to the two molecular spin orbitals,[29] so that $C_{Hr}^2 = C_{Hs}^2 = 0.5$. Substituting these in eq. 15 gives

$$\partial E/\partial C_{Hr} = 2C_{Hr}[B_H' + 0.5 A_H^- - E] +$$
$$(\partial E'/\partial C_{Hr}) = 0$$

In the secular equation which results from the variational treatment, the diagonal terms are formed mainly[30] from

$$B_H' + 0.5 A_H^- - E$$

Now

$$B_H' + 0.5 A_H^- = (I_H + E_H)/2$$

is the neutral electronegativity of the atom. Our treatment thus introduces electronegativity into the diagonal terms of the secular equation in a completely consistent way. This quantity can be defined only in a molecular context, and it is important to realize that it has the dimensions of energy; it is in fact the energy of an electron in the field of the other bonding electrons and the core. When two electrons only are involved in one homopolar bond, the electronegativity is

$$B_X + 0.5 A_X^- = (I_V + E_V)/2$$

for each electron around each atom.

It must be realized that electronegativity is not a measurable molecular constant, since it varies from molecule to molecule like the total energy (since it is a function of the variational parameters) and therefore a characteristic value cannot be given to it.

A neutral electronegativity can, nevertheless, be defined, which is the electronegativity of an atom in a homopolar molecule (where the C_{Xs}^2 for all the bonding electrons are equal to 0.5). With this restriction, the

(29) In the general case, C_X cannot be determined in advance, but starting with an initial arbitrary value the method can be made self-consistent.

(30) There is similarly a contribution from the bonding term, but this is small in comparison with the atomic term.

neutral electronegativity can be calculated. The formula developed above for atomic energies (eq. 15) is particularly suitable for these calculations, and hence the electronegativities for a large number of valency and hybridized orbitals can readily be obtained.

$$X_X = B_X' + \sum_{s \neq r} C_{Xs}^2 A_X^+ \delta_{rs} +$$
$$\sum_{s \neq r} C_{Xs}^2 A_X^- (1 - \delta_{rs})$$

These are given in Table VII.

TABLE VII

NEUTRAL ELECTRONEGATIVITY OF SOME COMMON ATOMS

Atom	Valence state	Orbital type	Electronegativity, e.v.	Atom	Valence state	Orbital type	Electronegativity, e.v.
H	s	s	7.17	N	s²p³	p	7.30
Li	s	s	3.10	P	s²p³	p	5.89
Na	s	s	2.80	O	s²p⁴	p	9.10
K	s	s	2.51	S	s²p⁴	p	7.16
C	sp³	s	12.38	F	s²p⁵	p	11.48
		p	5.19				
	didi ΠΠ	σ	8.79	Cl	s²p⁵	p	8.94
	trtrtr Π	σ	7.59	Br	s²p⁵	p	8.28
	tetetete	σ	6.99	I	s²p⁵	p	7.53
Si	sp³	s	10.50				
		p	4.16				
	didi ΠΠ	σ	7.33				
	trtrtr Π	σ	6.27				
	tetetete	σ	5.74				

As already pointed out, an exact calculation of the electronegativity and hence of the bond properties requires a knowledge of the coefficients of the atomic orbitals and of the molecular terms. These will be discussed in a forthcoming paper which describes a new self-consistent treatment of molecular structures.

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, INDIANA UNIVERSITY, BLOOMINGTON, IND.]

The Nature of the Two-Electron Chemical Bond.[1] V. Electron Pairing and H₃⁺

BY HARRISON SHULL

Data originally calculated by Hirschfelder, Eyring, and Rosen on linear symmetrical H₃⁺ are analyzed in terms of approximate natural orbitals. Every aspect of the analysis suggests that this form of H₃⁺ is best described as a relatively normal single bond in which is embedded a third proton. Hopton and Linnett (*J. Chem. Soc.*, 1553 (1962)) drew the conclusion from the same data (without, however, using natural orbitals) that H₃⁺ was best described by a nonpairing formulation. The present calculation and discussion does not support these authors' "propaganda against pairing."

Introduction

A recent paper by Hopton and Linnett[2a] discusses an old wave function of Hirschfelder, Eyring, and Rosen[2b] for linear H₃⁺ in several approximations which they class as molecular orbital (MO), valence bond (VB), and nonpairing (NP) schemes, there being three of the latter considered. Hopton and Linnett maxi-

(1) Supported in part by grants from the U. S. Air Force Office of Scientific Research and from the U. S. National Science Foundation.

