated, appearing as a degenerate pair amongst the symmetry coordinates.

It must next be shown how to modify the prescription if there are linear submolecules. It is not hard to see that each linear submolecule of length l (bonds), $l > 1$, reduces the total number of γ and τ by $l-1$, but introduces exactly $l-1$ coordinates of type ϕ' . Thus the net count

is unaffected. It should be noted that in some cases it will be necessary to include a torsion around the whole length of colinear bonds.

V. GENERAL MOLECULES

The number of vibrational degrees of freedom is

$$f = 3a - 6. \quad (14)$$

Initially it will be assumed that the molecule contains neither linear submolecules, nor atoms for which $m > 2$ at which all the incident bonds are coplanar. Under these conditions, the prescription of coordinates will take the following form.

(i) Let a bond stretch be defined for each bond; then

$$n_r = b. \quad (15)$$

(ii) A maximum of $m(m-1)/2$ coordinates of type ϕ can be defined at each atom of multiplicity m . However, it can be shown** that only $2m-3$ such angles are independent locally. If this number of angles be chosen† at each such atom, then the total number will be:

$$n_\phi = \sum_{m \geq 2} (2m-3)a_m = 4b - 3a + a_1. \quad (16)$$

(iii) As previously in the planar case, the number of torsions will be taken to correspond with the number of non-terminal bonds, which is

$$n_r = b - a_1. \quad (17)$$

Thus the following sum of coordinates is obtained:

$$\begin{aligned} n_r + n_\phi + n_\tau &= b + (4b - 3a + a_1) + (b - a_1) \\ &= f + 6\mu. \end{aligned} \quad (18)$$

Thus, in the general case, our prescription leads to 6μ redundancies, or no redundancies in the acyclic case. The proof that the f coordinates remaining in any case after the deletion of μ -bonds are independent is given, as noted above, in the Appendix.

It is now possible to eliminate the previous restriction which excluded cases in which the molecule contained linear submolecules, or atoms of multiplicity greater than two with all bonds coplanar. For each case of the first kind, when the linear submolecule is of length l

** This can be done by spherical trigonometry or by consideration of a molecule consisting of the atom in question plus m radially bonded atoms. The m bond stretches are independent of one another and of any ϕ 's which can be described in such a system (see Appendix). Since $3a-6$ is here $3(m+1)-6=3m-3$, it follows that $(3m-3)-m=2m-3$ angles are independent.

† It is to be noted that not every choice of $2m-3$ angles is correct. For $m=5$, seven ϕ 's might be chosen in such a way that all pairs for four of the bonds were used, giving 6ϕ 's, the seventh being chosen so as to include the fifth bond. Since this choice would be incorrect for the methane-like submolecule, it would also be incorrect for the larger molecule. In general, a choice which is shown in the Appendix to be independent can be made as follows: select three bonds which are not coplanar and define a ϕ between each pair; then in a stepwise fashion, define two additional non-coplanar ϕ 's for each additional bond, in each step using only the bonds which have been tied together at the end of the previous step.

bonds, the loss in definable τ 's is $l-1$, but this is exactly compensated by the addition of $l-1$ coordinates of type ϕ' . Here again, if the linear submolecule is not terminal, there will be one torsion which can still be defined extending across the entire linear submolecule.

When the second situation occurs, the $2m-3$ ϕ 's defined at the atom in question are no longer independent. However, it is merely necessary to substitute $m-2$ γ 's for ϕ 's (leaving $m-1$ ϕ 's) at each such atom so that there is no net loss of coordinates. Thus the general prescription becomes: choose as many τ 's as there are bonds; as many τ 's as there are non-terminal bonds, replacing as many τ 's as necessary by ϕ 's in the event of linear submolecules; finally, choose $2m-3$ ϕ 's at each atom of multiplicity m , but at each atom with $m > 2$ at which all bonds are coplanar, replace $m-2$ ϕ 's by γ 's. The resulting set of coordinates will consist of $f+6\mu$ coordinates in all, of which f are linearly independent.

VI. SOME EXAMPLES AND CONCLUSIONS

First, a few examples will be given to illustrate the count of redundancies and definition of complete sets of coordinates.

1. Sulfur hexafluoride:

$$\begin{aligned} a &= 7, & b &= 6, & \mu &= 0, & f &= 15, \\ n_r &= 6, & n_\phi &= 9, \\ n_r + n_\phi &= 15 = f. \end{aligned}$$

The nine ϕ 's may be chosen, for example, by taking all bond angles which are 90° at equilibrium except those bordering one octant.

2. Benzene:

$$\begin{aligned} a &= 12, & b &= 12, \\ f_i &= 21, & f_o &= 9; & \mu &= 1. \end{aligned}$$

In-plane modes:

$$\begin{aligned} n_r &= 12, & n_\phi &= 12, \\ n_r + n_\phi &= 24 = f_i + 3\mu = 21 + 3. \end{aligned}$$

Out-of-plane modes:

$$\begin{aligned} n_\gamma &= 6, & n_\tau &= 6, \\ n_\gamma + n_\tau &= 12 = f_o + 3\mu = 9 + 3. \end{aligned}$$

3. P_4O_6 :

Consider this molecule to be of tetrahedral form, with the phosphorus atoms at the vertices, the oxygen atoms midway along the edges.

$$\begin{aligned} a &= 10, & b &= 12; & f &= 24, & \mu &= 3, \\ n_r &= 12, & n_\phi &= 18, & n_\tau &= 6, & n_{\phi'} &= 6. \end{aligned}$$

In this example, three O-P-O ϕ 's are taken at each vertex and one P-O-P is taken as a ϕ at each O. The six torsions are about the six P-O-P bond sequences (each edge). The set ϕ' consists of six additional P-O-P bendings at the oxygens. The sum of the coordinates is:

$$n_r + n_\phi + n_\tau + n_{\phi'} = 42 = f + 6\mu = 24 + 18.$$

If the oxygen atoms are displaced from the lines between the various pairs of phosphorus atoms, $n_r = 12$, $n_\phi = 0$.

