Resolution of Crossed Bond Eigenfunctions in Terms of the Uncrossed Set

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Ammonium hexabromo-hypoantimonate, therefore, does not contain unpolymerized complexes involving a quadrivalent antimony atom, for such complexes would contain an odd number of electrons and hence give rise to strong paramagnetism. It is probable that the substance is a double salt containing one trivalent and one quinquivalent antimony atom corresponding to the formula $(NH_4)_4Sb^{III}Sb^VBr_{12}$. The observed diamagnetism could be made compatible with the presence of quadrivalent antimony by assuming that the quadrivalent antimony

atoms occur in groups of two joined by shared electron-pair bonds, Sb : Sb, similar to the group Hg : Hg^{++} in mercurous salts. This, however, seems improbable because the stoichiometric formula, $(NH_4)_2SbBr_6$, suggests that each antimony atom is surrounded by six bromine atoms which would prevent close approach of the antimony atoms.

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The Infrared Spectrum of Methyl Deuteride

As a consequence of its high degree of geometric symmetry the methane molecule, with nine degrees of freedom of vibration, has only two active fundamental absorption bands, each triply degenerate. While the character of these bands justifies the tetrahedral model, they yield very little information regarding the dimensions and elastic constants of the system. The replacement of one of the hydrogens by an atom of deuterium introduces a preferred axis, with respect to which the molecule is symmetrical, and increases the number of active vibrations from two to six. Of these, three are single, introducing electric moments parallel to the axis, and three are double, giving rise to perpendicular bands.

We have observed all of these fundamental bands, and have determined the rotational structure of one of them, the lowest frequency parallel vibration. This consists of a strong and narrow zero branch at approximately 1090 cm^{-1}, and the usual positive and negative branches, the intervals between rotation lines being about 4.5 cm^{-1}. From this interval the maximum moment of inertia may be computed at once, $I \sim 12.28 \times 10^{-40}$, and the H-H distances are about 2.51×10^{-8} cm. More bands must be analyzed and the molecular constants evaluated before these dimensions can be given with precision. Assuming the atomic distances to be the same for ordinary methane, its moment of inertia comes out approximately 10.45×10^{-40}. As

would be expected, this value is about twice as large as that determined from the rotational Raman effect by Dickinson, Dillon and Rasetti,[1] since they assumed that the successive lines have J values differing by two. They found $I = 5.17 \times 10^{-40}$.

Methyl deuteride is of especial interest in the study of rotational and vibrational interaction in perpendicular bands, since it is the first molecule available in which both moments of inertia may be determined precisely. Because the bands lie rather close together and overlap considerably, their analysis must await further study, and will be reported later.

A very interesting test of the assumption that the atomic distances are the same for both isotopes of hydrogen will be provided by the study of the methane molecule with three hydrogen atoms replaced by deuterium. These measurements we hope to publish within a short time, as well as the fundamental frequencies of tetra-deutero methane.

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April 13, 1934.

[1] Dickinson, Dillon and Rasetti, Phys. Rev. **34**, 582 (1929).

Resolution of Crossed Bond Eigenfunctions in Terms of the Uncrossed Set

The method of repeatedly applying the theorem for uncrossing any pair of bonds expressed by the relation

$$\times = | | + \asymp$$

is adequate for resolving every bond eigenfunction in terms of the linearly independent set. However, the labor of doing this rises rapidly as the number of bonds increases. Since in obtaining bases for irreducible representations[1] the resolution of crossed bond eigenfunctions is practically unavoidable, some simplification seems necessary. Very simple rules have been found for the cases usually encountered, i.e., those involving 5 bonds or fewer.

We assume we have a crossed bond eigenfunction A with $2n$ orbitals arranged symmetrically on a circle connected in pairs by n bonds.

Rule I

The number of times this process of uncrossing will yield a particular bond eigenfunction B with no crossed bonds equals the number of different ways a set of n continuous, entirely noncoincident (except perhaps at points), noncrossing paths may be drawn along the lines in A, such that they connect each pair of orbitals bound together in B. Ordinarily this rule enables one to determine coefficients 0 or 1 by inspection, but in any case the determination is very simple. A subsidiary rule is necessary in cases yielding larger coefficients. Such cases arise when there is a point common to more than three paths.

