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On the Use of Projection Operators in Molecular Dynamics

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Symmetry coordinates are easily constructed when operating in mass-weighted Cartesian space. Such coordinates can be used to block diagonalize automatically the secular equation occurring in the harmonic approximation of dynamics of large molecules. Examples of the usefulness of the method are given.

Key words: Symmetry in molecular dynamics – Projection operators and Cartesian coordinates

1. Introduction

Gwinn [1] has shown that Cartesian coordinates are more suitable when studying molecules with the help of computers. Advantages when using such coordinates are numerous. A N atom molecule has always a 3 N dimensional secular equation whatever the number of force constants introduced. Various types of fields can be used: the valence force field (Gwinn [1]), the Urey-Bradley force field (Hilderbrandt [2]), and the force field derived from analytical functions (Sanquer [3]). Furthermore, the word redundancy does not even need to appear anywhere. There are always six zero roots corresponding to rotations and translations of the molecule as a whole (in a non-linear molecule).

Group theory is very useful in molecular dynamics to reduce the size of the equations. But the use of computers and internal coordinates require skilled human operators to introduce, "by hand", the convenient relations in the machine. Moreover, in small molecules one spends very little time to diagonalize the secular equation matrix. The information needed to compare theory and experiment can be obtained by a look at the resulting eigenvectors. The classification of the frequencies according to the symmetry species can be done automatically (Dellepiane [4]).

However, in our study of large molecules, namely durene and its halogenoderivatives, a simplification of the secular equation was needed. A powerful procedure to introduce symmetry was found. The method has analogies with those so often used in solid state physics and is the transcription of the method by which Herzberg predicted, without any calculation, the form of vibrations in various molecules; this shows that the method has a real physical meaning independent of the particular force field used.

This formulation requires as supplementary data the introduction of symmetry operations in the form of 3 x 3 matrices and also the characters of the species as given in most textbooks on molecular dynamics [6]. We use symmetry at the start so that our way is quite different from those proposed by Dellepiane [4] and Gwinn [1].

2. The Method

We shall use the valence force field to expose the principles of the method; the arguments are identical for other force fields. Let $\boldsymbol{S}$ denote the column matrix of internal coordinates, $\boldsymbol{F}$ is the potential square matrix in these coordinates. Let $\boldsymbol{q}$ denote the column matrix of mass-weighted Cartesian coordinates. Wilson [5] has introduced a $\boldsymbol{B}$ matrix so that $\boldsymbol{S} = \boldsymbol{Bq}$.

Gwinn [1] showed that in the mass-weighted Cartesian system the kinetic energy matrix does not need to appear since it is the unit matrix and the frequencies are square-roots of eigenvalues of a $\boldsymbol{V}$ matrix, elements of which are computed through

$$V_{ij} = \sum_{lm} B_{li} B_{mj} F_{lm} \tag{1}$$

B_{li}, B_{mj} being elements of $\boldsymbol{B}$.

This expression essentially means that each element of $\boldsymbol{V}$ is a linear combination of elements of $\boldsymbol{F}$.

We now construct by some process a set of symmetry coordinates so that:

$$X_s = \sum_i C_{si} q_i, \tag{2}$$

In the new system one has, the transformation being unitary,

$$W_{rs} = \sum_{i,j} C_{ri} C_{sj} V_{ij}. \tag{3}$$

$\boldsymbol{W}$ is the potential energy matrix in the new system.

This can be written as

$$W_{rs} = \sum_{i,j,l,m} C_{ri} C_{sj} B_{li} B_{mj} F_{lm} \tag{4}$$

Once more the potential energy matrix terms can be evaluated as a sum of terms containing linearly the elements of F.

Of course W_{rs} needs to be evaluated only for X_r and X_s belonging to the same species.

3. Construction of Symmetry Coordinates

Let us denote by G the symmetry group of the molecule, i labelling some element of G. It is a well-known result of molecular dynamics that if atom 1 is sent to the emplacement of atom 2 by the symmetry operation i and that if the motion of atom 1 is known the motion of atom 2 is also known (to a phase factor). When dealing with symmetry it is usual to introduce "sets of equivalent nuclei". If, in a molecule of N atoms, there are n such sets it appears that the secular equation will break down in blocks, maximal dimension of which will be $3n$.