(2) (a) J. D. Hopton and J. W. Linnett, *J. Chem. Soc.*, 1553 (1962); (b) J. O. Hirschfelder, H. Eyring, and N. Rosen, *J. Chem. Phys.*, **4**, 130 (1936).

mize the overlap between the respective wave functions for these schemes and the one computed by the variation method. They conclude that since the overlap for the NP functions is 0.997–0.998 whereas the MO and VB overlaps are 0.982 the NP formalism is "best" and that there is "no particular and special energy effect involved in 'the pairing of the electrons'." This is adduced to be further support to a rather general discussion of many molecular systems in terms of a "nonpairing" formalism.[3]

(3) J. W. Linnett, *J. Am. Chem. Soc.*, **83**, 2643 (1961).

The purpose of the present paper is twofold. First, the analysis of Hopton and Linnett is vulnerable to criticism concerning the arbitrary nature of the basis functions involved. This vulnerability is in large part removed by using the natural expansion in the present paper. Second, even given the validity of the results of Hopton and Linnett, the author feels that the resulting discussion draws some unfounded conclusions concerning electron pairing. Hence some alternative statements of conclusion are presented here.

It was already known from the work of Hirschfelder, of course, that the ground state of H_3^+ has a triangular configuration, and recent calculations from this laboratory have confirmed it as being an equilateral triangle. Natural orbital analysis of the wave functions for the true ground-state configuration are in progress and will be submitted for publication soon. The present paper is confined to a discussion of points raised by Hopton and Linnett which can be answered from the viewpoint of the calculations for the fictitious linear configuration.

Ground State of Linear H_3^+.—The Hirschfelder, Eyring, Rosen calculation uses as basis orbitals, hydrogenic 1s-functions with orbital exponent unity centered upon three collinear equally spaced nuclei, a, b, and c. Using these letters to denote the normalized 1s-orbitals on the three centers, four normalized linearly independent $^1\Sigma_g^+$ wave functions can be constructed. The space portions of these are

$$\Psi_1 = N_1(a_1b_2 + b_1a_2 + b_1c_2 + c_1b_2)$$

$$\Psi_2 = N_2(a_1c_2 + c_1a_2) \qquad (1)$$

$$\Psi_3 = b_1b_2$$

$$\Psi_4 = N_2(a_1a_2 + c_1c_2)$$

The functions in (1) are normalized functions for which the $a - c$ separation is precisely twice that of the $a - b$ and $b - c$ separations. The overlap integrals Sab and Sac were taken from a tabulation of Hirschfelder and Linnett,[4] from which the normalization constants in (1) are easily derived. Hopton and Linnett carried through calculations only for the case that the distance $a - b$ is $2B$, but here we have extended this to three other distances so that the instructive trends toward the united and separated atoms may be observed. Each function in (1) is to be multiplied by the usual normalized singlet spin function: $(\alpha_1\beta_2 - \beta_1\alpha_2)/\sqrt{2}$.

Hirschfelder, Eyring, and Rosen presented a graph (Fig. 3 in their paper) of the coefficients, C_i, of the normalized Ψ_i of (1) as calculated from the usual Rayleigh–Ritz variation treatment

$$\Psi = \sum_i C_i\Psi_i \qquad (2)$$

The graph in the present author's copy of the journal resulted in the carefully measured values for the C_i reported in Table I. As read directly from the graphs, Ψ is not precisely normalized, probably from various errors creeping into the drawing, printing, and measurements of the graphs. In order to ensure that round-off and normalization inaccuracies were not affecting the results, the measured data were accurately renormal-

(4) J. O. Hirschfelder and J. W. Linnett, *J. Chem. Phys.*, **18**, 130 (1950).

TABLE I

COEFFICIENTS, C_i, OF $\Psi = \Sigma C_i\Psi_i$ OF THE HIRSCHFELDER, EYRING, AND ROSEN FUNCTION FOR H_3^+

$R_{a-b}{}^a$		1	2	3	4
Measured	C_1	1.0782	0.732	0.6953	0.7019
	C_2	−0.07308	.206	.3816	.5234
	C_3	.3393	.198	.1524	.0788
	C_4	− .3810	− .100	− .0385	− .0147
Renormalized	C_1	1.08476	.73554	.68995	.70096
	C_2	−0.07352	.20700	.37867	.52270
	C_3	.34136	.19896	.15123	.07870
	C_4	− .38332	− .10048	− .03829	− .01468

^{a} Internuclear separations given in Bohrs.

ized. The corrected coefficients, also given in Table I, are within the limits of error of the measurements.

