On the Classification of Symmetry Coordinates

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thetical. Even if one were found and prepared in suitable quantity and purity, there would still remain questions of its stability, reaction with window materials, and potency as a solvent (especially of complex organic compounds). The n-perfluoroparaffins promise to be satisfactory on all these counts.

[1] H. B. Klevens and J. R. Platt, J. Am. Chem. Soc. 69, 3055 (1947).
[2] Unpublished results of the authors.
[3] J. R. Platt and H. B. Klevens, Chem. Rev. 41, 301 (1947).
[4] Through the courtesy of Drs. H. M. Scholberg and W. H. Pearlson, Research Laboratories, Minnesota Mining and Manufacturing Company, St. Paul, Minnesota.
[5] W. C. Price, Chem. Rev. 41, 257 (1947).
[6] W. C. Price, J. Chem. Phys. 15, 614 (1947).
[7] J. R. Platt, H. B. Klevens, and G. W. Schaeffer, J. Chem. Phys. 15, 598 (1947).
[8] H. I. Schlesinger, D. M. Ritter, and A. B. Burg, J. Am. Chem. Soc. 60, 2297 (1938); and R. E. Moore, M. S. Thesis, University of Chicago, June, 1948.

The Average Boundaries of Statistical Chains

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September 17, 1948

THIS is to acknowledge my discovery that a problem which I solved as an example in a recent paper[1] had already been solved by W. Kuhn and H. Kuhn.[2] These authors give a result that differs from mine by only 5 percent. They also give values of various other parameters of branched as well as unbranched chains.

[1] C. A. Hollingsworth, J. Chem. Phys. 16, 544 (1948).
[2] W. Kuhn and H. Kuhn, Helv. Chim. Acta. 30, 1233 (1947).

On the Classification of Symmetry Coordinates*

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THE symmetry type or irreducible representations of the $3n-6$ vibrations of an n-atomic symmetrical molecule may be found by group theoretical methods which will be restated briefly. The atoms may be divided into sets equivalent under the point group of the molecule; the permutation matrices for any given set of equivalent atoms then form a reducible representation of the group, which may be reduced to a "sum" of irreducible representations by the standard orthogonality relation for group characters. The direct product of this sum by the sum of irreducible representations for translation yields the total contribution of this set of equivalent atoms. Summing the representations thus obtained over all sets of equivalent atoms in the molecule, and subtracting finally the representations for translation and rotation, yields the representations for the vibrations (with the sum of the dimensions equal to $3n-6$).

A similar procedure may be used to find *separately* the irreducible representations of the symmetry coordinates formed from equivalent internal coordinates, which are commonly taken as a starting point for normal coordinate analyses. It is a considerable advantage to be able to enumerate the irreducible representations of the symmetry coordinates without, or before, actually setting up the analytical expressions for these coordinates. Comparison of the representations for the sets of symmetry coordinates taken separately with the sum of representations for the $3n-6$ vibrations is usually sufficient to identify the redundant coordinates. In making frequency assignments, even when a normal coordinate analysis is not contemplated, a knowledge of the representations of the symmetry coordinates is useful in indicating the physical nature of the vibrations allowed in the spectra, and therefore in estimating probable frequencies. As is well known, each normal mode is formed only from symmetry coordinates belonging to the same representation.

In this communication the general principles of the method for symmetry coordinates are described. A paper now in preparation will give a fuller account and will contain tables by means of which the irreducible representations of most sets of equivalent internal coordinates may be obtained by inspection.

A set of equivalent internal coordinates may be divided into (equal) subsets such that each subset is associated with one point of an equivalent set of points, in the sense that the subsets permute among themselves in the same way as the points under the operations of the point group. The permutation matrices for this set of equivalent points form a reducible representation of the group, which may be reduced as discussed in the first paragraph. Those operations of the point group which do not permute a particular point of the set form a subgroup of the group. The operations of this subgroup will transform in some manner the members of the subset associated with this point; the introduction of subsets is necessary because, in general, the transformations of a subset under the subgroup cannot be represented by the permutations of a set of points. The case of most interest is that in which the coordinates of the subset belong to a single irreducible representation of the subgroup, the number of coordinates in the subset being equal to the dimension of the representation. In the case of the cyclic and dihedral groups the subgroup can contain only non-degenerate or one-dimensional representations, and each subset only one coordinate, unless the point lies on the principal symmetry axis and the latter is threefold or higher. In the latter case, and also in the case of tetrahedral and octahedral groups, when the point lies on a three- or fourfold axis, the subgroup will contain one or more two-dimensional representations, and the subset may contain one or two equivalent internal coordinates. There is also the relatively unimportant case in which the single point of the set lies at the origin, in which case three-dimensional representations occur for the tetrahedral and octahedral groups. There are, in addition, some cases of interest in which the subset lies in more than one representation of the subgroup. It should be noted that when the representation of the subset in the subgroup is one-dimensional, it may still not be totally symmetric.

The representation of the subset in the subgroup (the same for all subsets) may be obtained by inspection by considering the transformations under the subgroup of the s-vectors associated with the coordinates of the subset

which have been defined by Wilson.[1] One or more of the representations of the complete group (or, in a few cases, a linear combination of representations) will have characters identical with those of this representation of the subgroup, for those classes which contain operations in the subgroup. The direct product of any one of these representations (or combinations of representations) of the complete group with the sum of representations for the permutation matrices (of the set of equivalent points) will yield the required sum of irreducible representations for the complete set of equivalent internal coordinates. (If the subset lies in more than one representation of the subgroup, the contributions obtained for each taken separately are added.)

