Soviet-era science, translated into English

Physical Chemistry

1965

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Abstract

Full Text

Physical Chemistry

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Probability Distribution for an Internal Coordinate of a Polyatomic Molecule in a Vibrational Stationary State

(Presented by Academician Ya. K. Syrkin, 17 III 1965)

The application of transition-configuration theory to intramolecular rearrangements requires knowledge of the probability distribution for a certain internal coordinate in each vibrational stationary state ($^{1-2}$). The same is required by modern theoretical electronography (see, for example, (^{3})). Below, a solution of the problem is given for the case of harmonic vibrations.

Since any internal coordinate can be written in the form of a linear combination of normal coordinates, which in the case of harmonic vibrations are independent random variables, the problem of finding the probability distribution for a certain internal coordinate reduces to the problem of finding the distribution of the sum of independent random variables.

In accordance with (^{1}), the internal coordinate q_j is related to the dimensionless normal coordinates η_k by the relation

$$q_j = \sum_{k=1}^{n} \sqrt{2}\,\sigma_j^{(k)}\eta_k, \tag{1}$$

where

$$\sigma_j^{(k)} = \hbar^{1/2}\left(\frac{\partial\omega_k}{\partial u_{jj}}\right)^{1/2}. \tag{2}$$

The density of the distribution of η_k in the m-th stationary vibrational state of the molecule has, as is known (see, for example, (^{4})), the form

$$\rho_m(x) = \frac{1}{\sqrt{\pi}\,2^m m!}\exp(-x^2)H_m^2(x), \tag{3}$$

where H_m is the m-th Hermite polynomial. Therefore, the density of the distribution of the random variable $\sqrt{2}\sigma_j^{(k)}\eta_k$ in this same state is equal to

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$$\rho_m^\sigma(x) = \frac{1}{\sigma\sqrt{2\pi}\,2^m m!}\exp\left(-\frac{x^2}{2\sigma^2}\right)H_m^2\left(\frac{x}{\sigma\sqrt{2}}\right) \tag{4}$$

(the indices on σ have been omitted to simplify the notation).

The density of the distribution of the internal coordinate q_j in a vibrational stationary state of the molecule, characterized by the quantum numbers m_k ($k = 1, 2, \ldots, n$), is thus obtained by convolution (^{5}) of the corresponding expressions of the form (4), namely:

$$\rho_{m_1,\ldots,m_n}^{\sigma_1,\ldots,\sigma_n}(x) = \int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\cdots\int_{-\infty}^{\infty}\rho_{m_1}^{\sigma_1}(x-t_1)\rho_{m_2}^{\sigma_2}(t_1-t_2)\ldots$$

$$\ldots\rho_{m_n}^{\sigma_n}(t_{n-1})\,dt_1 dt_2\ldots dt_{n-1}. \tag{5}$$

For $n = 2$, the right-hand side of (5) can, using (4), be represented in the form $\exp(-x^2/2\sigma_{12}^2)P_{N_{12}}(x^2/2\sigma_{12}^2)$, where $\sigma_{12}^2 = \sigma_1^2 + \sigma_2^2$, and $P_{N_{12}}$ is a polynomial of degree $N_{12} = m_1 + m_2$. For arbitrary n, the right-hand side of (5) therefore has the form $\exp(-x^2/2\sigma_{1\ldots n}^2)P_{N_{1\ldots n}}(x^2/2\sigma_{1\ldots n}^2)$, where $\sigma_{1\ldots n}^2 = \sum_{i=n}^{n}\sigma_i^2$, and $P_{N_{1\ldots n}}$ is a polynomial of degree $N_{1\ldots n} = \sum_{i=1}^{n} m_i$ ($N_{1\ldots n}$ is the total quantum number of the vibrational stationary state).

Direct calculation of the coefficients of these polynomials is difficult even for $n = 2$ and not very large values of m_1 and m_2. It is still more difficult for $n > 2$. Even greater difficulties are encountered when attempting to compute directly the various moments of the distributions obtained. However, all these difficulties can be quite easily avoided if expression (5) is represented in the form

$$\rho_{m_1,\ldots,m_n}^{\sigma_1,\ldots,\sigma_n}(x) = \sum_{s=0}^{N_{1\ldots n}} a_s(m_1,\ldots,m_n;\sigma_1,\ldots,\sigma_n)\rho_s^{\sigma_{1\ldots n}}(x). \tag{6}$$

The possibility of such a representation follows from the fact that $P_{N_{1\ldots n}}$, being an even polynomial, can, as it turns out, be expanded in squares of Hermite polynomials.