Hopton and Linnett tabulate (for $R = 2B$) for the values: $C_1 = 0.378$, $C_2 = 0.208$, $C_3 = 0.203$, $C_4 = -0.100$. Only C_1 differs extensively from the values used here. It is hard to see how the number 0.378 was obtained unless there was an accidental transposition of digits or a subtle change of normalization. The former is the less likely since 0.378 is listed twice in the manuscript. In any case, this discrepancy seems not to have affected the results which are closely parallel to those given here.

In Table II, we list the overlap integrals used and the derived normalization constants as defined in

TABLE II

OVERLAP INTEGRALS OVER ATOMIC BASIS ORBITALS AND NORMALIZATION CONSTANTS FOR MOLECULAR BASIS FUNCTIONS

R_{a-b}	1	2	3	4
S_{ab}	0.858385	0.586453	0.348509	0.189262
S_{ac}	.586453	.189262	.0470963	.0101757
N_1	.285826	.364942	.440223	.480721
N_2	.609954	.694773	.706324	.707070

eq. 1 as a function of the internuclear separation, and in Table III are the overlap integrals between

TABLE III

OVERLAP INTEGRALS BETWEEN THE BASIS FUNCTIONS (EQ. 1) AND BETWEEN THE VARIATIONAL Ψ (TABLE I) AND THE INDIVIDUAL BASIS ORBITALS. THE FOUR VALUES ARE FOR THE DISTANCES 1, 2, 3, AND 4B, RESPECTIVELY

	Ψ_1	Ψ_2	Ψ_3	Ψ_4
Ψ_1	1.000000	0.949660	0.981395	0.949660
	1.000000	.707355	.856085	.707355
	1.000000	.453876	.613687	.453876
	1.000000	.259942	.363929	.259942
Ψ_2		1.000000	.898859	.872745
		1.000000	.477902	.365434
		1.000000	.171578	.093984
		1.000000	.050655	.020349
Ψ_3			1.000000	.898859
			1.000000	.477902
			1.000000	.171578
			1.000000	.050655
Ψ_4				1.000000
				1.000000
				1.000000
				1.000000
Ψ	0.985927	0.928928	0.995307	0.889506
	.981205	.785646	.879545	.590529
	.937289	.714178	.633060	.336487
	.861662	.708600	.359530	.182154

the basis functions (1) for the various internuclear distances. This table alone should give one great hesitation in drawing any conclusions about the im-

portance of the respective basis functions. It is very hard to interpret results when individual functions, far from being orthogonal, have overlap integrals approaching unity.

Natural Orbitals for Linear H_3^+.—To avoid the non-orthogonality interpretational problem and to take advantage of the known optimum convergence properties of natural orbitals,[5] we transform the basis in two steps. First we introduce orthogonal basis orbitals, $u = N(a - c)$, $p = N'(a + c)$, $q = N''(b + \lambda p)$, choosing λ so that q is orthogonal to p. By symmetry, p and q are each orthogonal to u. It is then straightforward to express first the Ψ_i and then Ψ itself in terms of u, p, and q. The resultant expression for Ψ is nondiagonal, and it may be diagonalized by well known techniques to find the natural orbitals (in terms of p, q, and u and hence ultimately in terms of a, b, and c) and the expansion of Ψ in terms of the natural orbitals. The technique is precisely the same as that used earlier for H_2.[6] In Table IV we collect the

TABLE IV
THE NATURAL EXPANSION FOR THE H_3^+ FUNCTIONS. SEE EQ. 2
AND 4 FOR DEFINITION OF COEFFICIENTS

R_{a-b}	1B	2B	3B	4B
C_1	0.996408	0.982669	0.951633	0.903254
C_2	− .078144	− .173198	− .280578	− .376100
C_3	− .032535	− .066019	− .125187	− .206594
t_{11}	.068905	.313145	.428886	.510878
t_{12}	.881171	.582271	.540197	.520828
t_{23}	1.099569	.785316	.724370	.710732
t_{31}	2.104233	.948228	.661672	.521295
t_{32}	−3.645215	−1.425768	−1.005115	− .897257

pertinent coefficients. Thus we can write the natural expansion

$$\Psi = c_{1g}\chi_{1g}(1)\chi_{1g}(2) + c_{2u}\chi_{2u}(1)\chi_{2u}(2) + c_{3g}\chi_{3g}(1)\chi_{3g}(2) \quad (3)$$

noting that $c_{1g}^2 + c_{2u}^2 + c_{3g}^2 = n_1 + n_2 + n_3 = 1$ where the n's are the occupation numbers of the respective natural orbitals. The natural orbitals themselves can be expressed in terms of the original 1s basis orbitals by

$$\chi_i = t_{i1}(a + c) + t_{i2}b + t_{i3}(a - c) \quad (4)$$

where the various nonzero t_i are also listed in Table IV. It should be noted that t_{13}, t_{21}, t_{22}, and t_{33} are identically zero by symmetry at every distance.

