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On the Helical Configuration of a Polymer Chain

TAKEHIKO SHIMANOUCI AND SAN-ICHIRO MIZUSHIMA

Chemical Laboratory, Faculty of Science, Tokyo University, Hongo, Tokyo, Japan

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A mathematical expression for the helical configuration of a polymer chain has been derived as a function of the bond lengths, bond angles, and internal rotation angles. The result of the calculation has been applied to the determination of stable configurations of several polymer chains.

I. INTRODUCTION

A GENERAL interest has been aroused in helical configurations of chain molecules in the field of high polymers, especially of proteins,¹ nucleic acids,² starches,³ etc. It would, therefore, be interesting to derive a mathematical expression of chain configurations as a function of bond lengths, bond angles, and internal rotation angles, since in setting up a polymer model we can try with different values of these parameters lying in a range of values predicted from the study of simpler molecules as a structural unit of the corresponding polymer. The last parameter is concerned with the internal rotation about a single bond as axis, which has been considered to be free in many mathematical papers dealing with various problems of polymer chains. However, considerable evidence has been accumulated to indicate that the barrier to internal rotation has a height of few kilocalories per mole or more and the chain tends to have a configuration corresponding to the minima of the hindering potential.⁴ Therefore, if the configuration does not correspond to these minima, the internal forces, such as internal hydrogen bonds, should be strong enough to compensate the excess of energy arising from the hindering potential to internal rotation.

We have already published a note⁵ dealing with a special case of this problem. Since then an interesting paper by Low and Grenville-Wells⁶ on the mathematical treatment of polypeptide configurations became available to us. However, this paper did not take the internal rotation angle as a parameter and, furthermore, it referred to a special case of polypeptides as our previous note,⁵ we, therefore, would like to discuss a more general mathematical formulation in the present communication.

II. DERIVATION OF THE GENERAL EXPRESSION

Suppose that the skeleton of a polymer chain has a configuration as shown in Fig. 1 and let the bond length, bond angle, and internal rotation angle be denoted by r_{ij} , ϕ_{ijk} , and τ_{ijkl} , respectively, where i, j, k , and l are any four consecutive numbers specifying skeletal atoms. These atoms lie on a helix which can be described by three coordinates, ρ_i , θ_{ij} , and d_{ij} , where ρ_i is the distance of the i th atom from the axis of the helix and θ_{ij} and d_{ij} are, respectively, the angle of rotation about the axis and the translation along the axis on passing from the i th atom to the j th. (See Fig. 2.)

The mathematical treatment is simplest, if the skeleton contains only one kind of atom where the values of r , ϕ , τ , ρ , θ , and d are all independent of subscripts. It is, however, evident that even for two or more than two kinds of skeletal atoms, a similar treatment can be made, if we take account of a specific atom in the structural unit of the polymer chain. We shall first obtain the expression of ρ , θ , and d as a function of r , ϕ , and τ in the simplest case.

Let us choose sets of right-handed rectangular coordinate systems in the following way (see Fig. 3). The origin of the coordinate system i coincides with the position of the i th atom with its X_i axis on $r_{i, i+1}$ or the

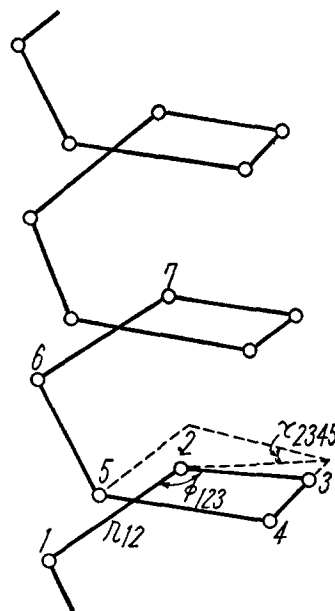


FIG. 1. Helix and internal coordinates.

¹ See, for example, a discussion on the structure of proteins Proc. Roy. Soc. (London) **B141**, 1-103 (1953).