As a simple example, the torsions about the carbon-carbon single bonds in benzene (point group D_{6h}) will be considered. The six torsions permute in the same way as the set of six midpoints of the sides of the carbon hexagon. The representation of the permutations is $A_{1g}+B_{2u}+E_{1u}+E_{2g}$. The subgroup at a point of the set is C_{2v}, and the representation of the torsion in the subgroup is A_2 (corresponding to a rotation about the C_2 axis). The corresponding representations of D_{6h} are A_{1u} and B_{2g}. The direct product of either of these with the representation of the permutations yields $A_{1u}+B_{2g}+E_{1g}+E_{2u}$ as the representation of the set of six equivalent torsions.

[1] E. B. Wilson, Jr., J. Chem. Phys. 9, 76 (1941), Eq. (2). The s-vectors are the coefficients in the linear functions connecting the internal coordinates with the vector displacements of the atoms. The only non-vanishing s-vectors for a given internal coordinate are those attached to the few atoms whose relative motion changes the coordinate. The orientation of the s-vectors with respect to the symmetry elements may be obtained by inspection by noting that the s-vector for a given internal coordinate attached to a given atom lies in the direction in which this atom must move, all other atoms remaining fixed, to produce the maximum positive rate of change of the coordinate per linear distance traveled. For the present purpose the magnitudes of the s-vectors are not important, but only the equality or inequality of the magnitudes, which is obvious from symmetry considerations.

Note on the Energy of a Rotating Molecule

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August 27, 1948

THE quantum-mechanical problem of the energy levels of a molecule has been attacked by Born and Oppenheimer,[1] who expanded the accurate Hamiltonian operator about the equilibrium configuration of the nuclei in powers of k; $K^4 = m/M \approx 10^{-4}$, the ratio of the electronic mass to a nuclear mass. They show that the energy can be decomposed into contributions from the electronic, the vibrational, and the rotational motion, which first enter in the zeroth-, second-, and fourth-order corrections, respectively. In higher orders of approximation, which these authors did not examine in detail, the three types of motion interact. Wilson and Howard,[2] and Nielsen,[3] and Darling and Dennison[4] have investigated the interaction of rotational and vibratory motion. They conclude that the rotational energy levels are those of an effective asymmetric rotor, appropriate to a given vibrational state, and differing somewhat from the equilibrium rotor; a small term that

can be described as centrifugal distortion perturbs the motion of this rotor. These authors do not make clear the magnitude of the corrections to be expected. The recent interest in pure rotational spectra which are observed in the microwave region has made it imperative that the higher order terms in the Hamiltonian be examined from a consistent point of view. With this in mind, the procedure of Born and Oppenheimer[1] has been continued.[5]

The results of the perturbation calculation will now be briefly summarized. The Hamiltonian operator which determines rotational fine structure of a given non-degenerate electronic and vibrational state can be written

$$H_R = H_R{}^{(4)} + H_R{}^{(6)} + H_R{}^{(8)} + \cdots,$$

where the superscripts describe the magnitude of a term in powers of k relative to the electronic energies. H_R is a function of angular momentum operators P which can act only on a rotational wave function. Electronic and vibrational labels on these operators are understood.

The leading term, $H_R{}^{(4)}$, is the Hamiltonian of a rigid rotator whose moments of inertia are those of the equilibrium configuration of the nuclei (electronic masses not included). In a system of principal axes it is

$$H_R{}^{(4)} = \Sigma_\alpha \mu_{\alpha\alpha}{}^0 P_\alpha{}^2, \quad \alpha = x, y, z$$

$$1/\mu_{\alpha\alpha}{}^0 = I_\alpha = \text{equilibrium moment of inertia},$$

$H_R{}^{(4)}$ is independent of vibrational and electronic properties.

The largest correction, $H_R{}^{(6)}$, is also a homogeneous quadratic polynomial in the angular momentum operators. It therefore merely introduces corrections to the equilibrium rotational constants. By insertion of the appropriate quantities, the results of Nielsen's calculation, contained in the corrections $x_{s\sigma}$, $y_{s\sigma}$, $z_{s\sigma}$, reference 3, Eqs. (27) and (28), have been verified exactly. They contain the quadratic and cubic potential constants, but are independent of the electronic structure.

The next correction, $H_R{}^{(8)}$, considerably complicates the description of the system, because it is the sum of a homogeneous quadratic and a homogeneous quartic polynomial in the operators P. The latter is the centrifugal distortion which has been discussed by several authors.[2-4,6] The former provides further corrections to the rotational constants; it depends on quadratic, cubic, quartic, and quintic potential constants, and also includes terms that depend on the electronic structure. These are given by

$$\mu_{\alpha\alpha}{}^0 P_\alpha{}^2 \sum_{n'} (\mu_{\alpha\alpha}{}^0 (P_\alpha)_{nn'} (P_\alpha)_{n'n})/(E_n - E_{n'}),$$

(n, n' are electronic quantum numbers). They may very simply be shown to appear when the electronic wave equation is solved in a rotating coordinate system.[7,8]

In conclusion, it should be mentioned that the expansion which has been discussed is reliable only when the energy differences between electronic or vibrational states are of the same magnitude as the energies themselves. If the differences are much smaller (near-degeneracy), some corrections to the energy will be larger than their place in the series in the first equation would indicate.

The author wishes to express his appreciation to Pro-