Molecular Orbital Calculations of Vibrational Force Constants. I. Ethylene

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As a preliminary to the theoretical evaluation of certain out-of-plane vibrational force constants of benzene, the energy levels and twisting frequency of ethylene are calculated by the method of antisymmetric molecular orbitals, no empirical data being used other than molecular dimensions. The problem is oversimplified to a two-electron one, and yet encouraging results are obtained.

BECAUSE electronic velocities on the average far surpass nuclear velocities, it is permissible in the calculation of vibrational energy levels of molecules to picture the nuclei vibrating in the time-average potential field of the electrons. The force constant associated with the nth normal mode of vibration then turns out to be equal to the curvature at the equilibrium position of the plot of electronic energy *versus* the nth normal coordinate. It is therefore possible, in principle at least, to find the vibrational force constants of a molecule from its electronic energy as a function of nuclear configuration.

The problem of determining the electronic energy of a polyatomic molecule is, in general, extremely difficult, because exact solution of the many-body wave equation is out of the question —very crude approximation methods must be used. Nevertheless, considerable success has been attained in the semiquantitative calculation of electronic energy levels. Up to now very few attempts have been made to calculate electronic energies as functions of configuration, however. The present papers are a try at this: in I the twisting force constant of ethylene is computed from the electronic energy as a function of the twisting angle; in II two analogous force constants of benzene are computed in similar manner.

Of the various approximate methods available for the calculation of electronic energies, the so-called method of molecular orbitals, in the form employed by Goeppert-Mayer and Sklar,[1] appears the most suitable for quantitative calculation on ethylene and benzene. Goeppert-Mayer

and Sklar have calculated the energy levels of the equilibrium configuration of benzene, Hartmann,[2] the levels of the equilibrium (planar) form of ethylene; straightforward extension of these calculations should yield the energies for small distortions from equilibrium (and hence the force constants).

In the Goeppert-Mayer-Sklar modification of the molecular orbital method, the wave functions for the various states of an n-electron system are written as products of n one-electron wave functions (called molecular orbitals). The latter are found by the method of variation of parameters as best linear combinations of orbitals on individual atoms (called atomic orbitals); the energies are calculated on the assumption that each electron moves independently in the potential field of the nuclear framework. The wave function for the ground state of the n-electron system is constructed by the placing of electrons in the molecular orbitals of lowest energy, two at a time until all n electrons are used up. The energy of the ground state is then calculated from this wave function, with an n-electron Hamiltonian which includes electronic repulsion terms. Excited states are similarly treated, care always being taken to multiply the wave functions by suitable spin factors and to make them completely antisymmetric as regards electron interchange.

THE ENERGY LEVELS OF ETHYLENE[3]

Anticipating enough trouble with benzene treated as a six-electron problem, one starts by

[1] M. Goeppert-Mayer and A. L. Sklar, J. Chem. Phys. 6, 645 (1938).
[2] H. Hartmann, Zeits. f. physik. Chemie B53, 96 (1943).
[3] The treatment given in this and the following sections is, like Hartmann's (see reference 2), in the classification

considering ethylene as a two-electron problem, knowing full well that this is not strictly justified.[4] The electrons considered are the "unsaturation" electrons which pair to form the second "double" or "$\pi\pi$" carbon-carbon bond. If the carbon atoms are labeled A_1 and A_2 [in general A_n] and the $2p\pi$-wave functions for electron ν on A_1 and A_2 are denoted by $\alpha_1(\nu)$ and $\alpha_2(\nu)$ [in general $\alpha_n(\nu)$], the problem is to calculate the energy levels of the two electrons which occupy the molecular orbitals which are linear combinations of α_1 and α_2, as a function of the angle φ between the major axes of α_1 and α_2. The position $\varphi=0$ corresponds to the equilibrium, planar configuration of ethylene; the second derivative of the energy with respect to φ, evaluated at $\varphi=0$, is the force constant for twisting about the double bond.

The atomic orbitals α_1 and α_2 are taken to be real, normalized, Zener-type, hydrogen-like functions.[5] They therefore depend upon an effective nuclear charge Z of a carbon nucleus towards a $2p\pi$-electron. Also, by the vector property of p orbitals,[6]

$$\alpha_1 = a_1, \quad \alpha_2 = a_2\cos\varphi + a_{2s}\sin\varphi, \quad (1)$$

where a_2 is a p orbital parallel to (but not coaxial with) a_1, and a_{2s} is a p orbital perpendicular both to a_1 and the carbon-carbon internuclear axis.

From analogy with the hydrogen molecule,[6] the linear combinations of the α_n which are proper molecular orbitals for the distorted molecule are

$$\phi_+(\nu) = (2\sigma_+)^{-\frac{1}{2}}[\alpha_1(\nu) + \alpha_2(\nu)],$$
$$\phi_-(\nu) = (2\sigma_-)^{-\frac{1}{2}}[\alpha_1(\nu) - \alpha_2(\nu)]. \quad (2)$$

of Mulliken [R. S. Mulliken, Chem. Rev. 41, 203 (1947)] an "approximate theoretical" one; Mulliken's "semiempirical" treatment of ethylene [R. S. Mulliken and C. C. J. Roothaan, Chem. Rev. 41, 219 (1947)] is formally similar, but appeals to experiment rather than calculation for values of certain integrals.