² J. D. Watson and F. H. C. Crick, Nature **171**, 737 (1953).

³ R. E. Rundle and R. R. Baldwin, J. Am. Chem. Soc. **65**, 554 (1943); R. E. Rundle and D. French, *ibid.* 1707 (1943).

⁴ As to the summary of this work, see, for example Mizushima, Morino, and Shimanouchi, J. Phys. Chem. **56**, 324 (1952); S. Mizushima, *Structure of Molecules and Internal Rotation* (Academic Press, Inc., New York, 1954).

⁵ T. Shimanouchi and S. Mizushima, J. Chem. Soc. Japan **74**, 755 (1953).

⁶ B. W. Low and H. J. Grenville-Wells, Proc. Natl. Acad. Sci. **39**, 785 (1953).

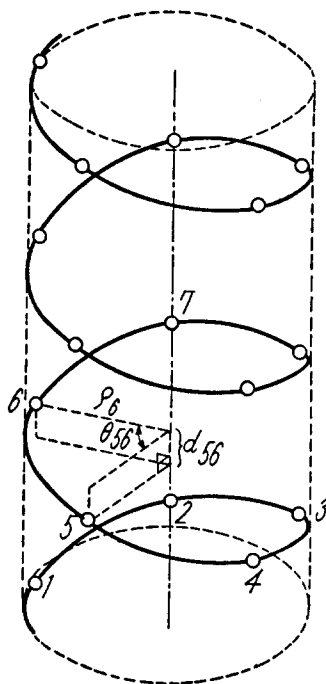


FIG. 2. Helix and cylindrical coordinates.

bond connecting the i th atom to the $i+1$ th. The Y_i axis lies in the plane determined by the two bonds $r_{i,i+1}$ and $r_{i-1,i}$ in such a way that the angle between $r_{i-1,i}$ and the positive direction of Y_i is acute. The positive direction of Z_i axis is so taken as to make the coordinate system right-handed, as referred to in the foregoing. Then it can be shown (according to the calculation of Eyring⁷) that the transformation of the i th coordinates (X_i, Y_i, Z_i) into the $i-1$ th $(X_{i-1}, Y_{i-1}, Z_{i-1})$ is expressed as

$$\mathbf{X}_{i-1} = \mathbf{A}\mathbf{X}_i + \mathbf{B}, \quad (1)$$

where \mathbf{X}_i is a column vector with elements X_i, Y_i , and Z_i ,

$$\mathbf{A} = \begin{bmatrix} -\cos\phi & -\sin\phi & 0 \\ \sin\phi \cos\tau & -\cos\phi \cos\tau & -\sin\tau \\ \sin\phi \sin\tau & -\cos\phi \sin\tau & \cos\tau \end{bmatrix} \quad (2)$$

and

$$\mathbf{B} = \begin{bmatrix} r \\ 0 \\ 0 \end{bmatrix}. \quad (3)$$

Let us choose other sets of right-handed rectangular coordinate systems (ξ_i, η_i, ζ_i) as follows (see Fig. 3). The origin of the i th coordinates coincides with the foot of the perpendicular to the axis of the helix drawn from the i th atom. The ξ_i axis being on this perpendicular with its positive direction pointing towards the i th atom. The ζ_i axis lies on the axis of the helix and the η_i axis is perpendicular to both ξ_i and ζ_i . Then the transformation of the i th coordinates (ξ_i, η_i, ζ_i) into

the $i-1$ th can be expressed as

$$\xi_{i-1} = \mathbf{N}\xi_i + \mathbf{L}, \quad (4)$$

where ξ_i is a column vector with elements ξ_i, η_i , and ζ_i ,

$$\mathbf{N} = \begin{bmatrix} \cos\theta & -\sin\theta & 0 \\ \sin\theta & \cos\theta & 0 \\ 0 & 0 & 1 \end{bmatrix}, \quad (5)$$