The data of Table IV cover a range of internuclear distance sufficient to run almost from the united atom to the separated atom case. Thus, at a distance of $1B$, the first occupation number (C_1^2) is as high as 0.992829, and the first natural orbital is very largely b with just a little a and c mixed in. But, of course, each of the latter overlap b so much (0.858, Table II) that there is not a great distinction between b and $N(a + c)$. In fact, the overlap, $\int bN(a + c)d\tau$, is 0.964. The united atom for H_3^+ is Li^+. Unfortunately the author does not currently have occupation number information on Li^+, but the results should not be very different from He where the first occupation number is ~ 0.992.

At the other extreme at $4B$ for R_{a-b}, the first occupation number has already dropped to 0.815868 with

(5) P.-O. Löwdin and H. Shull, *Phys. Rev.*, **101**, 1730 (1955).
(6) H. Shull, *J. Chem. Phys.*, **30**, 1405 (1959).

the remaining occupation going competitively between the second and third natural orbital. In the first orbital, the weights of a, b, and c have already become almost equal $(t_{11} = t_{12})$. For the basis functions used here, the correct limiting function at $R = \infty$ is $(1/\sqrt{6}) \cdot (ab + ac + bc + ba + ca + cb)$. This leads to three natural orbitals. The first is $(1/\sqrt{3})(a + b + c)$, having an occupation number of $2/3$ and the other two being $(a - c)/\sqrt{2}$, $(a - 2b + c)/\sqrt{6}$ (or some linear combination of these) with degenerate occupation numbers of $1/6$. Even at $4B$, the occupation numbers of 0.816, 0.141, and 0.043 and the given orbital forms quite clearly are approaching rapidly the limiting case. That these two are degenerate at infinity can most easily be seen by noting that another linearly independent pair of the same two orbitals is $(a - b)/\sqrt{2}$ and $(b - c)/\sqrt{2}$.

The Truncated Expansions.—The basis set used by Hirschfelder, Eyring, and Rosen is, of course, a very limited one. There are only three functions of g type and one of u, and hence these reduce in natural orbital form to two of g type and one of u. Well known theorems on the truncated expansions[4] may be applied even in this limited case, although just how close the results will be to those from a more definitive calculation remains to be seen. In any case, within the very limited basis, we can find the "optimum" functions of rank 1, 2, and 3 by truncating the natural expansion after 1, 2, and 3 terms, respectively, and then renormalizing.

The best function of rank 1 is precisely

$$\Phi_1 = \chi_1(1)\chi_1(2) \quad (5)$$

whereas that of rank 2 may be written

$$\Phi_2 = [c_1\chi_1(1)\chi_1(2) + c_2\chi_2(1)\chi_2(2)]/(c_1^2 + c_2^2)^{1/2} \quad (6)$$

Since Ψ is of rank 3, it itself is the rank 3 function with maximum overlap (of unity). In Table V we list the renormalized coefficients of Φ_2 and the overlap integrals (optimum) $\int \Phi_1 \Psi d\tau$, $\int \Phi_2 \Psi d\tau$. Comparing these results with the overlaps computed by Hopton and Linnett, we find (at $R = 2B$) that the optimum rank 1 function has an overlap slightly better than either the VB or MO function quoted by these authors, and the rank 2 function has an overlap just slightly higher than any of the so-called nonpairing approximations used by these authors.