[4] Thus the neglect of non-unsaturation electrons makes the calculations immediately subject to the "nightmare of inner shells"—the error resulting from the failure to construct wave functions for the unsaturation electrons which are orthogonal to the wave functions for the other electrons (in stabler orbitals).

[5] Cf., for example, Eyring, Walter, and Kimball, Quantum Chemistry (John Wiley and Sons, Inc., New York, 1944), pp. 89–90.

[6] Eyring, Walter, and Kimball, Quantum Chemistry (John Wiley and Sons, Inc., New York, 1944), Chapter XII.

Here

$$\sigma_+ = 1 + S_{\alpha_1\alpha_2} \quad \sigma_- = 1 - S_{\alpha_1\alpha_2}, \quad (3)$$

where

$$S_{\alpha_1\alpha_2} = \int \alpha_1(1)\alpha_2(1)dv_1 \quad (4)$$

is the overlap integral between α_1 and α_2.

The various states of the two electrons result from putting two electrons into ϕ_+ and ϕ_- in all possible ways. This yields the following four wave functions:

$$\psi_1 = \phi_+(1)\phi_+(2),$$
$$\psi_V = 2^{-\frac{1}{2}}[\phi_+(1)\phi_-(2) + \phi_+(2)\phi_-(1)],$$
$$\psi_T = 2^{-\frac{1}{2}}[\phi_+(1)\phi_-(2) - \phi_+(2)\phi_-(1)],$$
$$\psi_2 = \phi_-(1)\phi_-(2). \quad (5)$$

All but the third of these are symmetric in the electrons and therefore require antisymmetric spin factors of the form

$$X_s = 2^{-\frac{1}{2}}[\delta_+(1)\delta_-(2) - \delta_+(2)\delta_-(1)], \quad (6)$$

where $\delta_+(\nu)$ and $\delta_-(\nu)$ are possible orthonomal spin functions for the νth electron. The third is antisymmetric in the electrons and so must be combined with a symmetric spin factor

$$X_t = \begin{cases} 2^{-\frac{1}{2}}[\delta_+(1)\delta_-(2) + \delta_+(2)\delta_-(1)], \\ \text{or} \quad \delta_+(1)\delta_+(2), \\ \text{or} \quad \delta_-(1)\delta_-(2). \end{cases} \quad (7)$$

Completely antisymmetric wave functions for the four states thus are[7]

$$\Psi_1 = \psi_1 X_s \quad \text{(singlet, energy } E_1\text{)},$$
$$\Psi_V = \psi_V X_s \quad \text{(singlet, energy } E_V\text{)},$$
$$\Psi_T = \psi_T X_t \quad \text{(triplet, energy } E_T\text{)},$$
$$\Psi_2 = \psi_2 X_s \quad \text{(singlet, energy } E_2\text{)}. \quad (8)$$

Now Ψ_1 and Ψ_2 are both totally symmetric in the nuclei. They therefore interact to give the two states

$$\Psi_N = C_1\Psi_1 + C_2\Psi_2$$
$$\text{(singlet, energy } E_N \leqslant \min\{E_1, E_2\}) \quad (9)$$

and

$$\Psi_Z = D_1\Psi_1 + D_2\Psi_2$$
$$\text{(singlet, energy } E_Z \geqslant \max\{E_1, E_2\}). \quad (10)$$

Ψ_N turns out to be the best wave function for the ground state of planar ethylene obtainable from this approach.

[7] At this point Hartmann (reference 2) is in error—his (12b) is not a singlet but a mixed singlet and triplet wave function.

The Hamiltonian for the system may be written

$$\mathbf{H} = \mathbf{T}(1) + \mathbf{T}(2) + \mathbf{H}_0(1) + \mathbf{H}_0(2) + (e^2/r_{12}), \quad (11)$$

where $\mathbf{T}(\nu)$ is the kinetic energy of electron ν, $\mathbf{H}_0(\nu)$ is the mutual potential energy of electron ν and the single-bonded $H_2C - CH_2$ framework, and e^2/r_{12} is the repulsive potential between electrons 1 and 2. Consequently,

$$\begin{aligned} E_1 &= \int \Psi_1 \mathbf{H} \Psi_1 dv = \int \psi_1 \mathbf{H} \psi_1 dv \\ &= \int \phi_+(1)\phi_+(2)\mathbf{H}\phi_+(1)\phi_+(2)dv \\ &= 2\epsilon_+ + \gamma_{++}, \end{aligned} \quad (12)$$

where

$$\begin{aligned} \epsilon_+ &= \int \phi_+(1)\phi_+(2)[\mathbf{T}(1)+\mathbf{H}_0(1)]\phi_+(1)\phi_+(2)dv \\ &= \int \phi_+(1)[\mathbf{T}(1)+\mathbf{H}_0(1)]\phi_+(1)dv, \end{aligned} \quad (13)$$

and

$$\gamma_{++} = \int \phi_+(1)\phi_+(2)(e^2/r_{12})\phi_+(1)\phi_+(2)dv. \quad (14)$$