and

$$\mathbf{L} = \begin{bmatrix} 0 \\ 0 \\ d \end{bmatrix}. \quad (6)$$

Let us now discuss the relation between the two kinds of coordinate systems referred in the foregoing. The transformation of ξ_i into \mathbf{X}_i can be calculated as

$$\mathbf{X}_i = \mathbf{T}(\xi_i + \mathbf{S}), \quad (7)$$

where

$$\mathbf{T} = \begin{bmatrix} t_{11} & t_{12} & t_{13} \\ t_{21} & t_{22} & t_{23} \\ t_{31} & t_{32} & t_{33} \end{bmatrix} \quad (8)$$

and

$$\mathbf{S} = \begin{bmatrix} -\rho \\ 0 \\ 0 \end{bmatrix}. \quad (9)$$

Here \mathbf{T} is an orthogonal matrix whose elements are determined so as to make the three relations (1), (4), and (7) consistent.

From (1) and (7), we have

$$\mathbf{T}(\xi_{i-1} + \mathbf{S}) = \mathbf{A}\mathbf{T}(\xi_i + \mathbf{S}) + \mathbf{B}, \quad (10)$$

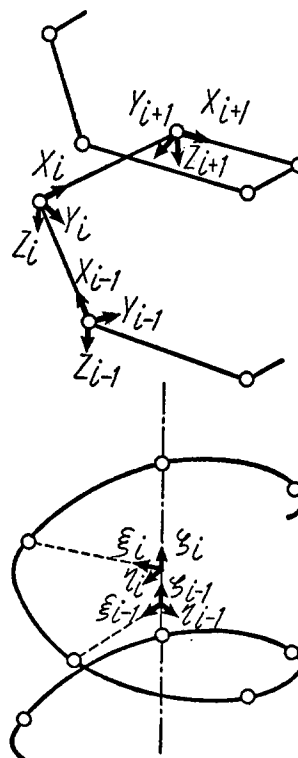


FIG. 3. The two sets of rectangular coordinate systems.

⁷ H. Eyring, Phys. Rev. 39, 746 (1932).

which can be rewritten as

$$\xi_{i-1} = \mathbf{T}^{-1} \mathbf{A} \mathbf{T} \xi_i + (\mathbf{T}^{-1} \mathbf{A} \mathbf{T} - \mathbf{E}) \mathbf{S} + \mathbf{T}^{-1} \mathbf{B}, \quad (11)$$

where \mathbf{E} is a unit matrix. This equation should be identical with Eq. (4) and, accordingly, we have

$$\mathbf{N} = \mathbf{T}^{-1} \mathbf{A} \mathbf{T} \quad (12)$$

$$\mathbf{L} = (\mathbf{T}^{-1} \mathbf{A} \mathbf{T} - \mathbf{E}) \mathbf{S} + \mathbf{T}^{-1} \mathbf{B}. \quad (13)$$

We see from Eq. (12) that the orthogonal transformation applied to \mathbf{A} gives \mathbf{N} and, therefore, the sum of diagonal elements of these two matrices should be the same. Accordingly, we have from Eqs. (2) and (5)

$$1 + 2 \cos \theta = -\cos \phi - \cos \phi \cos \tau + \cos \tau. \quad (14)$$

The final result is obtained by combining Eqs. (3), (6), (9), (13), and (14):

$$\cos \theta = \frac{1}{2} [-\cos \phi + \cos \tau - \cos \phi \cos \tau - 1], \quad (15)$$

$$d^2 = r^2 (1 - \cos \tau) (1 - \cos \phi) / (3 + \cos \phi - \cos \tau + \cos \phi \cos \tau), \quad (16)$$

$$\rho^2 = 2r^2 (1 + \cos \phi) / (3 + \cos \phi - \cos \tau + \cos \phi \cos \tau)^2. \quad (17)$$

These three equations determine the configuration of the helix in terms of bond lengths r , bond angles ϕ , and internal rotation angles τ .

