THE CONSTITUTIVE CHANGES OF THE COVALENT LINKAGES, THEIR NATURE AND CAUSE.

By A. Burawoy.

Organic chemists, unable to interpret the variations of bond properties within different substances by modifying the classical conceptions of chemical linkages, have sought to describe the obscure actual structures or the required structural modifications in terms of the principles of the classical (atomic or electronic) structural theories.   This has finally led to the hypothesis of *mesomerism*.   As a basis for a quantitative approach, theoretical physicists have developed the same simplifying hypothesis. In an attempt to apply the quantum mechanical principle of resonance to this problem, Pauling [1] identified linkages with certain constant values of bond properties : all observed changes in the bond energies of atomic distances of covalent linkages from such idealised values (as observed in simple substances such as methane, ethylene, or acetone) were attributed to a rather obscure qualitative structural change of the molecules interpreted as *resonance among several (idealised) valence bond structures*.   Their interaction was made responsible for the increased stability, the *resonance energy*.

Theoretical experience shows, however, that even in a simple molecule such as H_2 not less than 15 % of the bond energy is due to deformation effects.[1]   Such effects also considerably influence the bond properties of other covalent linkages.[2]   They might be expected to be more complicated and variable in polyatomic molecules, but, unfortunately, do not lend themselves to a quantitative treatment by the available methods of theoretical physics.   It is not justifiable, however, to overcome this difficulty by neglecting and arbitrarily replacing it by a new conception of chemical structures, because it allows of a quantitative treatment.

It is, therefore, not surprising that this conception, a speculative application of the principle of quantum-mechanical resonance, is at variance with numerous important facts.   This may be illustrated by a few examples.

1. The shortened C—F distance in CH_2F_2 and CF_4 as compared with CH_3F has been attributed to resonance [1,3] involving structures of the type $F^-HC=F^+$.   The smaller shortening of the C—Cl distance in CH_2FCl, CHF_2Cl and CCl_4 (and the unchanged C—Br distances in CH_3Br and CBr_4) has been explained [1] by a decreasing power of the halogen atoms to form double bonds in the series $F > Cl > Br > I$.   This interpretation neglects the fact that I has the greatest tendency to be in a higher valency

[1] Pauling, *The Nature of the Chemical Bond*, New York, 1940.

[2] Burawoy, *Trans. Faraday Soc.*, 1943, **39**, 79.

[3] Broackway, *J. Physic. Chem.*, 1937, **41**, 747, 185.

state and to form cations in its "trivalent" state, and it cannot be accepted. The arbitrary and unsatisfactory nature of the claim that the halogen atoms in these substances have a tendency to form double bonds is clearly illustrated by the numerous contradictory statements with regard to the relative degree of double bond formation. It has been claimed to *increase* or *decrease* in the order F, Cl, Br, I or to remain constant, as required by the facts.

2. The shortened C—Hlg distances in benzene-, ethylene-, and acetylene-halides (Table III) have been attributed to the same types of resonance involving structures such as H_2C^-—CH=X^+ and HC^-=C=X^+. However, since the halogen atoms possess a much higher electron affinity than a C atom, the contribution of structures Hlg^--H_2C=Hlg^+ should have been much greater than that of structures H_2C^-—CH=Hlg^+ or HC^-=C=Hlg^+, and the shortening in the former molecules much greater, whereas the opposite is the case. Moreover, in contrast to the findings in the case of the aliphatic halides, *all* C—Hlg linkages are shortened by similar absolute amounts. The claimed decreasing power of the halogens to form double bonds in the series $F > Cl > Br > I$ is not observed (at least not to the same extent). This clearly indicates that the cause of the shortening is different in both cases, as will be explained later.

3. The shortening of the C—C distances in substances containing conjugated systems, such as butadiene, diacetylene or cyanogen, has been claimed as evidence for their interpretation as resonance hybrids involving structures H_2C=CH—CH=CH_2, H_2C^-—CH=CH—CH_2^+ (2 structures),

$\overset{|}{C}H_2$—CH=CH—$\overset{|}{C}H_2$ or HC≡C—C≡CH, $H\overset{-}{C}$=C=C=$\overset{+}{C}H$ (2),
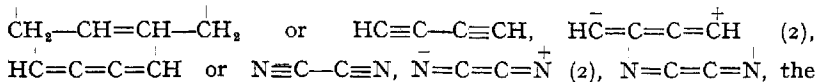
HC=C=C=CH or N≡C—C≡N, $\overset{-}{N}$=C=C=$\overset{+}{N}$ (2), N=C=C=N, the

C—C linkages acquiring double bond character. However, this interpretation should also demand an increase of the bond lengths of the C=C, C≡C C≡N linkages, since the later should obtain a single or double bond character respectively, whereas the values observed are unchanged.