Further simplifications are derived from the fact that some atoms lie on symmetry elements which influence Cartesian coordinates of atoms in special positions to disappear from equations attached to some species. We shall then use the well-known projection expression [6]

$$X_s^p = L \sum_i C_i^p \cdot A_i \cdot q_s \tag{5}$$

L is a normalization factor. It is known from group theory that $L \sim \sqrt{d/g}$, where d is the dimension of the p irreducible representation, g the order of the group, i.e. the number of symmetry operations belonging to the molecule.

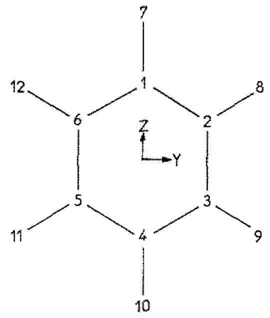

Fig. 1. Labelling of atoms in an hexagonal molecular model

q_s is a mass-weighted Cartesian coordinate associate with a representative atom of a set of equivalent nuclei.

C_i^p is the character associated with i in the p irreducible representation.

The summation is to be carried out on all operations i of the group G with possible redundancies. $A_i \cdot q_s$ then denotes the result of operation i on q_s.

4. Study of an Hexagonal Molecule (Benzene)

The benzene molecule has twelve atoms. There is no difficulty to treat such a molecule without accounting for the symmetry but its simple structure made it a good test for our method.

Moreover good valence force fields are available for this molecule. We used the field given by Scherer [7, 8] in his work on the chlorobenzenes. The full symmetry group of benzene is D_{6h} [6]; we shall not give character tables as these are available in many places. This model has two sets of equivalent nuclei, one formed by all C atoms the other by all H atoms. Let us choose as the representatives of the two sets atom 1 and atom 7 (see Fig. 1). It appears that in A_{1g} species of D_{6h} the only possible displacement of 1 and 7 is along the z axis, this is obtained automatically by applying Eq. (5) to the subgroup of G which leaves 1 and 7 invariant. All coefficients of Eq. (2) are then obtained by repeated application of operation C_6. Thus in the A_{1g} species of benzene one has to diagonalize a 2 x 2 matrix.

This can be repeated for all species of D_{6h}. Degenerate modes, however, need special attention. These modes cannot be expressed in terms of one linear term; moreover they transform themselves in a somewhat different manner in C_n or S_n operations: there is a supplementary rotation (Herzberg [5]). Such a transformation is quite predictable from the characters of the corresponding species and the correct coefficients of Eq. (2) are quite easy to obtain. But when calculating mean-square displacements one must take into account the arbitrariness of the starting choice as this procedure can give only one frequency and one eigenvector for the degenerate pair (Cyvin [9]). Triply degenerate species were not considered. One advantage of this approach is to permit an easy study of the molecule within one subgroup of its full symmetry group, e.g. subgroups of D_{6h} which may present some chemical interest are $D_{3h}, D_{2h}, C_{2v}, C_i$. The restriction of a group to one of its subgroups is obtained by suppressing symmetry operations, thus increasing the number of sets of equivalent nuclei. In D_{2h} symmetry atoms 1 and 2 no longer belong to the same set of equivalent nuclei. The correspondence between the species of various symmetry groups could be predicted by the correlation table of Wilson [6].

The asymmetric molecule can be treated as a special case with only one species, each atom being one set of equivalent nuclei by itself, all zero roots falling in the unique species.

A Fortran IV programe[1] has been written and tested on benzene and chlorobenzenes in the valence force field approximation: calculated mean-square displacements for individual atoms of the benzene molecule (D_{6h} symmetry or its subgroups) are in agreement with those of Johnson [10]. Other possibilities, such as the use of other currently available force fields and least-square adjustment of force constants, will soon be added.

4. Conclusion

The projection operator technique is very easy to use when dealing with Cartesian coordinates; this is essentially because these coordinates transform themselves in a very simple and uniform manner under the symmetry operations. Although Gwinn [1] has pointed out that some large molecules have no symmetry at all we think that this new method of study is very useful. So many molecules have at least a centre of inversion or a plane of reflexion leading to tractable dimension of the secular equation. This method can also be useful in a least-square treatment which limits itself to some species of a small molecule of high (or low) symmetry. Results of particular applications to the durene molecule and its halogen derivatives will be published later.

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[1] Available on request from the authors.