III. STABLE CONFIGURATIONS OF *n*-PARAFFINS AND POLYOXYMETHYLENE

Let us first apply the three expressions to the determination of stable configurations of long chain *n*-paraffins. The equilibrium τ values of *n*-paraffins have been shown to be 180° (*trans*) or about $\pm 60^\circ$ (*gauche*) by our spectroscopic measurement.⁴

For $\tau = 180^\circ$, Eq. (2) is reduced to

$$\mathbf{A} = \begin{bmatrix} -\cos \phi & -\sin \phi & 0 \\ -\sin \phi & \cos \phi & 0 \\ 0 & 0 & -1 \end{bmatrix}$$

and from Eq. (15), we have

$$\theta = 180^\circ.$$

The corresponding configuration is the extended form in which all the molecules of solid *n*-paraffins have been shown to exist by our Raman measurement.⁸

For $\tau = 60^\circ$, we have

$$\mathbf{A} = \begin{bmatrix} -\cos \phi & -\sin \phi & 0 \\ 1 & 1 & \sqrt{3} \\ -\frac{\sin \phi}{2} & -\frac{\cos \phi}{2} & -\frac{1}{2} \\ \frac{\sqrt{3}}{2} \sin \phi & -\frac{\sqrt{3}}{2} \cos \phi & \frac{1}{2} \end{bmatrix}$$

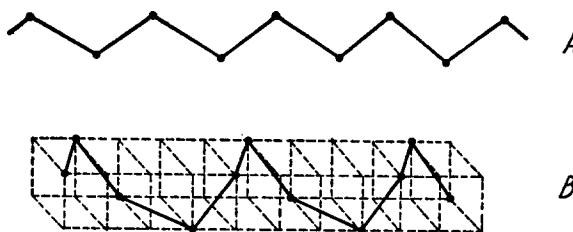


Fig. 4. The two configurations of *n*-paraffin and polyoxymethylene.

and Eqs. (15), (16), (17) become

$$\cos \theta = -(1 + 3 \cos \phi) / 4$$

$$d = \{ (1 - \cos \phi) / (5 + 3 \cos \phi) \}^{1/2} r$$

$$\rho = 2\sqrt{2} (1 + \cos \phi)^{1/2} r / (5 + 3 \cos \phi).$$

Assuming ϕ to be tetrahedral, we have

$$\theta = 90^\circ$$

$$d = r / \sqrt{3}.$$

The helix having these values of parameters is shown in Fig. 4B. Actually we have no corresponding example in the case of *n*-paraffins. However, polyoxymethylene has been shown to have a helical configuration with

$$\theta = 80^\circ$$

$$d = 1.93 \text{ \AA}.$$

Assuming the C—O bond length to be 1.49 Å, we have

$$r / \sqrt{3} = 1.71 \text{ \AA}.$$

Therefore, all the stable positions of internal rotation in polyoxymethylene can be concluded to be almost the *gauche*. This is in agreement with the experimental result obtained for Cl—CH₂—O—CH₂—Cl which has a configuration similar to polyoxymethylene.¹⁰

IV. STABLE CONFIGURATIONS OF POLYPEPTIDE CHAIN

The polypeptide chain contains three kinds of internal rotation axes, —CO—NH—, —CHR—CO—, and —NH—CHR—, the corresponding azimuthal angle being designated by τ_1 , τ_2 , and τ_3 , respectively. Further let us denote bond distances r_1 , r_2 , r_3 and bond angles ϕ_1 , ϕ_2 , ϕ_3 in the unit of the chain as shown in Fig. 5. Then the values of θ , d , and ρ of an α -carbon atom can be calculated similarly as above except for the expressions of \mathbf{A} and \mathbf{B} in Eqs. (2) and (3), which are changed to

$$\mathbf{A} = \mathbf{A}_3 \mathbf{A}_1 \mathbf{A}_2, \quad (18)$$

$$\mathbf{B} = \mathbf{A}_3 \mathbf{A}_1 \mathbf{B}_2 + \mathbf{A}_3 \mathbf{B}_1 + \mathbf{B}_3, \quad (19)$$

⁸ E. Sauter, Z. physik chem. **B21**, 186 (1933).