The equation

$$R = \frac{x_1 k_1 R_1 + x_2 k_2 R_2 + x_3 k_3 R_3}{x_1 k_1 + x_2 k_2 + x_3 k_3},$$

where x_1, $_2$, $_3$ are the partial contributions of 3 structures to the hybrid of the molecule, k_1, $_2$, $_3$ the force constants assumed to be in the ratio $1 : 3 : 6$ for single, double and triple bonds, R_1, $_2$, $_3$ the bond distances, has been suggested for the calculation of the amount of double bond character of the C—C linkage.[1] It has been empirically derived from the known C=C and C—C distances in ethylene and ethane (1·34 and 1·54 A) corresponding to 100 % double and single bond character and those of graphite and benzene (1·42 and 1·39 A respectively) corresponding to 1/3 and 1/2 double bond character, the assumption, of course, being that the changes are due to the phenomenon of resonance. Table I shows the percentage contribution of the double bonded structures calculated by this equation from the observed C—C distances.

The table also shows the observed interatomic distances of the multiple linkages as well as those by utilising the amount of the double bonded (radical or ionic) structures calculated from the same equation. The expected changes should be in many cases much greater than any possible experimental error of the methods. *This interpretation of conjugated systems is therefore excluded.* Moreover, unstable structures such as

$\overset{|}{C}H$=C=C=$\overset{|}{C}H$ and N=C=C=N with three adjacent double bonds should add up to 70 %, *i.e.* should be more stable than the conventional structures HC≡C—C≡CH and N≡C—C≡N.

4. The shortened C—C distance in methyl acetylene and methyl cyanide necessitated the assumption of conjugation between a methyl

TABLE I.

Substance.	C—C Distance.	Double Bond Character.	C=C or C≡C Distance.	
			Calc.	Obs.
	(A)			
$H_2C=CH-CH=CH_2$	1·46	18 %	1·354	1·35
$Ph-CH=CH-Ph$.	1·44	25 %	1·36	1·33
$HC≡C-C≡CH$	1·36	75 % (70 %)[4]	1·284 (1·275)	1·19
$Ph-C≡C-Ph$ . .	1·40	44 % (36 %)	1·24 (1·23)	1·19
$Me-C≡C-H$ . .	1·46	18 % (14 %)	1·214 (1·21)	1·20

group and the multiple linkage (interpreted as resonance), involving [1, 6] the unlikely structures H^+ $CH_2=C=CH^-$ and H^+ $CH_2=C=N^-$. The shortened C—H distance in acetylene and HCN (1·06 A) necessitated, finally, the admission that the C atomic radius of a triple linkage is changed, since no resonance is possible.[1, 5]

5. As recently shown,[8] the facts connected with the light absorption of organic compounds are *qualitatively* incompatible with the interpretation of organic compounds or conjugated systems as resonance hybrids among several valence bond structures.[9]

In order to maintain this postulate (mesomerism), not only have unlikely idealised structures been suggested, but also sundry auxiliary hypotheses have been introduced, *e.g.* the formal charge effect, the correction due to the incompleteness of the valency shell, the decreasing atomic radius of a C atom belonging to a triple bond, and the adjacent charge rule. In spite of its considerable ambiguity, it is *qualitatively* in disagreement with numerous important facts. The constitutive changes in the linkages and their bond properties cannot be accounted for quantitatively or described qualitatively in terms of idealised additive structures.

The resonance hypothesis permits quantitative treatment of the variations of covalent linkages, but the value of such treatments based on simplifying assumptions unconnected with realities is open to doubt. In purporting to possess a quantitative, mathematical background they are, indeed, misleading. In view of the necessity of introducing numerous approximations and simplifications in the mathematical treatment of polyatomic molecules, agreement between calculated and observed values is in itself no evidence for the qualitative assumptions made.