Similarly,

$$E_2 = 2\epsilon_- + \gamma_-, \quad (15)$$

$$E_V = \epsilon_+ + \epsilon_- + \gamma_{+-} + \delta_{+-}, \quad (16)$$

$$E_T = \epsilon_+ + \epsilon_- + \gamma_{+-} - \delta_{+-}, \quad (17)$$

where

$$\epsilon_- = \int \phi_-(1)[\mathbf{T}(1)+\mathbf{H}_0(1)]\phi_-(1)dv, \quad (18)$$

$$\gamma_{\pm-} = \int \phi_\pm(1)\phi_-(2)(e^2/r_{12})\phi_\pm(1)\phi_+(2)dv, \quad (19)$$

$$\delta_{+-} = \int \phi_+(1)\phi_-(2)(e^2/r_{12})\phi_-(1)\phi_+(2)dv. \quad (20)$$

E_N and E_Z are the two roots of the secular equation

$$\begin{vmatrix} E_1 - E & \int \psi_1 \mathbf{H} \Psi_2 dv \\ \int \Psi_1 \mathbf{H} \Psi_2 dv & E_2 - E \end{vmatrix} = 0. \quad (21)$$

But

$$\begin{aligned} \int &\Psi_1 \mathbf{H} \Psi_2 dv \\ &= \int \psi_1 \mathbf{H} \psi_2 dv = \int \phi_+(1)\phi_+(2)\mathbf{H}\phi_-(1)\phi_-(2)dv \\ &= \int \phi_+(1)\phi_+(2)[\mathbf{T}(1)+\mathbf{T}(2)+\mathbf{H}_0(1) \\ &\qquad + \mathbf{H}_0(2) + (e^2/r_{12})]\phi_-(1)\phi_-(2)dv \\ &= \int \phi_+(1)\phi_+(2)(e^2/r_{12})\phi_-(1)\phi_-(2)dv \\ &= \delta_{+-} = (1/2)(E_V - E_T). \end{aligned} \quad (22)$$

Hence

$$\begin{aligned} E_N &= (1/2)(E_2+E_1) - (1/2)(E_2-E_1) \\ &\quad \times [1 + (E_V-E_T)^2(E_2-E_1)^{-2}]^{\frac{1}{2}} \end{aligned} \quad (23)$$

and

$$\begin{aligned} E_Z &= (1/2)(E_2+E_1) + (1/2)(E_2-E_1) \\ &\quad \times [1 + (E_V-E_T)^2(E_2-E_1)^{-2}]^{\frac{1}{2}}. \end{aligned} \quad (24)$$

For $\varphi = \pi/2$, E_1 and E_2 coalesce and the perturbation is at a maximum. In this case (23) and (24) give

$$E_N{}^{\perp} = E_1{}^{\perp} - (1/2)(E_V{}^{\perp} - E_T{}^{\perp}) \quad (25)$$

and

$$E_Z{}^{\perp} = E_1{}^{\perp} + (1/2)(E_V{}^{\perp} - E_T{}^{\perp}), \quad (26)$$

where the superscript $\perp$ denotes the position $\varphi = \pi/2$.

The above formulas give the energies in terms of integrals over molecular orbitals. The next step is to express these in terms of integrals over atomic orbitals through the use of (2). One finds, after the use of a little algebra,

$$\begin{aligned} \gamma_{++} = 2(2\sigma_+)^{-2}[&(\alpha_1\alpha_1;\alpha_1\alpha_1) + (\alpha_1\alpha_1;\alpha_2\alpha_2) \\ &+ 2(\alpha_1\alpha_2;\alpha_1\alpha_2) + 4(\alpha_1\alpha_1;\alpha_1\alpha_2)], \end{aligned}$$

$$\begin{aligned} \gamma_{--} = 2(2\sigma_-)^{-2}[&(\alpha_1\alpha_1;\alpha_1\alpha_1) + (\alpha_1\alpha_1;\alpha_2\alpha_2) \\ &+ 2(\alpha_1\alpha_2;\alpha_1\alpha_2) - 4(\alpha_1\alpha_1;\alpha_1\alpha_2)], \end{aligned}$$

$$\begin{aligned} \gamma_{+-} = (2\sigma_+\sigma_-)^{-1}[&(\alpha_1\alpha_1;\alpha_1\alpha_1) \\ &+ (\alpha_1\alpha_1;\alpha_2\alpha_2) - 2(\alpha_1\alpha_2;\alpha_1\alpha_2)], \end{aligned}$$

and

$$\delta_{+-} = (2\sigma_+\sigma_-)^{-1}[(\alpha_1\alpha_1;\alpha_1\alpha_1) - (\alpha_1\alpha_1;\alpha_2\alpha_2)], \quad (28)$$

where, in c.g.s. units,[8]

$$\begin{aligned} (\alpha_i\alpha_j;\alpha_k\alpha_l) &= \int \alpha_i(1)\alpha_k(2)(e^2/r_{12})\alpha_j(1)\alpha_l(2)dv \\ &= (\alpha_k\alpha_l;\alpha_i\alpha_j). \end{aligned} \quad (29)$$