⁹ S. Mizushima and T. Shimanouchi, J. Am. Chem. Soc. **71**, 3411 (1949).

¹⁰ M. Katayama and Y. Morino, Repts. Radiation Chem. Research Inst. **4**, 1 (1949).

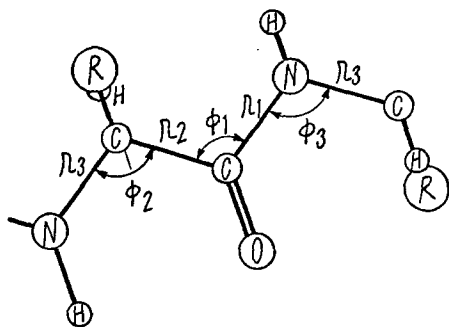


FIG. 5. The polypeptide chain.

where

$$\mathbf{A}_i = \begin{bmatrix} -\cos\phi_i & -\sin\phi_i & 0 \\ \sin\phi_i \cos\tau_i & -\cos\phi_i \cos\tau_i & -\sin\tau_i \\ \sin\phi_i \sin\tau_i & -\cos\phi_i \sin\tau_i & \cos\tau_i \end{bmatrix}, \quad (20)$$

$$\mathbf{B}_i = \begin{bmatrix} r_i \\ 0 \\ 0 \end{bmatrix}, \quad (21)$$

$$i = 1, 2, 3.$$

With the relations (18) and (19) of \mathbf{A} and \mathbf{B} we have the expressions for \mathbf{N} and \mathbf{L} identical with Eqs. (12) and (13).

The equations for θ , d , and ρ referred to in our previous paper⁵ can then be derived from Eqs. (15), (16), and (17) by denoting the elements of \mathbf{A} and \mathbf{B} as follows:

$$\mathbf{A} = \begin{bmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{bmatrix} \quad (22)$$

$$\mathbf{B} = \begin{bmatrix} b_1 \\ b_2 \\ b_3 \end{bmatrix}. \quad (23)$$

Then we have

$$\cos\theta = (a_{11} + a_{22} + a_{33} - 1)/2, \quad (24)$$

$$d^2 = [b_1(a_{13} + a_{31}) + b_2(a_{23} + a_{32}) + b_3(a_{33} - a_{11} - a_{22} + 1)]^2 / (3 - a_{11} - a_{22} - a_{33}) \times (a_{33} - a_{11} - a_{22} + 1), \quad (25)$$

$$\rho^2 = (b_1^2 + b_2^2 + b_3^2 - d^2) / (3 - a_{11} - a_{22} - a_{33}). \quad (26)$$

The helical configuration of a polypeptide chain is determined from Eqs. (24), (25), and (26), if we know the values of r , ϕ , and τ . The values of the former two parameters (or the bond lengths and bond angles) lie in a narrow range, but that of the last parameter can take two quite different values except for τ_1 or the azimuthal angle of internal rotation about $-\text{CO}-\text{NH}-$ axis which always take a value corresponding to the planar *trans* configuration of the peptide bond.¹¹ The

¹¹ Mizushima, Shimanouchi, Nagakura, Kuratani, Tsuboi Baba, and Fujioka, J. Am. Chem. Soc. **72**, 3490 (1950).

equilibrium values of τ_2 and τ_3 correspond either to the *trans*-configuration or to the *gauche*-configuration, where the latter differs from the former by a τ value not much different from 120° . These different values of τ give rise to different stable configurations of a polypeptide chain.