TABLE V
COEFFICIENTS OF THE RANK 2 TRUNCATED FUNCTION AND OVER-
LAPS BETWEEN TRUNCATED FUNCTIONS AND Ψ

R_{a-b}	1B	2B	3B	4B
$n_1^{1/2} = c_1/(c_1^2 + c_2^2)^{1/2}$	0.99694	0.98482	0.95918	0.92317
$n_2^{1/2} = c_2/(c_1^2 + c_2^2)^{1/2}$	− .07819	− .17358	− .28280	− .38439
$\int \Psi \Phi_1 d\tau$	.99641	.98267	.95163	.90325
$\int \Psi \Phi_2 d\tau$	.99947	.99782	.99213	.97843

If we look momentarily at Hopton and Linnett's MO function, we see that it is the most general form of rank 1 function in this basis set. Their parameter k should be equal to our t_{12}/t_{11}, and indeed $k = 1.87$ whereas $t_{12}/t_{11} = 1.859$ for $R = 2$ (Table I). The slight difference represents only a slight variation in the input coefficients as read from the graphs, and hence the slight improvement in overlap for our rank 1 function as compared to the MO function is not significant.

Brief examination of Hopton and Linnett's non-pairing functions A and B shows that each is of (u, v) form and hence of rank 2. In fact we may rewrite them instructively as

$$\text{NP } A = [(a + 2b + c)(1)(a + 2b + c)(2) -$$
$$(a - c)(1)(a - c)(2)]/2$$
$$\text{NP } B = [(a + 2kb + c)(1)(a + 2kb + c)(2) - \quad (7)$$
$$(a - c)(1)(a - c)(2)]/2$$

Clearly neither A nor B is the most general form of rank 2 function since A has no arbitrary constants and neither A nor B permits the relative amounts of the two configurations to reach an optimum value. The degree of "goodness" of functions A and B as compared to our rank 2 function is then clearly a function of how closely the fixed ratio between the two configurations approximates the true one, and how closely 2 and $2k$ in the two cases approach t_{12}/t_{11}. The "best" value of the latter has already been shown to be 1.859, not far from 2 for A, and only a little farther from the optimum $2k = 1.790$ reported for B. This rationalizes the excellent overlaps Hopton and Linnett found for A and B of 0.9972 and 0.9978 compared to our rank 2 overlap of 0.99782.

Finally, it is easily established that both the VB function and the NP function C of Hopton and Linnett are of rank 3, but with nongeneral coefficients for the various configurations. The most general function of rank 3 is Ψ itself in this case, and the optimum overlap is precisely 1. It is interesting to note that NP C is not as good as B even though it is of rank 3. Even more interestingly, the VB function is significantly poorer despite its rank of 3.

The latter is easily explained if one expands the function as a sum of square terms, for the important configuration $(a - c)(1)(a - c)(2)$ comes in with coefficient $+k$ in the VB function, but with coefficient $-k$ in the NP C function. This forces k slightly negative in the VB function in contrast to its high positive value in all the other approximate functions.

Electron Pairing.—We now wish to examine carefully the arguments of Hopton and Linnett with respect to electron pairing. Hopton and Linnett argue essentially that since NP A, B, and C functions have higher overlaps than either the MO and VB functions, this is significant evidence against electron pairing.

In part, the discussion is a semantic one. Hopton and Linnett seem to adopt the viewpoint that by electron pairing we mean only the presence of a pair of electrons in a "bond" or bonding region identified by a pair of rather arbitrarily chosen atomic orbitals. The nonpairing functions are then distinguished by having one electron in one such "bond" and the second electron in another, or the reverse. This viewpoint is susceptible to the very strong criticism that the concept of "bond" used by Hopton and Linnett has little if any significance in the context of a molecule with three centers and two electrons. Similar cases are involved in the bridge hydrogen bonds of the boron hydrides or in aromatic compounds where electrons are almost completely delocalized. Despite the delocalization, it is not proper to say that the electrons are *unpaired*.

We have already suggested[7,8] that a more fruitful approach is to consider the optimum *geminal* description of a molecule

$$\Psi = \lambda_1 O_{op}\Lambda_1(1,2)\Lambda_2(3,4) \ldots + \text{other terms} \quad (8)$$

in analogy to a natural expansion in the two electron case. Here O_{op} is an operator which guarantees appropriate antisymmetry properties, spin and spatial symmetries, and normalization. The forms of the geminals Λ_i are to be freely varied over space and spin coordinates so as to make λ_1 a maximum. We would say that the *geminal* description is a valid one if λ_1 approaches unity, and we have shown, for example, that this is clearly so for Be.

Each geminal is a function of both space and spin variables of two electrons. Consequently, each Λ_i may be written as a sum of a singlet and a triplet term. If the former term heavily dominates (*i.e.*, has a coefficient approaching unity in the normalized geminal), we would say that the electrons are largely *paired*.