The evaluation of the $\epsilon_\pm$ is not so easy.[9] Neglecting the hydrogen atoms, one first assumes that

$$\mathbf{H}_0(\nu) = \mathbf{H}_{A1}(\nu) + \mathbf{H}_{A2}(\nu), \quad (30)$$

where $\mathbf{H}_{An}(\nu)$ is the potential representing attraction of electron ν by the nth carbon nucleus plus repulsion of electron ν by the other five electrons of that nucleus. Then

$$[\mathbf{T}(\nu)+\mathbf{H}_{An}(\nu)]\alpha_n(\nu) = W_{2p}\alpha_n(\nu), \quad (31)$$

where W_{2p} is the energy of a $2p$ electron in a

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[8] Note that in atomic units (distances in units of the first Bohr radius $a_0 = 0.5292$A, energies in units of $e^2/2a_0 = 13.602$ ev)

$$(\alpha_i\alpha_j;\alpha_k\alpha_l) = \int \alpha_i(1)\alpha_k(2)(2/r_{12})\alpha_j(1)\alpha_l(2)dv.$$

[9] The procedure adopted here is due to Goeppert-Mayer and Sklar (reference 1).

TABLE I. Values of integrals over atomic orbitals (atomic units).

Integral	ρ	6	8.13	8.37	10
$S_{a_1a_2}$		0.46800	0.27723	0.25995	0.16396
$Z^{-1}(A_1:a_2a_2)$		0.0773	0.02287	0.01976	0.00703
$Z^{-1}(A_1:a_1a_2)$		0.1200	0.04768	0.04364	0.02090
$Z^{-1}(a_1a_1;a_1a_1)$		0.3914	0.3914	0.3914	0.3914
$Z^{-1}(a_1a_1;a_2a_2)$		0.2616	0.2140	0.2086	0.1806
$Z^{-1}(a_1a_1;a_{2s}a_{2s})$		0.2484	0.2080	0.2036	0.1774
$Z^{-1}(a_1a_2;a_1a_2)$		0.0730	0.0250	0.0220	0.0082
$Z^{-1}(a_1a_{2s};a_1a_{2s})$		0.0035	0.0015	0.0012	0.0004
$Z^{-1}(a_1a_1;a_1a_2)$		0.1538	0.0827	0.0766	0.0448

TABLE II. Values of integrals over molecular orbitals (atomic units).

Integral	ρ	6	8.13	8.37	10
$\varphi=0$: $Z^{-1}(\epsilon_+ - W_{2p})$		−0.4174	−0.2876	−0.2767	−0.2176
$Z^{-1}(\epsilon_- - W_{2p})$		−0.1224	−0.1474	−0.1462	−0.1458
$Z^{-1}\gamma_{++}$		0.3281	0.3023	0.2993	0.2833
$Z^{-1}\gamma_{--}$		0.3247	0.3107	0.3082	0.2927
$Z^{-1}\gamma_{+-}$		0.3246	0.3008	0.2981	0.2855
$Z^{-1}\delta_{+-}$		0.0831	0.0961	0.0980	0.1083
$\varphi=\pi/2$: $Z^{-1}(\epsilon_+ + W_{2p})$		−0.3257	−0.2309	−0.2234	−0.1844
$Z^{-1}(\epsilon_- - W_{2p})$		−0.3257	−0.2309	−0.2234	−0.1844
$Z^{-1}\gamma_{++}$		0.3234	0.3012	0.2987	0.2848
$Z^{-1}\gamma_{--}$		0.3234	0.3012	0.2987	0.2848
$Z^{-1}\gamma_{+-}$		0.3164	0.2982	0.2963	0.2840
$Z^{-1}\delta_{+-}$		0.0715	0.0917	0.0939	0.1070

carbon atom in its valence state; and Eqs. (2), (13), and (18) give

$$\epsilon_\pm = (2\sigma_\pm)^{-1} \int [\alpha_1(\nu)\pm\alpha_2(\nu)][T(\nu)+H_{A1}(\nu) \\ H_{A2}(\nu)][\alpha_1(\nu)\pm\alpha_2(\nu)]dv_\nu \\ = W_{2p}+(2\sigma_\pm)^{-1} \int [\alpha_1(1)+\alpha_2(1)] \\ \times [H_{A1}(1)\alpha_2(1)+H_{A2}(1)\alpha_1(1)]dv_1. \quad (32)$$