[1] Eyring, Frost and Turkevich, J. Chem. Phys. **1**, 777 (1933).

Rule II

Draw the shortest set of n paths of the kind described in rule I. If there is a point common to p paths (only points for which p is 3 or greater are to be considered) the number of times B will occur in uncrossing A is $(p-2)$. In determining p we note that frequently for an eigenfunction A parts of the lines in A are not traversed by the set of n paths. All points connected by untraversed lines are for this purpose to be counted as one point. Having done this one further procedure may be necessary in applying rule II. Any path which passes through a point and which with the perimeter circle separates other paths common to the point into two groups is omitted in determining p for the point. This discarding is continued until there are no more such paths.

The coefficients for all uncrossed bonds are positive if the convention is adopted in every B and A of arranging the orbitals in order around a circle and always directing the arrow representing a bond toward the orbitals with the higher ordinal number.

These rules have been checked for all possible patterns of 5 bonds or less. A more complicated rule is required for direct application to more than 5 bonds. However, eigenfunctions involving 6 or more bonds are readily reduced by comparatively few uncrossings to cases to which our simple rules apply.

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On Diffusion Equilibria of Electrolytes

A study of the fundamental elements contained in the theory of electrolytic conductivity which will be reported later, has led among others, to some results about the limiting case, i.e., diffusion equilibrium under the influence of external forces.

Consider for the purpose of illustration the distribution of charged colloidal particles and ions in a gravitational field. If there are only very few ions present which carry charges of the same sign as those present on the colloidal particles, the problem can be solved with sufficient accuracy for dilute solutions. It is found that there occur large deviations from the Boltzmann distribution which tend to make the latter more uniform. At the same time the rate of establishment of equilibrium is greatly reduced. An increase in concentration tends to diminish the deviation

from the Boltzmann distribution. The presence of ions carrying charges of the same sign as the colloidal particles acts in the same direction.

Similarly it can be shown that the diffusion potential in electrolytes does not assume its classical value.

These effects can perhaps be described by the statement that the activity coefficients of the charged particles lead to an apparent reduction in the value of their diffusion coefficient.

The writer hopes to be able to present shortly a more detailed account of these investigations.

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Observations on the Synthesis of Tetra-Deutero Methane

In the course of the synthesis of tetra-deutero methane with the object of studying its physical properties, we have made some observations on the relative velocities of reactions between the proto water and aluminum carbide and the deutero water and aluminum carbide.

Carefully prepared aluminum carbide in fairly finely divided form was placed in a sealed container fitted with a small reflux condenser, and the proto water added at low temperatures. The whole system was evacuated and the mixture allowed to come to room temperature. Gas bubbles formed at ordinary temperatures and in the course of 10 or 15 minutes raised the pressure in the apparatus to atmospheric. The mixture was then raised to about 80°C and the methane generated collected over mercury. It required on the average 2 minutes to collect 100 cc of methane.

With the same apparatus and aluminum carbide from the same batch and of the same fineness of division, the same method was attempted using the deutero water. At room temperatures, no reaction took place in the course of two hours. We then filled the apparatus with CO_2 at atmospheric pressure and raised the temperature

to 80°. It now required 46.5 minutes to collect the first 100 cc of methane gas. This gives a ratio of the velocities for the two reactions of approximately 23. This seems to be the highest ratio so far observed for reactions involving compounds of the two hydrogens. Not until the reaction vessel was heated to about 65° were we able to see any bubbles of methane form in the reaction vessel. The next 100 cc were collected at 90°. At this temperature, the rate of evolution of the gas was about three times that at 80°.

The temperatures were controlled by maintaining the temperature of a water bath within a degree or two of the temperatures given. There is a possibility, of course, of slight error in this way, but that there is an enormous difference in the velocities of the reactions cannot be doubted.

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