Finally, the spatial portions of each geminal may be localized in the region of one nucleus (as in an inner shell of an atom), or localized in the region associated mostly with two nuclei (as the chemist's single bond), or delocalized over the region of several nuclei (as in benzene). Clearly there will exist all varieties of approximations to these and intermediate forms as well. But we can expect that the entity the chemist calls a chemical bond will be associated with an optimum geminal when that concept has any general validity. We have given a sketch of an argument[7] for believing that such geminal functions will be transferable from molecule to molecule in just those cases in which a chemist finds the chemical bond concept to be transferable.

Applied to H_3^+, this viewpoint suggests that since the exact Ψ is a two-electron function, it is a perfect geminal. Furthermore, since the ground state is a pure singlet, the electrons are perfectly paired. No arguments based on approximations to this function can be construed as evidence that the electrons are not *paired*.

But we can ask—just as we can in the H_2 molecule to what extent is the pair of electrons correlated and, if so, how? To do this, we return to the natural expansion in the two cases and examine it term by term. If we do this at the same level of approximation, we find that the first natural orbital for H_2 is given by $(a + c)/[2(1 + Sac)]^{1/2}$, using the same symmetry notation as for linear H_3^+. In the latter case, the first natural orbital as given above varies from almost pure b at $R = 1B$ to an almost equal distribution over a, b, and c at $R = 4B$. Furthermore this first natural orbital has an overlap of about 0.99 with the best wave function in this approximation for H_2 at the equilibrium distance for this calculation. In H_3^+, from Table V, we see that this overlap varies from 0.99641 at $R = 1$ to 0.90325 at $R = 4$. Thus the MO *pair* description of H_3^+ is as valid (and that is very valid indeed!) as that for H_2 in the equilibrium region. The description is well known to become inappropriate in either case in the asymptotic limit of large R.

(7) T. L. Allen and H. Shull, *J. Chem. Phys.*, **35**, 1644 (1961).
(8) T. L. Allen and H. Shull, *J. Phys. Chem.*, **66**, 2281 (1962).

Next we consider the rank 2 function in each case obtained by adding the second natural orbital configuration. This is completely equivalent to a (u, v) description which, for H_2, has one electron localized near one nucleus when the other electron is near the other nucleus. We can obtain a measure of this spatial correlation by considering the overlap between the normalized u and v functions found in this way. This can easily be shown to be $(c_1 - c_2)/(c_1 + c_2)$. For H_2, this is about 0.80, and for H_3^+ at the four internuclear distances of 1, 2, 3, 4B, respectively, it is 0.8546, 0.7003, 0.5446, and 0.4120. It is clearly seen that in the equilibrium region, the amount of delocalization in H_3^+ is *not significantly different* from that in H_2. Of course, as the distance becomes larger, the u, v separation becomes more distinct in either case. Higher terms in either H_2 or H_3^+ would introduce additional electron correlation perpendicular to the axis.

Ionic Character.—Since linear symmetric H_3^+ falls in the same symmetry class as H_2, the author's earlier arguments[9] concerning ionic character of H_2 may also be applied to the present molecule. In the two-term truncated natural expansion, it was shown that there existed in the homopolar case a pair of functions l, r (earlier called u, v) such that

$$\Psi_A = N[(l(1)r(2) + r(1)l(2)] \tag{9}$$

was the optimum embodiment of the intuitive left–right or alternant correlation associated with Pauling's covalent concept,[10] and simultaneously the function

$$\Psi_I = N[l(1)l(2) + r(1)r(2)] \tag{10}$$

was the optimum embodiment of the intuitive ionic concept. The "optimum" here refers in the first case to giving maximum weight to that part of configuration space in which the two electrons are on opposite sides of a plane perpendicular to the molecular axis and dividing it in two equivalent parts, and in the second case, giving the maximum weight to that part of configuration space in which the electrons are both on the same side of this plane.

It was shown that in the optimum case for both eq. 9 and eq. 10

$$l = (\chi_1 + \chi_2)/\sqrt{2} \tag{11}$$

$$r = (\chi_1 - \chi_2)/\sqrt{2}$$

Finally, the total two-term truncated wave function may be expressed as

$$\Psi = \lambda_A \Psi_A + \lambda_I \Psi_I \tag{12}$$

where λ_A^2 and λ_I^2 may be considered as the fraction alternant and ionic character, respectively. In the case of H_2, it seemed appropriate also to call the former "atomic" character, but that seems less appropriate here. It can easily be shown that

$$\lambda_A^2 = \frac{1}{2} + (n_1 n_2)^{1/2} \tag{13}$$

where the n_i are taken from Table V, and $\lambda_I^2 = 1 - \lambda_A^2$. We have collected these parameters in Table VI together with the very instructive expansions

(9) H. Shull, *J. Am. Chem. Soc.*, **82**, 1287 (1960).

