

Erratum: Relation between Vapor Pressure and Viscosity of Liquids

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tion of the field gradient at the nucleus. The problem is thereby reduced to an atomic orbital one, with the filling of the atomic orbitals being influenced by bond properties such as ionic character and hybridization. This procedure was employed for derivation of the specialized formulas by Gordy et al.3 It is unsatisfactory in that it does not account for the covalent bond energy, just as methods which have been used successfully to calculate the covalent bond energy do not give correctly the nuclear coupling. The more desirable comprehensive treatment requires a set of wave functions which give the correct charge distribution both near the nucleus and in the overlap region—but such a treatment has not yet been made.

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Command.

¹ W. Gordy, J. Chem. Phys. 19, 792 (1951).

² C. H. Townes and B. P. Dailey, J. Chem. Phys. 17, 782 (1949).

³ Gordy, Smith, and Trambarulo, *Microwave Spectroscopy* (John Wiley and Sons, Inc., New York, 1953), p. 272. See also Ch. VII.

⁴ Robinson, Dehmelt, and Gordy, J. Chem. Phys. 22, 511 (1954).

⁵ P. N. Schatz, J. Chem. Phys. 22, 695 (1954); 22, 755 (1954).

Erratum: Concentration Dependence of Differential Capacity in Electrolytes at the Electrocapillarity Maximum

[J. Chem. Phys. 22, 763-764 (1954)] J. Ross Macdonald Texas Instruments Incorporated, Dallas, Texas

Ross McDonald should read J. Ross Macdonald.

Erratum: Relation between Vapor Pressure and Viscosity of Liquids

[J. Chem. Phys. 22, 349 (1954)] Shashanka Shekhar Mitra

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QUATION (1) should be read as

 $\log P + n \log_{\eta} + n'(\log_{\eta})^2 = C,$

instead of

 $\log P + n \log \eta = n' (\log \eta)^2 = C.$

On the Transformation of Internal Coordinates

E. J. O'REILLY, JR. 1425 Kanawha Street, Hyattsville, Maryland (Received June 1, 1954)

I N constructing the elements of the secular equation according to the method of Wilson! it is necessarily to the method of Wilson¹ it is necessary to determine the transformation properties of the internal coordinates under the operations of the symmetry group to which the molecule belongs. Tobin² has indicated in a general fashion these transformation properties. To minimize error, however, where complex internal coordinates are encountered it has been found convenient to first determine the transformation properties of the unit bond vectors which define the internal coordinate. Then explicit transformation of the internal coordinate qi under the operation R yields qi'. The transformed coordinate qi' is readily associated with the untransformed coordinates q_i in terms of the e vectors by means of the relations of vector analysis.

Examples may be drawn from the case of a hexatomic planar system of V_h symmetry (Fig. 1). Torsion about the central bond may be defined after Günthard³ by the coordinate $r\Delta\delta_1$, the change in the dihedral angle between planes (1, 3, 2) and (5, 4, 6). The transformation properties of the i-th internal coordinate under the symmetry group operation R_k may be characterized by the term f_{ij}^{k} . The operation R_{k} is mathematically equivalent to multiplication by an orthogonal rotation matrix whose determinant has the value $f = \pm 1$. Further by definition,

$$r\Delta\delta_i = r(\delta_i - \delta_i^*),$$

where δ_i is the value of the coordinate in the equilibrium position, and δ_i * is its corresponding value in the distorted position. Since

$$R_k[r\Delta\delta_i] = f_{ij}^k r\Delta\delta_i$$

and

$$R_k[r(\delta_i-\delta_i^*)]=f_{ij}^kr(\delta_j-\delta_j^*),$$

it follows that the transformation properties $f_{ij}{}^k$ of $r\Delta\delta_i$ are identical to those of $r\delta_i$.

For this example, δ_1 may be defined³ as

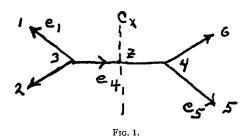
$$\delta_1 = \cos^{-1}\{\mathbf{e}_4 \times [\mathbf{e}_4 \times (\mathbf{e}_1 \times \mathbf{e}_2)] \cdot \mathbf{e}_4 \times (\mathbf{e}_5 \times \mathbf{e}_6)\}.$$

The operations C_z , i, and C_x , on δ_1 yield, respectively,

$$\delta_1' = \cos^{-1}\{-\mathbf{e}_4 \times [-\mathbf{e}_4 \times (\mathbf{e}_5 \times \mathbf{e}_6)] \cdot -\mathbf{e}_4 \times (\mathbf{e}_1 \times \mathbf{e}_2) p^n\}$$

$$\delta_1'' = \cos^{-1}\{-\mathbf{e}_4 \times [-\mathbf{e}_4 \times (\mathbf{e}_5 \times \mathbf{e}_6)] \cdot -\mathbf{e}_4 \times (\mathbf{e}_1 \times \mathbf{e}_2) p^n\}$$

$$\delta_1''' = \cos^{-1}\{-\mathbf{e}_4 \times [-\mathbf{e}_4 \times (\mathbf{e}_6 \times \mathbf{e}_5)] \cdot -\mathbf{e}_4 \times (\mathbf{e}_2 \times \mathbf{e}_1) p^n\}.$$



Here n is the number of cross products in the expression, and p is +1 or -1 for a proper or improper rotation, respectively. The factor p^n arises from the formal identity of the cross product as a pseudovector, where

$$\mathbf{c} = \mathbf{a} \times \mathbf{b}; \quad c_k = \delta_{ijk} a_i b_j$$

and δ_{ijk} is the unit skew-symmetric tensor, which changes sign under an improper rotation.

Use of the various identity relations among the terms of a scalar triple product relate the transformed coordinates

$$\delta_1 = \cos^{-1}(\mathbf{A} \times \mathbf{B} \cdot \mathbf{C})$$

$$\delta_1' = \cos^{-1}(-\mathbf{A} \times -\mathbf{C} \cdot -\mathbf{B})(1) = \delta_1$$

$$\delta_1'' = \cos^{-1}(-\mathbf{A} \times -\mathbf{C} \cdot -\mathbf{B})(-1) = -\delta_1$$

$$\delta_1''' = \cos^{-1}(-\mathbf{A} \times \mathbf{C} \cdot \mathbf{B})(1) = \delta_1.$$

The wagging of the extreme atoms may be described by two coordinates $r\Delta\gamma_1$ and $r\Delta\gamma_2$ which designate the change in the angles formed between the central bond and the normals to planes (132) and (546), respectively. γ_i is defined as

$$\gamma_1 = \cos^{-1}(\mathbf{e}_4 \cdot \mathbf{e}_1 \times \mathbf{e}_2)$$

 $\gamma_2 = \cos^{-1}(-\mathbf{e}_4 \cdot \mathbf{e}_5 \times \mathbf{e}_6).$

Under the operations C_x , i, and C_x , γ_1 transforms to

$$\begin{split} &\gamma_1{}' = \cos^{-1}(-e_4 \cdot e_5 \times e_6)(1) = \gamma_2 \\ &\gamma_1{}'' = \cos^{-1}(-e_4 \cdot e_5 \times e_6)(-1) = -\gamma_2 \\ &\gamma_1{}''' = \cos^{-1}(-e_4 \cdot e_6 \times e_5)(1) = -\gamma_2. \end{split}$$

E. B. Wilson, J. Chem. Phys. 7, 1047 (1939); 9, 76 (1941).
 M. C. Tobin, J. Chem. Phys. 20, 1980 (1952).
 H. Günthard et al., Helv. Chim. Acta, 32, 1784 (1949).