Now from (6) and the linearity of the convolution operation one obtains the recurrence relations:

$$\rho_{m_1,\ldots,m_n,m_{n+1}}^{\sigma_1,\ldots,\sigma_n,\sigma_{n+1}}(x) =$$

$$= \sum_{s=0}^{N_{1\ldots n}} a_s(m_1,\ldots,m_n;\sigma_1,\ldots,\sigma_n)\rho_{s,m_{n+1}}^{\sigma_{1\ldots n},\sigma_{n+1}}(x) \quad (n = 2, 3, \ldots) \tag{7}$$

or else

$$a_s(m_1, \dots, m_n, m_{n+1}; \sigma_1, \dots, \sigma_n, \sigma_{n+1}) =$$

$$= \sum_p a_p(m_1, \dots, m_n; \sigma_1, \dots, \sigma_n) a_s(m_{n+1}, p; \sigma_{n+1}, \sigma_{1\dots n}) \tag{8}$$

(the summation is performed over all nonnegative values of p from the interval $s - m_{n+1} \leq p \leq N_{1\dots n}$; $n = 2, 3, \dots$).

It follows from (6) that for any n and any values of $n, m_1, \dots, m_n$ and $\sigma_1, \dots, \sigma_n$, the coefficients a_s satisfy the condition

$$\sum_{s=0}^{N_{1\dots n}} a_s(m_1, \dots, m_n; \sigma_1, \dots, \sigma_n) = 1. \tag{9}$$

From the commutativity of the convolution operation it follows that these coefficients do not change under an arbitrary, but identical, permutation in the sets m_i and σ_i.

The derivation of the expression for $a_s(m_1, m_2; \sigma_1, \sigma_2)$ uses the formula for expanding the product of two Hermite polynomials in Hermite polynomials [6], the "addition theorem" for Hermite polynomials [7], and also the formula obtained by the author of the present article for expanding an even Hermite polynomial in squares of Hermite polynomials, which has the form:

$$H_{2n}(x) = \sum_{l=0}^{n} (-1)^l 2^l l! \binom{n}{l}^2 H_{n-l}^2(x). \tag{10}$$

As a result of rather cumbersome calculations one obtains

$$a_s(m_1, m_2; \sigma_1, \sigma_2) = (-1)^s \sum_k \sum_l (-1)^{k+l} \binom{k+l}{s} \binom{k+l}{k} \binom{m_1}{l} \binom{m_2}{k} {\sigma'_1}^{2l} {\sigma'_2}^{2k}, \tag{11}$$

where ${\sigma'_1}^2 = \sigma_1^2/\sigma_{12}^2$ and ${\sigma'_2}^2 = \sigma_2^2/\sigma_{12}^2$.

In the particular case $m_2 = 0$, from (11) it follows that

$$a_s(m_1, 0; \sigma_1, \sigma_2) = \binom{m_1}{s} {\sigma'_1}^{2s} {\sigma'_2}^{2(m_1 - s)}. \tag{12}$$

For $m_1 = m_2 = 0$, (12) gives

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$$a_0(0, 0; \sigma_1, \sigma_2) = 1. \tag{13}$$

Now from the recurrence relations (8) it follows that

$$a_0(0, \dots, 0; \sigma_1, \dots, \sigma_n) = 1 \tag{14}$$

and from formula (6)

$$\rho^{\sigma_1,\dots,\sigma_n}_{0,\dots,0}(x) = \rho^{\sigma_{1\dots n}}_0(x) \tag{15}$$

(a known result stating that, in the ground vibrational state of a molecule, each internal coordinate is normally distributed).