(10) L. Pauling, "The Nature of the Chemical Bond," 2nd Ed., Cornell University Press, Ithaca, N. Y., 1960.

TABLE VI
ALTERNANT AND IONIC CHARACTER IN H_3^+

R_{ab}	1	2	3	4
λ_A^2	0.57795	0.67094	0.77126	0.85486
λ_I^2	.42205	.32906	.22874	.14514
$l_a{}^a$	.82624	.77673	.81548	.86381
$l_b{}^a$	.62308	.41173	.38198	.36828
$l_c{}^a$	− .72950	− .33388	− .20894	− .14132
$u_a{}^b$	.36288	.59272	.72256	.81462
$u_b{}^b$	.84852	.53688	.47473	.43763
$u_c{}^b$	− .23017	− .01526	+ .03125	+ .04391

^{a} Coefficients in the expansion $l = l_a a + l_b b + l_c c$. ^{b} Coefficients in the expansion $u = u_a a + u_b b + u_c c$.

of l, r, and the normalized u and v functions (see eq. 16 of ref. 6 in terms of the original basis orbitals a, b, and c. The functions r and v are symmetrically related to l and u, respectively, and their coefficients have not been explicitly listed.

First, we can compare the coefficients λ_A^2 and λ_I^2 in H_3^+ (Table VI) with those found in H_2.[8] For the Wang function, λ_I^2 was 0.3205; for the Weinbaum function, 0.3854; and for the Rosen function, 0.3765. If Hopton and Linnett's contentions concerning the appropriate description of the bonds in H_3^+ were correct, we would expect very much higher values in this case. Clearly in the bonding region, Table VI shows there is *no significant difference* between H_2 and linear H_3^+.

If there is still any feeling that examination of coefficients of arbitrary basis sets has any validity, examination of the l_i and u_i of Table VI should dispel it completely. Examining $R = 2$, we might well conclude that the expansion of u in terms of a, b, and c lends strong weight to the Hopton–Linnett description of H_3^+, for a and b enter with almost equal coefficients, and c with almost zero coefficient; whereas, of course, v has the same equal weight for b and c with low weight for a. It is at first hard to believe that l with coefficients of 0.78 for a, 0.41 for b, and -0.33 for c and r, symmetrically related, correspond actually to considerably greater electron separation than the former. What is not obvious from simple inspection of the coefficients is the manner in which the negative c coefficient subtracts weight from the right side of b which already has a lower weight than a. This thereby greatly lowers the two-electron population on b itself which the (u, v) form has a good deal of. Even the symmetric nature of a and b, so attractive in the (u, v) case for $R = 2$, disappears at all other internuclear distances.

Discussion and Conclusions

Finally we would add a brief comment concerning the existence of a "special energetic effect" associated with a pair of electrons. In this connection, we believe that the arguments given by Pauling[10] showing the existence of such an effect in H_2 are not valid. In particular, the wave function associated with a single "structure" in H_2 does not belong to the complete set of functions used in the variation theorem, and it is improper to use the latter to draw conclusions about the energy lowering between a function outside the antisymmetric class of functions and one within this class. This particular criticism does not apply to more complex cases cited by Pauling (*e.g.*, benzene) where the individual structures themselves belong to the correct class of functions. It seems preferable to the present author, as it has to

Hopton and Linnett, to discuss energetic effects in terms of the more classical electrostatic interactions plus correlation effects.

We would conclude from consideration of the natural orbital analysis of H_3^+ that in the bonding region, linear H_3^+ has many similarities to H_2. In particular, the description of "nonpairing" offered by Hopton and Linnett is no different in kind from the electron correlation in H_2, and we believe it an unfortunate choice of terminology to refer to this as nonpaired. We would prefer to retain the concept of the one-electron bond for those cases in which there is a single electron in a bonding region which is *largely spin uncorrelated* with other electrons, and this situation does not apply for H_3^+. Because there are two effective bonding regions in linear H_3^+ and only two electrons, it follows that on the average there is only one electron in each region, but it does not follow that the electrons are paired in any sense different from that in the case of the hydrogen molecule.