Now $H_{An}(1)$ is the potential on electron 1 due to the *neutral* carbon atom A_n minus one $2p$ electron in the orbital $\alpha_n(\nu)$:

$$H_{An}(1)=H_{An}^*(1) - \int (e^2/r_{12})\alpha_n^2(2)dv_2. \quad (33)$$

Here $H_{An}^*(1)$ is the (assumed) spherically symmetric potential of a neutral carbon atom A_n. Substituting this in (32), one finds

$$\epsilon_\pm = W_{2p}-(\sigma_\pm)^{-1}[(A_1:\alpha_2\alpha_2)\pm(A_1:\alpha_1\alpha_2) \\ +(\alpha_1\alpha_1;\alpha_2\alpha_2)\pm(\alpha_1\alpha_1;\alpha_1\alpha_2)], \quad (34)$$

where

$$(A_1:a_p\alpha_{p'}) = -\int H_{A1}^*(\nu)\alpha_p(\nu)\alpha_{p'}(\nu)dv_\nu \\ = (A_1:\alpha_{p'}\alpha_p). \quad (35)$$

There remains to make explicit the dependence of the various integrals on the angle φ. To do this, one may note from (1) that

$$S_{\alpha_1\alpha_2} = \cos\varphi S_{a_1a_2}, \\ (A_1:\alpha_2\alpha_2) = (A_1:a_2a_2), \\ (A_1:\alpha_1\alpha_2) = \cos\varphi(A_1:a_1a_2), \\ (\alpha_1\alpha_1;\alpha_1\alpha_1) = (a_1a_1;a_1a_1), \\ (\alpha_1\alpha_1;\alpha_2\alpha_2) = \cos^2\varphi(a_1a_1;a_2a_2) \quad (36) \\ \qquad +\sin^2\varphi(a_1a_1;a_{2s}a_{2s}), \\ (\alpha_1\alpha_2;\alpha_1\alpha_2) = \cos^2\varphi(a_1a_2;a_1a_2) \\ \qquad +\sin^2\varphi(a_1a_{2s};a_1a_{2s}), \\ (\alpha_1\alpha_1;\alpha_1\alpha_2) = \cos\varphi(a_1a_1;a_1a_2).$$

[Integrals such as $S_{a_1a_{2s}}$, $(a_1a_1;a_2a_{2s})$, and $(A_1:a_1a_{2s})$ are zero by symmetry.] Hence

$$\epsilon_\pm = W_{2p}-(1\pm\cos\varphi S_{a_1a_2})^{-1} \\ \times \{(A_1:a_2a_2)\pm\cos\varphi[(A_1:a_1a_2) \\ +(a_1a_1;a_1a_2)]+\cos^2\varphi(a_1a_1;a_2a_2) \\ +\sin^2\varphi(a_1a_1;a_{2s}a_{2s})\}, \quad (37)$$

$$\gamma_{\pm\pm} = (1/2)(1\pm\cos\varphi S_{a_1a_2})^{-2} \\ \times \{(a_1a_1;a_1a_1)\pm 4\cos\varphi(a_1a_1;a_1a_2) \\ +\cos^2\varphi[(a_1a_1;a_2a_2)+2(a_1a_2;a_1a_2)] \\ +\sin^2\varphi[(a_1a_1;a_{2s}a_{2s}) \\ \qquad +2(a_1a_{2s};a_1a_{2s})]\}, \quad (38)$$

$$\gamma_{+-} = (1/2)(1-\cos^2\varphi S_{a_1a_2}^2)^{-1} \\ \times \{(a_1a_1;a_1a_1)+\cos^2\varphi[(a_1a_1;a_2a_2) \\ -2(a_1a_2;a_1a_2)]+\sin^2\varphi[(a_1a_1;a_{2s}a_{2s}) \\ \qquad -2(a_1a_{2s};a_1a_{2s})]\}, \quad (39)$$

$$\delta_{+-} = (1/2)(1-\cos^2\varphi S_{a_1a_2}^2)^{-1} \\ \times \{(a_1a_1;a_1a_1)-\cos^2\varphi(a_1a_1;a_2a_2) \\ \qquad -\sin^2\varphi(a_1a_1;a_{2s}a_{2s})\}. \quad (40)$$

Combination of these expressions as required by (12), (15)–(17), and (23)–(24) gives the energy levels as function of φ.

