

## Erratum and Further Comments: Radiation Damage in Organic Crystals. III. Long Polyene Radicals

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with that of the capillaries. The electron current to the collector cylinder was amplified by a vibrating reed electrometer and the output signal was differentiated by a simple  $R$ - $C$  circuit, the resultant function being recorded as the retarding field was varied linearly from 0 to  $\sim 15$  V. This gives an electron energy distribution curve. Figure 1 [(a), (b), (c)] shows the records obtained for argon, krypton, and xenon, by which the potential scale was calibrated. It can be seen that the doublet separation in  $\text{Xe}^+$  (1.3 V) could be resolved and that in  $\text{Kr}^+$  distinguished. All other substances so far examined have given complex spectra. The curves for carbon disulphide and nitrogen dioxide are included in the figure [(d), (e)] the potentials derived from other sources<sup>3,4</sup> being indicated by arrows. In these and in all curves for molecules, so far examined the effect of Franck-Condon prohibition upon the formation of the  $\text{O} \rightarrow \text{O}$  (vibrationless) ion is evident. We are attempting to refine the grid design to improve the energy resolution and so resolve close-lying levels.

\* The support of the Gulbenkian Foundation is gratefully acknowledged.

<sup>1</sup> W. W. Lozier, *Phys. Rev.* **36**, 1285 (1930).

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## Comments and Errata

### Erratum and Further Comments: Radiation Damage in Organic Crystals. III. Long Polyene Radicals

[*J. Chem. Phys.* **37**, 361 (1962)]

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THE theoretical and experimental equations for the second moments in this paper employ different normalizations, and are thus inconsistent. Equation (19) and all equations based on this equation should be divided by a factor of 4. This then makes the theoretical moment equations consistent with the experimental moments, which employ the conventional definition with a line shape normalized to one. In Table III of the above paper, all the theoretical moments should be divided by a factor of four.

The experimental moments in Table III are then much larger than the corrected theoretical moments. If, however, one now assumes that the carbonyl group

TABLE I. Comparison of experimental second moments with moments calculated from modified Eq. (22) and Hückel, Hartree-Fock and valence-bond spin densities. The values assume no carbonyl group participation, therefore, the values of  $m$  are reduced by one.

$m$	Exp.	Second moments, $\langle(\Delta\nu)^2\rangle_A$ , in gauss <sup>2</sup>		
		Hückel	Hartree-Fock	Valence bond
1	134	102	145.9	197.4
2	228	60.6	102.8	162.2
3	174	42.6	80.4	140.9
4	161	32.8	67.2	126.5
6	122	22.2	... <sup>a</sup>	115.2

<sup>a</sup> Impossible to calculate because of breakdown of perturbation treatment for large  $m$ .

does *not* act like a carbon-carbon double bond, a new set of theoretical moments can be calculated. The results are shown here in Table I. It will be observed that the theoretical moments that take into account spin correlation—especially the valence bond calculation—give results in reasonably good agreement with the experimental results. This is not surprising in view of the fact that the radicals under consideration are odd alternate. It is also reasonable that the carbonyl be neglected in view of the fact that previous experimental evidence on spin distributions in malonic<sup>1</sup> and succinic acid<sup>2</sup> radicals show no  $\pi$ -electron spin transfer onto the carbonyl groups (of carboxyl groups) even though the carboxyl group has the proper orientation for conjugation.

The present discussion still supports our previous conclusion that the spin in these long polyene radicals is distributed over the whole chain. We are indebted to Professor G. Vincow for a helpful discussion.

<sup>1</sup> H. M. McConnell, C. Heller, T. Cole and R. W. Fessenden, *J. Am. Chem. Soc.* **82**, 766 (1960).

<sup>2</sup> C. Heller and H. M. McConnell, *J. Chem. Phys.* **32**, 1535 (1960).

### On Pople's Molecular-Orbital Theory of Diamagnetism\*†

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(Received August 22, 1962)

RECENTLY Pople<sup>1</sup> proposed an approximate theory of molecular diamagnetic susceptibilities based on the use of GIAO (gauge invariant atomic orbitals<sup>2-4</sup>). The theory implicitly assumes the existence of a reliable molecular wave function, which is obtained as an antisymmetrized product of linear combinations of atomic orbitals. We take it that this

TABLE I. Values of atomic integrals that occur in susceptibility calculations of  $H_2$ , HF, and  $N_2$ . On the left are the one-center terms, on the right are two-center terms.