In fact, every facet of our analysis suggests that there is not any difference in kind between linear H_3^+ and H_2. The former might therefore be better considered as a relatively normal (albeit lengthened) single bond in which is embedded an additional proton. Of course, it should be borne in mind that the present analysis is for the hypothetical (nonequilibrium) linear symmetric case using a relatively crude calculation. More accurate calculations are in progress, and we hope eventually to make a more definitive analysis. Even in the linear case, however, we can expect some significant changes. For example, the calculation of Hirschfelder, Eyring, and Rosen did not allow orbital exponents to vary. We can expect a significant increase in bond concentration toward the axis in H_3^+ as compared to H_2 at comparable distances, but the present crude calculations are not sufficiently refined to show this. We do expect, however, that this concentration will not have any significant effect upon the importance of electron correlation as discussed here.

Dynamic Mechanical Properties of Poly-γ-benzyl-L-glutamate in a Helicogenic Solvent

BY N. W. TSCHOEGL AND JOHN D. FERRY

The storage (G') and loss (G'') shear moduli have been measured over a wide frequency range for dilute solutions of poly-γ-benzyl-L-glutamate in *m*-methoxyphenol, a helicogenic solvent, using the apparatus of Birnboim and Ferry. A few measurements were also obtained in dichloroacetic acid, which produces the random coil configuration. The temperature dependence of the viscoelastic properties was satisfactorily described by the method of reduced variables, from 0 to 50° in *m*-methoxyphenol (1 and 2% polymer), and at −6 and 0° in dichloroacetic acid (2% polymer). The frequency dependence of G' and G'' in the *m*-methoxyphenol solutions was qualitatively intermediate between the predictions of the Kirkwood–Auer theory for rigid rods and the Zimm theory for flexible random coils with dominant hydrodynamic interaction. A fit to the Kirkwood–Auer theory at low frequencies gave values for the molecular weight and relaxation time which were not unreasonable considering that there must be substantial intermolecular interaction even at 1% concentration. A fit to the Zimm theory gave unacceptable values for the molecular weight and terminal relaxation time. Thus the hydrodynamic behavior revealed at low frequencies is essentially rodlike, but the deviations from the Kirkwood–Auer theory at high frequencies indicate some flexibility of the helix. In dichloroacetic acid, the data are of limited scope; the magnitude of the terminal relaxation time is much too small for rigid rods but is somewhat larger than that predicted by the Zimm theory for coils.

Introduction

The characteristic hydrodynamic behavior of synthetic polypeptides in the helical form, associated with a stiff rodlike configuration, has been investigated by several types of measurements, including non-Newtonian viscosity[1] and electrical birefringence.[2,3] It should also be manifested in viscoelastic measurements. Kirkwood and Auer[4] showed over a decade ago that a solution of thin rodlike molecules should reveal viscoelastic properties when subjected to sinusoidal deformations, and they calculated the frequency dependence of both viscous and elastic components of the mechanical response in terms of molecular parameters.

We describe here some viscoelastic measurements of dilute solutions of poly-γ-benzyl-L-glutamate in a helicogenic solvent, and compare the results with the Kirkwood–Auer theory. A few data are also presented for the same polypeptide in a solvent which favors the random coil configuration.

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(2) I. Tinoco, Jr., *ibid.*, **79**, 4336 (1957).

(3) G. Boeckel, J.-C. Genzling, G. Weill, and H. Benoit, *J. chim. phys.*, **59**, 999 (1962).

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Theory

The viscoelastic properties of a dilute macromolecular solution are conveniently described by the contributions of the solute to the components of the complex shear modulus, $\mathbf{G}^* = G' + iG''$. The storage modulus G' is due entirely to the solute; the portion of the loss modulus contributed by the solute is $G'' - \omega v_1 \eta_s$, where ω is the circular frequency, v_1 the volume fraction of solvent (usually negligibly different from unity), and η_s the solvent viscosity. According to the Kirkwood–Auer theory[4] for a rodlike macromolecule, these quantities are given by

$$G' = (3cRT/5M)\omega^2\tau^2/(1 + \omega^2\tau^2) \qquad (1)$$

$$G'' - \omega v_1 \eta_s = (3cRT/5M)\omega\tau[1/(1 + \omega^2\tau^2) + {}^1\!/_3] \qquad (2)$$

where c is concentration of solute in g./cc., M is the molecular weight, and τ, the relaxation time, is given by

$$\tau = \pi\eta_s L^3/18kT \ln (L/b) \qquad (3)$$

Here L is the length of the rod, and b the length of the