As atomic wave functions one may take[5]

$$a_1(\nu) = (Z^5/32\pi)^{\frac{1}{2}}a_{1\nu} \\ \times\exp(-Za_{1\nu}/2)\sin\theta_{a_{1\nu}}\cos\phi_\nu, \\ a_2(\nu) = (Z^5/32\pi)^{\frac{1}{2}}a_{2\nu} \\ \times\exp(-Za_{2\nu}/2)\sin\theta_{a_{2\nu}}\cos\phi_\nu, \quad (41) \\ a_{2s}(\nu) = (Z^5/32\pi)^{\frac{1}{2}}a_{2\nu} \\ \times\exp(-Za_{2\nu}/2)\sin\theta_{a_{2\nu}}\sin\phi_\nu,$$

where $a_{n\nu}$, $\theta_{a_{n\nu}}$, ϕ_ν are polar coordinates of electron ν with respect to a coordinate system fixed at nucleus A_n. One then finds that all of the integrals which appear in (37)–(40) are to be found in the literature or can be calculated by methods given in the literature. These integrals will be discussed in detail elsewhere; suffice it here to tabulate the ones needed as functions of the screening constant Z and the

TABLE III. Energy levels of planar and perpendicular ethylene (electron volts) for $R = 1.353$Å.

Level		Z	2.35	3.18	3.27	3.91
			Energy-energy of planar N level (electron volts)			
Planar	1	0.3	1.3	1.4	3.0	
	2	19.1	13.8	13.4	11.2	
	N	0	0	0	0	
	T	7.0	3.1	2.8	2.2	
	V	12.3	11.5	11.5	12.7	
	Z	19.4	15.0	14.8	14.1	
Perpendicular	1	6.0	6.2	6.1	6.6	
	2	6.0	6.2	6.1	6.6	
	N	3.7	2.2	1.9	0.9	
	T	3.5	2.1	1.8	0.9	
	V	8.1	10.0	10.2	12.3	
	Z	8.3	10.1	10.3	12.3	

parameter

$$\rho = ZR, \qquad (42)$$

where R is the carbon-carbon distance. This is done in Table I.

In Table II the integrals (37)–(40) over molecular orbitals are tabulated as functions of ρ and Z both for planar ($\varphi = 0$) and perpendicular ($\varphi = \pi/2$) ethylene. Energies of the various states of the molecule relative to the ground state N of the planar configuration calculated for $R = 1.353$Å (the experimental value for the internuclear distance in the ground state[10]) from the integrals in Table II, are given in Table III, and plotted in Fig. 1 for $Z = 3.18$. The value of Z is quite arbitrary; 3.18 was found by Zener[11] to be the best value in an isolated carbon atom, but may not be the best value for carbon in a molecule. Moreover, both R and Z probably change[12,13] between normal and excited states. Lacking further information one may as well assume constant values for both.
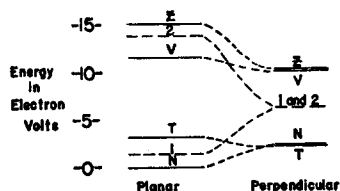
FIG. 1. Energy levels of ethylene: $R = 1.353$Å, $Z = 3.18$.

[10] W. S. Gallaway and E. F. Barker, J. Chem. Phys. 10, 88 (1942).
[11] C. Zener, Phys. Rev. 36, 51 (1930).
[12] R. S. Mulliken and C. A. Rieke, Rev. Mod. Phys. 14, 259 (1942).
[13] R. S. Mulliken, J. Chem. Phys. 3, 517 (1935).

Table III and Fig. 1 indicate that the planar configuration is more stable than the perpendicular one, as is generally accepted. Qualitatively, Fig. 1 agrees very well with the energy level scheme found by Mulliken,[3] but quantitatively it leaves something to be desired. Experimentally,[3]

$$[E_V - E_N]_{\varphi=0} = 7.6 \text{ ev.}$$

The calculated value for $Z = 3.18$ is 11.5 volts.[14] Also the calculated $T - V$ splitting is too large. This result is typical of molecular orbital calculations.[1] The dotted lines in the figure indicate how the $\varphi = 0$ levels pass continuously into the $\varphi = \pi/2$ ones. (Actual values of the energies for any given value of φ could be calculated from the formulas given above.)

THE TWISTING FORCE CONSTANT AND TWISTING FREQUENCY OF ETHYLENE

Twisting force constants for the various states of the ethylene molecule may be defined as second derivatives of the energy:

$$k_N = (\partial^2 E_N / \partial \varphi^2)_{\varphi=0}, \qquad (43)$$

$$k_1 = (\partial^2 E_1 / \partial \varphi^2)_{\varphi=0}, \qquad (44)$$

etc. From (23), the relation between k_N and the other force constants is found to be

$$2k_N = (k_1 + k_2) + (1 + \kappa^2)^{-\frac{1}{2}}(k_1 - k_2) \\ - \kappa(1 + \kappa^2)^{-\frac{1}{2}}(k_V - k_T) \qquad (45)$$

where

$$\kappa = [(E_V - E_T)(E_2 - E_1)^{-1}]_{\varphi=0}. \qquad (46)$$

If κ were zero, k_N would be equal to k_1.