$H_2$			
$\langle u_a   r_a^{-2}   u_a \rangle$	2.321 564	$\langle u_a   r_a^{-2}   u_b \rangle$	2.369 811
HF			
$\langle h   r_H^{-2}   h \rangle$	3.000 000	$\langle h   r_F^{-2}   s \rangle$	1.051 620
$\langle s   r_F^{-2}   s \rangle$	1.159 527	$\langle h   r_H^{-2}   s \rangle$	1.541 153
$\langle p_z   r_F^{-2}   p_z \rangle$	1.109 467		
$N_2$			
$\langle s_a   r_a^{-2}   s_a \rangle$	2.054 832	$\langle s_a   r_a^{-2}   s_b \rangle$	1.514 861
$\langle p_{za}   r_a^{-2}   p_{za} \rangle$	1.972 387	$\langle s_a   r_b^{-2}   p_{zb} \rangle$	1.653 428

condition is satisfied. In fact, if we use the term "exact" in the following we disregard possible deviations in the results due to this approximation. Pople's theory is subsequently developed by replacing the atomic orbitals by GIAO and by introducing some additional approximations, labeled A, B, C, D, and E.

In a recent series of papers we derived an exact theory<sup>5</sup> of the diamagnetic susceptibilities of diatomic molecules from SCF LCAO MO functions by introducing GIAO, the general formulas were applied to calculations of the magnetic susceptibilities of hydrogen fluoride<sup>6</sup> and of the nitrogen molecule<sup>7</sup>; the magnetic shielding constant and susceptibility of the hydrogen molecule had been calculated previously.<sup>8</sup> Since all contributions to the susceptibilities of these molecules were calculated explicitly we are in a position to investigate the validity of the assumptions A, C, D, and E made by Pople.<sup>1</sup>

It appears that the deviations caused by approximations A, C, and D are not unimportant but that they are small compared with the errors introduced by approximation E. In Table I we have reported some atomic integrals for  $H_2$ , HF, and  $N_2$  obtained from references 4, 8, 6, and 7. On the left-hand side we have listed some atomic integrals that give major contributions to the susceptibilities and on the right-hand side are some atomic integrals that may be neglected according to Pople's approximation E. It follows that the approximation is incorrect. This is most dramatically illustrated for  $H_2$  where the term that is supposed to be negligible is larger than the main contribution to the susceptibility.

In addition, Pople's theory neglects the contribution to the susceptibility from the quantity  $Q$ , defined by Eq. (27) of reference 5 or by Eq. (33) of reference 8. For the hydrogen molecule this contribution is small, only 1%, but for HF and  $N_2$  the contributions are 30% and 13%, and not negligible.

We conclude that it is generally not possible to express a molecular diamagnetic susceptibility as a

sum of atomic contributions since the interatomic terms are of major importance. How then are we to explain the success of Pascal's rules<sup>9</sup> where the molecular magnetic susceptibility is calculated from a set of atomic susceptibilities? We believe that there is an alternative explanation which rests on a sounder theoretical foundation. As we have pointed out earlier<sup>10</sup> it is more profitable from a theoretical point of view to introduce the concept of bond susceptibility and to write the susceptibility of a molecule as a sum of contributions from the various bonds. This neglects the susceptibilities due to the inner-shell electrons of the atoms, but these are usually quite small. It appears now that we may introduce a set of atomic constants so that each bond susceptibility may approximately be written as a sum of the two corresponding atomic contributions; the difference is accounted for by a correction term representing the bond. In fact, this explanation agrees satisfactorily with the Pascal rules, where molecular susceptibilities are obtained as sums of atomic terms, representing the atoms in the molecules, and of bond correction terms, representing the bonds. It has been shown<sup>10</sup> that a higher degree of accuracy may be obtained by subsequently considering interactions between adjacent bonds.

It seems that Pascal's rules do not necessarily rest on the concept of atomic susceptibilities and that the significance of this concept is not supported by theoretical evidence.

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## Reply to Letter by H. F. Hameka

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**I** SHOULD like to make three points in reply to the letter by Dr. Hameka.

(1) The value of quantum mechanical theories of properties of large molecules should not always be judged by the numerical accuracy of the approximations. Indeed, there are many examples of mathemati-