Let us designate by $\angle t$ and $\angle g$ the values of τ corresponding to the *trans*- and the *gauche*-configurations. Then the equilibrium values of τ_1 , τ_2 , and τ_3 for some of the polypeptide models are expressed as follows:

(a) $\tau_1 = \tau_2 = \tau_3 = \angle t$ for the extended configuration corresponding to the structure of β keratin proposed by Meyer and Mark.¹²

(b) $\tau_1 = \angle t$, $\tau_2 = -\angle g$, and $\tau_3 = \angle g$ for the folded configuration corresponding to the structure of α protein proposed by Shimanouchi and Mizushima¹³ and by Ambrose *et al.*¹⁴

(c) $\tau_1 = \angle t$, $\tau_2 = \angle g$, and $\tau_3 = -\angle g$ for the folded configuration proposed by Huggins.¹⁵

(d) $\tau_1 = \angle t$, $\tau_2 = \angle g$, and $\tau_3 = \angle g$ or $\tau_1 = \angle t$, $\tau_2 = -\angle g$, and $\tau_3 = -\angle g$ for α helices of Pauling and Corey.¹⁶

The details of the discussion on the relative stability of these configurations and of others will be given elsewhere.¹⁷

V. STABLE CONFIGURATIONS OF CELLULOSE

The molecules of cellulose consist of pyranose rings. If we number the atoms of a cellulose molecule as shown in Fig. 6, the azimuthal angles of internal rotation

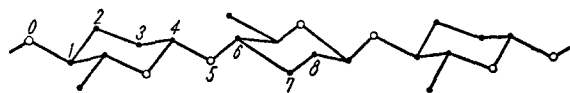


FIG. 6. The atomic arrangement in cellulose.

become:

$$\begin{aligned} \tau(0123) &= 180^\circ, \\ \tau(1234) &= 60^\circ, \\ \tau(2345) &= 180^\circ, \\ \tau(3456) &= -120^\circ, \\ \tau(4567) &= -120^\circ. \end{aligned}$$

¹² K. H. Meyer and H. Mark, Ber. deut. chem. Ges. **61**, 1932 (1928).

¹³ T. Shimanouchi and S. Mizushima, Kagaku **17**, 24, 52 (1947); Bull. Chem. Soc. Japan **21**, 1 (1948).

¹⁴ E. J. Ambrose and W. E. Hanby, Nature **163**, 483 (1949); Ambrose, Elliot, and Temple, Nature **163**, 859 (1949).

¹⁵ M. L. Huggins, Chem. Revs. **32**, 195 (1943).

¹⁶ Pauling, Corey, and Branson, Proc. Natl. Acad. Sci. **37**, 205 (1951).

¹⁷ A part of this discussion has been given in reference 5. See also S. Mizushima, *Advances in Protein Chemistry* (Academic Press, Inc., New York, 1954), Vol. IX.

Furthermore, if we rewrite Eq. (1) as

$$\mathbf{X}_{i-1} = \mathbf{A}_{i-1, i} \mathbf{X}_i + \mathbf{B}_{i-1, i},$$

we have

$$\mathbf{A} = \mathbf{A}_{12} \mathbf{A}_{23} \mathbf{A}_{34} \mathbf{A}_{45} \mathbf{A}_{56},$$

$$\mathbf{B} = \mathbf{A}_{12} \mathbf{A}_{23} \mathbf{A}_{34} \mathbf{A}_{45} \mathbf{B}_{56} + \mathbf{A}_{12} \mathbf{A}_{23} \mathbf{A}_{34} \mathbf{B}_{45} + \mathbf{A}_{12} \mathbf{A}_{23} \mathbf{B}_{34} + \mathbf{A}_{12} \mathbf{B}_{23} + \mathbf{B}_{12}$$

in place of Eqs. (18) and (19) of the preceding section.

Using τ values just shown and assuming the bond angle ϕ to be tetrahedral angle and bond lengths of C—C and C—O to be 1.54 Å, we can calculate the θ

and d values of the cellulose helix as

$$\theta = 180^\circ,$$

$$d = (10.9/2)A.$$

The latter can be considered to be in good agreement with the value $(10.3/2)A$ (or half the fiber period) obtained from the diffraction experiment on cellulose,¹⁸ if we take into account the approximation made in this calculation.

¹⁸ See, for example, K. H. Meyer and H. Mark, *Hochpolymere Chemie II* (Akademische Verlagsgesellschaft, Leipzig, Germany, 1940).