In conclusion, two points should be emphasized. The first is, that for reasons of symmetry, numerous additional redundancies may be introduced *locally*:^{††} the present analysis makes it possible to distinguish these redundancies from the cyclic ones. The second point to be made is, that although the sets of coordinates prescribed in this paper have been shown to be complete, there are molecular examples in which simpler, more symmetrical prescriptions can be shown to be complete. The P_4 molecule, with atoms as vertices and bonds as edges of a tetrahedron is of this type, since the set of the six bond stretches alone is a complete set.

APPENDIX

It is desired to prove that the f coordinates remaining in any molecule after deletion of $\mu = b - a + 1$ bonds are linearly independent.

If the i -th such coordinate be designated by S_i , then the set of coordinates will be linearly independent if and only if the only set of constants, c_i , which satisfy

$$\sum_{i=1}^f c_i S_i = 0 \quad (19)$$

are

$$c_i = 0, \quad i = 1, 2, \dots, f. \quad (20)$$

Using concepts introduced by Wilson,¹ the internal coordinates may be expressed in terms of independent displacement vectors, $\rho_1, \rho_2, \dots, \rho_a$ of the several atoms in the form

$$S_i = \sum_{\sigma=1}^a \mathbf{s}_{i\sigma} \cdot \rho_{\sigma}. \quad (21)$$

where $\mathbf{s}_{i\sigma}$ is a vector which indicates the direction in which the displacement of the σ -th atom makes the maximum contribution to S_i . The condition for linear independence can then be formulated as follows: Combining (19) and (21)

$$\sum_{i=1}^f c_i \sum_{\sigma=1}^a \mathbf{s}_{i\sigma} \cdot \rho_{\sigma} = \sum_{\sigma=1}^a \sum_{i=1}^f c_i \mathbf{s}_{i\sigma} \cdot \rho_{\sigma} = 0. \quad (22)$$

But, owing to the independence of the ρ_{σ} , (22) holds if and only if

$$\sum_{i=1}^f c_i \mathbf{s}_{i\sigma} = 0, \quad \sigma = 1, 2, \dots, a. \quad (23)$$

Therefore, linear independence of the f coordinates requires that the only solution of the a equations of (23) be that in which all c_i vanish.

The proof will be given by mathematical induction. It will be shown that:

(i) The prescribed set of coordinates for the case, $a = 2$, is linearly independent;

^{††} Local redundancies in this sense must be taken to include those introduced, for example, in ethane by taking more than one r about the carbon-carbon bond.

(ii) If the set of coordinates prescribed for the case $a = n$ is assumed linearly independent, then the prescribed set for $a = n + 1$ is necessarily linearly independent.

The proof of (i) is trivial: the prescribed set for the diatomic molecule consists solely of the single bond stretching coordinate, which, as is well known, represents the single vibrational degree of freedom in such a case.

In order to prove (ii), first consider every possible way by which the addition of one atom to a set of n atoms augments the prescribed set of coordinates. Note that only acyclic molecules need be considered. Depending upon the multiplicity of the atom to which the additional atom is attached, and also upon the possibility that the new bond may be colinear or coplanar with bonds in the original molecule, the new coordinates must constitute a set of one of the following five types:[‡]

- (1) $r, \phi, \tau,$
- (2) $r, \phi, \phi',$
- (3) $r, \phi, \phi,$
- (4) $r, \phi, \gamma,$
- (5) $r, \phi.$

A detailed examination of the $\mathbf{s}_{i\sigma'}$ vectors for the new atom ($\sigma' = n + 1$), shows that for each of the above five sets, the vectors are linearly independent. For example, for the first set $\mathbf{s}_{r\sigma'}$ is along the new bond, $\mathbf{s}_{\phi\sigma'}$ is perpendicular to the new bond and in the plane defined by the new bond and a (terminal) bond of the original molecule, $\mathbf{s}_{\tau\sigma'}$ is perpendicular to both $\mathbf{s}_{r\sigma'}$ and $\mathbf{s}_{\phi\sigma'}$. Case (3), on the other hand, gives rise to an $\mathbf{s}_{r\sigma'}$ which is along the new bond, and to $\mathbf{s}_{\phi_1\sigma'}$ and $\mathbf{s}_{\phi_2\sigma'}$ which are perpendicular to the new bond but not themselves colinear.

Case (5) holds for the transition from a linear to a planar molecule.

It is now evident that (23) can only hold in the augmented molecule at the new atom if the c_i corresponding to the new coordinates are all zero. Therefore, any linear dependence for the augmented molecule must involve only the original coordinates, which by hypothesis, are linearly independent. This shows that the set of coordinates prescribed for the augmented molecule is linearly independent if that for the original molecule was. This completes the proof of the independence of the coordinates prescribed for any acyclic molecule.

[‡] This statement holds even when the addition of an atom changes the molecule from linear to planar, or from planar to non-planar, with one exception, namely the case where the new atom is bonded to a planar molecule at an atom of multiplicity m greater than two in such a way as to produce a non-planar molecule. For this special case, the strict use of the coordinate prescription yields one new r , m new ϕ 's, and results in a loss of $m - 2$ γ 's. This difficulty may be eliminated by the observation that any final acyclic configuration may be reached from the diatomic molecule by steps of addition of one atom in which the special step just described is not required. Thus, for any atom which is ultimately to have m bonds not coplanar, we may imagine the atoms added in such an order that the first three are bonded to the central one by non-coplanar bonds, subsequently adding as many as desired in a given plane.