k_1, k_2, k_V, and k_T may be obtained from (12) and (15)–(17). Indeed,

$$k_1 = 2k_{\epsilon+} + k_{\gamma++}, \\ k_2 = 2k_{\epsilon-} + k_{\gamma--}, \\ k_V = k_{\epsilon+} + k_{\epsilon-} + k_{\gamma+-} + k_{\delta+-}, \\ k_T = k_{\epsilon+} + k_{\epsilon-} + \gamma_{+-} - k_{\delta+-}; \qquad (47)$$

where, by (37)–(40),

$$k_{\epsilon\pm} = (\partial^2 \epsilon_{\pm} / \partial \varphi^2)_{\varphi=0} \\ = (1 \pm S_{a_1 a_2})^{-2} \{ [\pm (A_1 : a_1 a_2) \\ + 2(a_1 a_1 ; a_2 a_2) - 2(a_1 a_1 ; a_{2s} a_{2s}) \\ \pm (a_1 a_1 ; a_1 a_2)] \pm S_{a_1 a_2} [-(A_1 : a_1 a_2) \\ + (a_1 a_1 ; a_2 a_2) - 2(a_1 a_1 ; a_{2s} a_{2s})] \},$$

[14] Hartmann's value (corrected as required by reference 7) is 8.54 ev, but he used values for certain integrals different from those given in Table I.

$$k_{\gamma\pm\pm} = (\partial^2\gamma_{\pm\pm}/\partial\varphi^2)_{\varphi=0}$$
$$= (1\pm S_{a_1a_2})^{-3}\{[\mp 2(a_1a_1; a_1a_2)$$
$$- (a_1a_1; a_2a_2) - 2(a_1a_2; a_1a_2)$$
$$+ (a_1a_1; a_{2s}a_{2s}) + 2(a_1a_{2s}; a_1a_{2s})]$$
$$\pm S_{a_1a_2}[(a_1a_1; a_1a_1)\pm 2(a_1a_1; a_1a_2)$$
$$+ (a_1a_1; a_{2s}a_{2s}) + 2(a_1a_{2s}; a_1a_{2s})]\}, \quad (48)$$

$$k_{\gamma+-} = (\partial^2\gamma_{+-}/\partial\varphi^2)_{\varphi=0}$$
$$= (1 - S_{a_1a_2}{}^2)^{-2}\{[-(a_1a_1; a_2a_2)$$
$$+ 2(a_1a_2; a_1a_2) + (a_1a_1; a_{2s}a_{2s})$$
$$- 2(a_1a_{2s}; a_1a_{2s})] + S_{a_1a_2}{}^2[-(a_1a_1; a_1a_1)$$
$$- (a_1a_1; a_{2s}a_{2s}) + 2(a_1a_{2s}; a_1a_{2s})]\},$$

$$k_{\delta+-} = (\partial^2\delta_{+-}/\partial\varphi^2)_{\varphi=0}$$
$$= (1 - S_{a_1a_2}{}^2)^{-2}\{[(a_1a_1; a_2a_2)$$
$$- (a_1a_1; a_{2s}a_{2s})] + S_{a_1a_2}{}^2[(a_1a_1; a_{2s}a_{2s})$$
$$- (a_1a_1; a_1a_1)]\}.$$

The force constants are thus all expressible in terms of the quantities in Tables I and II; Table IV gives them as functions of ρ and Z.

The formula relating twisting frequencies ω and force constants k is[15]

$$\omega = (1/\pi c)(k/I)^{\frac{1}{2}}, \quad (49)$$

where c is the velocity of light, I is the total moment of inertia about the carbon-carbon axis, and ω is in wave numbers (cm^{-1}). With $R = 1.353$A, HCH angle $= 119° 55'$ and CH distance $= 1.071$A,[10] one finds $I = 5.7535\times 10^{-40}$ g/cm^2, and then obtains from (49)[16]

$$\omega = 2066k^{\frac{1}{2}}, \quad (50)$$

where k is in atomic units and ω in wave numbers (cm^{-1}). Values of ω for the pseudo-ground state Ψ_1 and the ground state Ψ_N calculated by (50) from the force constants in Table IV, with $R = 1.353$A, are given in Table V and plotted in Fig. 2.

The actual (experimental) value of ω is in doubt. The value usually accepted[17] is *ca.* 825 cm^{-1}, but Rasmussen and Brattain have pointed out that 950 cm^{-1} is also possible.[18] The present results are too approximate to aid in settling the assignment.

[15] W. G. Penney, Proc. Phys. Soc. **46**, 333 (1934).
[16] One atomic unit $= 2.1792\times 10^{-11}$ ergs, $c = 2.9977\times 10^{10}$ cm/sec.
[17] G. Herzberg, *Infrared and Raman Spectra of Polyatomic Molecules* (D. Van Nostrand Company, Inc., New York, 1945), p. 328.
[18] R. S. Rasmussen and R. R. Brattain, J. Chem. Phys. **15**, 120 (1947).

TABLE IV. Force constants of planar ethylene (atomic units).