If only one, say (without loss of generality) the first normal vibration is excited, then, using (12), we obtain, with account taken of (4), the following expression for the distribution density of the internal coordinate:

$$\rho^{\sigma_1,\sigma_2,\dots,\sigma_n}_{m_1,0,\dots,0}(x) = \frac{1}{\sigma_{1\dots n}\sqrt{2\pi}} \exp\left(-\frac{x^2}{2\sigma^2_{1\dots n}}\right) \times$$

$$\times \sum_{s=0}^{m_1} \binom{m_1}{s} \sigma_1'^{\,2s} \sigma_{2\dots n}'^{\,2(m_1-s)} \cdot \frac{1}{2^s s!} H_s^2\left(\frac{x}{\sigma_{1\dots n}\sqrt{2}}\right), \tag{16}$$

where $\sigma_1'^2 = \sigma_1^2/\sigma^2_{1\dots n}$ and $\sigma'^2_{2\dots n} = \sum_{i=2}^{n} \sigma_i^2/\sigma^2_{1\dots n}$.

Expression (11) can be represented in several more convenient equivalent forms, for example in the form

$$a_s(m_1, m_2; \sigma_1, \sigma_2) = \binom{N_{12}}{m_2}\binom{N_{12}}{s}^{-1} \sigma_1'^{\,2(s-m_2)} \sigma_2'^{\,2(s-m_1)} \times$$

$$\times \left[\sum_{k=0}^{\min(N_{12}-s, m_1)} (-1)^k \binom{N_{12}-k}{s}\binom{m_1}{k} \sigma_1'^{\,2(N_{12}-s-k)}\right]^2. \tag{17}$$

It follows from (17) that the coefficients $a_s(m_1, m_2; \sigma_1, \sigma_2)$ are nonnegative for any values of the parameters. From the recurrence relations (8) it therefore follows that the coefficients a_s possess this same property for any n. Thus, on the basis of (9), the coefficients a_s, for any n and any values of $m_1, \dots, m_n$ and $\sigma_1, \dots, \sigma_n$, form discrete distributions.

From (17) there also follow the following curious properties of the coefficients $a_s(m_1, m_2; \sigma_1, \sigma_2)$, the use of which makes it possible to reduce considerably the computational work in the practical calculation of these coefficients, namely:

$$a_s(m_1, m_2; \sigma_1, \sigma_2) = a_{m_1}(s, N_{12} - s; \sigma_1, \sigma_2) = a_{m_2}(N_{12} - s, s; \sigma_1, \sigma_2). \tag{18}$$

It is convenient to present these properties in the form

$$c^{(N_{12})}_{m_2,s} = c^{(N_{12})}_{s,m_2} = c^{(N_{12})}_{N_{12}-s,N_{12}-m_2}, \qquad (m_2, s = 0, 1, 2, \dots, N_{12}), \tag{19}$$

where $c^{N_{12}}_{m_2,s} \equiv a_s(m_1, m_2; \sigma_1, \sigma_2)$ are elements of a square matrix of order $(N_{12}+1)$ corresponding to some definite value of the total quantum number N_{12} ($N_{12} = 0, 1, 2, \dots$).

Relations (19) mean that each such matrix is doubly symmetric (symmetric with respect to both main diagonals), and, consequently, also centrosymmetric. Moreover, on the basis–

Under the existence of the properties indicated earlier, all elements of these matrices are nonnegative, and their sum in any row (and in any column) is equal to unity; that is, these matrices are doubly stochastic.

The number of distinct elements to be calculated in the matrix corresponding to the total quantum number N_{12} is equal to $\left({}^1/_2 N_{12} + 1\right)^2$ if N_{12} is even, and to ${}^1/_4(N_{12} + 1)(N_{12} + 3)$ if N_{12} is odd.

In practical calculations it is convenient, taking (4) into account, to write formula (6) in the form

$$\rho^{\sigma_1,\dots,\sigma_n}_{m_1,\dots,m_n}(x) = \frac{1}{\sigma_{1\dots n}\sqrt{2\pi}} \exp\left(-\frac{x^2}{2\sigma^2_{1\dots n}}\right) \times$$

$$\times \sum_{s=0}^{N_{1\dots n}} a_s(m_1, \dots, m_n; \sigma_1, \dots, \sigma_n) \frac{1}{2^s s!} H_s^2\left(\frac{x}{\sigma_{1\dots n}\sqrt{2}}\right).$$

It is also useful to bear in mind that $\rho^{\sigma_1,\dots,\sigma_n}_{m_1,\dots,m_n}(x)$, as it turns out, does not exceed $(\sigma_{1\dots n}\sqrt{2\pi})^{-1}$.

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Received
12 III 1965

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