On the Electronic Structure and Electronic Spectra of Ethylene-Like Molecules*†

ROBERT G. PARR,‡ *Department of Chemistry, Carnegie Institute of Technology, Pittsburgh, Pennsylvania,*
and *Department of Theoretical Chemistry, University of Cambridge, Cambridge, England*

AND

RUDOLPH PARISER, *Jackson Laboratory, E. I. duPont de Nemours and Company, Wilmington, Delaware*

(Received July 9, 1954)

A previously given theory of the electronic spectra and electronic structure of complex unsaturated molecules is applied to *ethylene-like molecules*, molecules such as ethylene itself, propylene or formaldehyde, which have two π electrons and two atomic π orbitals available for π -bond formation. Relations are derived among electronic excitation energies, intensities of electronic transitions, extra-ionic resonance energies and dipole moments of such molecules. Relative electronegativities are shown to play an important role in these relations, where the *effective electronegativity* of an atom is Mulliken's electronegativity (the mean of the appropriate atomic valence-state ionization potential and electron affinity) plus the total attraction of the valence electron of the atom for all other atoms in the molecule.

The analysis yields the result that the dipole moment due to a slight bond heteropolarity is proportional to the electronegativity difference of the bonded atoms, the extra-ionic resonance energy to its square. Proportionality factors are given absolutely by the theory. It is pointed out that the theory of a two-electron σ bond is formally the same, moreover, so that a derivation is provided

for the familiar electronegativity relations of Pauling. Theoretical and empirical values for the proportionality factors are found to agree reasonably well for both π bonds and σ bonds.

The formulas given cover multiple perturbations of any type which may be considered not to add (or subtract) π electrons or π orbitals. They thus provide a scheme for quantitative evaluation of *inductive effects* in ethylene-like molecules. Systematic consideration of *mesomeric effects* is deferred, but an outline of the procedure which may be used for their study is given, using mono-substituted ethylene as an example.

To illustrate the use of the formulas, to bring out the relationships between the method and the work of other authors, and to see whether the method has promise for σ -electron systems, calculations are made of the electronic spectrum of ethylene, the twisting force constant of ethylene, the ionization potential and electron affinity of ethylene, the electronic spectrum and dipole moment of formaldehyde, and the electronic spectrum, ionization potential, and binding energy of the hydrogen molecule.

I. INTRODUCTION

RECENTLY there have been presented the elements of a theory designed for the quantitative correlation and prediction of those properties of complex unsaturated organic molecules, such as color, intensity of color, and resonance energy, which are qualitatively attributable to the unsaturation, or π electrons of these molecules.¹⁻³

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† Contribution No. 166 from Jackson Laboratory, E. I. duPont de Nemours and Company, Wilmington, Delaware.

‡ John Simon Guggenheim Memorial Foundation Fellow and Fulbright Research Scholar at the University of Cambridge, 1953-1954.

¹ R. Pariser and R. G. Parr, *J. Chem. Phys.* **21**, 466 (1953).

² R. Pariser and R. G. Parr, *J. Chem. Phys.* **21**, 767 (1953). The argument given on p. 769 of this paper in favor of using lower

The theory differs from conventional ones in several important ways, some rather subtle, and it is a semi-empirical theory which may require modification as experience with its application accumulates. In order that the crucial points involved may be fully bared, Sec. II of the present paper is devoted to a summary of the main ideas and approximations in the theory.

Sections III-V give the application of the theory to two- π -electron, ethylene-like molecules (e.g., propylene or formaldehyde). Section III contains a derivation of

penetration integral values than calculated theoretically is not correct. The actual formal relation between the electron affinity A and self-penetration integral (1:11) is $A = (1:11) - T$, where T is the kinetic energy of a π electron in the negative ion (a relatively large quantity). The authors are indebted to Dr. F. O. Ellison for pointing out this error.

³ F. G. Fumi and R. G. Parr, *J. Chem. Phys.* **21**, 1864 (1953). In Table I of this paper, for boldface g read \tilde{g} .