Force constant	ρ	6	8.13	8.37	10
$Z^{-1}k_{\epsilon+}$		+0.07143	+0.04907	+0.04625	+0.03129
$Z^{-1}k_{\epsilon-}$		−0.35739	−0.10730	−0.09755	−0.04233
$Z^{-1}k_{\gamma++}$		−0.00415	−0.00266	−0.00234	−0.00020
$Z^{-1}k_{\gamma--}$		−0.02222	−0.02317	−0.02188	−0.01352
$Z^{-1}k_{\gamma+-}$		−0.02098	−0.00568	−0.03396	−0.00303
$Z^{-1}k_{\delta+-}$		−0.02971	−0.00950	−0.00884	−0.00270
$Z^{-1}k_1$		+0.13871	+0.09548	+0.09016	+0.06238
$Z^{-1}k_2$		−0.73700	−0.23777	−0.21698	−0.09818
$Z^{-1}(k_V - kT)$		−0.05942	−0.01900	−0.01768	−0.00540
$Z^{-1}k_N$		+0.13021	+0.07283	+0.06604	+0.03062

DISCUSSION

Penney[19] discussed the ethylene molecule many years ago in some detail, employing both the HLSP method and a molecular orbital procedure. Considering the problem as a twelve-electron one, he showed by both methods that the stable configuration of the molecule is the planar structure involving sp^2 hybridization and $\pi\pi$-bonding (as assumed above). From his HLSP treatment, Penney obtained the dependence of the energy on the angle φ, finding approximately that

$$E_\varphi - E_0 = (3/2)J\sin^2\varphi, \quad (51)$$

where J is a certain exchange integral that had been previously evaluated by Bartlett.[20] To the simple harmonic approximation, (51) gives for the twisting force constant

$$k = 3J, \quad (52)$$
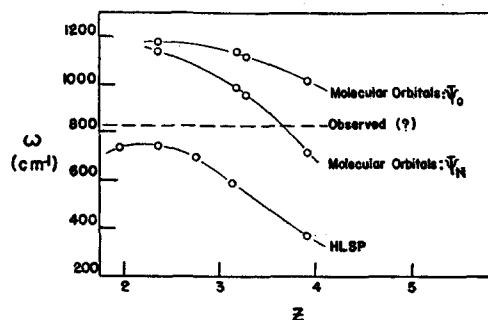
so that by (50)

$$\omega = 3578J^{\frac{1}{2}}. \quad (53)$$

FIG. 2. Calculated twisting frequency of ethylene. Upper curve should be labeled Ψ_1.

[19] W. G. Penney, Proc. Roy. Soc. **A144**, 166 (1934); also reference 15.
[20] J. H. Bartlett, Phys. Rev. **37**, 507 (1931). In Bartlett's notation $J = I_2$.

TABLE V. Twisting frequency of ethylene (cm⁻¹) calculated by the method of molecular orbitals for $R=1.353A$.

State	Z	2.35	3.18	3.27	3.91
Ψ_1		1180	1140	1120	1020
Ψ_N		1140	995	960	715

TABLE VI. Twisting frequency of ethylene (cm⁻¹), calculated by HLSP method for $R=1.353A$.

Z	J[a]	ω
1.17	−0.096	imaginary
1.96	0.0425	738
2.35	0.0430	742
2.74	0.0381	698
3.13	0.0269	587
3.91	0.0109	374

[a] J values are from Bartlett, reference 20, and are in atomic units.

Penney used this formula to determine J. Alternatively, one can employ it to compute theoretical values of ω from calculated values of J. Results of some calculations using this approach are given in Table VI and plotted in Fig. 2.

It is interesting, but probably not significant, that the molecular orbital and HLSP results bracket the observed value of ω. Decrease of ω with increase in Z for large Z might have been expected in both methods because an increase in Z causes a shrinkage of the $2p\pi$-orbitals and consequently a decrease in the overlap between them and the strength of the $\pi\pi$-bond.

The molecular orbital results are definitely encouraging, especially in view of the following considerations:

(1) One might expect Z in ethylene to be slightly larger than the optimum value 3.18 for an isolated carbon atom. For the electrons in the trigonal bonds in the planes of the CH_2 group should have relatively little screening effect on the $2p\pi$-electrons in orbital perpendicular to those planes.

(2) The amount of perturbation of the state Ψ_1 by the state Ψ_N is largely determined by the quantity κ, which is directly proportional to the T-V splitting. Because the latter comes out too large, κ is too

large, and the calculated decrease in force constant too great. The best molecular orbital curve therefore probably lies between the two curves in Fig. 2.

(3) For the distorted ethylene molecule the true $\pi\pi$-bond is not a simple combination of $2p$ orbitals perpendicular to the CH_2 groups (as assumed in the calculation above) but a mixed bond which involves p orbitals in the planes of these groups. This gives rise to an increased stability of the distorted molecule, as has indeed been shown by Mulliken.[3] Since this has not been included in the above calculation, the computed frequency would on this account be expected to be high.

For immediate results on ethylene, the semi-empirical approach of Mulliken[3] should be preferred to the present approach. The latter uses fewer extra-geometrical empirical results, however, and so is a step towards the ideal "first principle" treatment.