The variations of bond properties within different molecules do not involve modifications in the *type* of linkages. They are accounted for by the principles of the empirical classical (atomic and electronic) structural theories : existence of single, double and triple bonds represented by two, four and six electrons contributed equally by the two atoms of a linkage, of unshared electron pairs and lone electrons ; the possibility of uneven distribution of shared electrons between the two nuclei. These theories, of course, have never demanded that any particular

[4] Bracketted values are calculated with a correction of 0·02 A for the radius of a C atom belonging to a triple linkage.[5]

[5] Pauling, Springall and Palmer, *J. Am. Chem. Soc.*, 1939, 61, 927.

[6] Hugill, Coop and Sutton [7] have already pointed out that the chemical properties are against the assumption of such a structure.

[7] *Trans. Faraday Soc.*, 1938, 34, 1518.

[8] Burawoy, *Chem. and Ind.*, 1940, 52, 855.

[9] The results of the present paper show that the speculative electronic formulæ suggested by the author [9a] for the absorbing states of organic compounds cannot be maintained. This will be discussed elsewhere.

[9a] Burawoy, *J.C.S.*, 1939, 1177.

covalent linkages are *quantitatively* equivalent in all molecules : they are influenced by all the other linkages and atoms present in the molecule, which vary them by virtue of electron displacements due to changes in the *effective size* and the electron attracting power of individual nuclei. These changes may be caused (*a*) by a varying *withdrawal of electrons* by an inductive mechanism within the other linkages in which the nucleus participates ; (*b*) by the *replacement of electrons* belonging to a single linkage either *by the more weakly held polarisable electrons* belonging to a multiple linkage or by unshared or lone electrons. Another important factor is a varying *steric repulsive interaction* of atomic orbitals within the molecule. This total effect may be called a *stereomeric effect*, which may be negative (— St) or positive (+ St) in the case of a decreasing or increasing effective atomic radius, due to the replacement or removal of a hydrogen atom. These effects are more complicated than but are comparable with the deformation effects assumed in the quantitative treatment of the H_2 molecule.

Variations of Bond Distances and Bond Energies due to Changes of Substituents.

The C—F distance, which is 1·42 A. in CH_3F, is shorter in CH_2F_2 and CF_4 (1·36 A.), the C—Cl distance, which is 1·77 A. in CH_3Cl, is shorter in CH_2FCl (1·76 A.), CHF_2Cl (1·73 A.), and CCl_4 (1·755 A.). Similarly, the Si—Cl distance decreases in the order SiH_3Cl (2·06 A.), SiH_2Cl_2 (2·02 A.) $SiHCl_3$ (2·01 A.), $SiCl_4$ (2·00 A.). On the other hand, the C—Br distances in CH_3Br and CBr_4 are almost [3] unchanged (1·91 A.). This can be attributed to the replacement of H atoms by the stronger electron attracting F and Cl atoms. The increased positive charge at the C or Si atom respectively will be responsible for a smaller effective size, greater attraction of the electrons participating in the other linkages, and a shortening of the C—Hlg and Si—Hlg distances. This effect should, and does, decrease in the order of decreasing electron attraction F > Cl > Br > I. The increasing repulsive steric interaction of the substituents may be an additional factor. It may also account for the negligible effect of the third and fourth F atoms in CF_4. In agreement with this interpretation the shortening of the C—Hlg bond distances is accompanied by increased bond energies [10] and decreased polar character.[11]

The varying C—C and C—H bond energies in aliphatic hydrocarbons [12] are similarly explained. They cannot be accounted for by the resonance hypothesis or the conception of hyperconjugation.[13]

Variations due to the Presence of Multiple Linkages.

A considerable shortening of bond distances and corresponding increase of bond energies [16, 17] is observed, if one or both atoms of a single linkage are part of a double or triple bond. Two factors contribute mainly to the decrease of the bond distances.

1. *Presence of strongly polarizable electrons* at the atoms of multiple linkages. Repulsive interaction of the electron pairs of a multiple linkage will decrease the hold on these electrons by the nuclei, as indicated by the

[10] Henne *et al.*, *J. Am. Chem. Soc.*, 1936, **58**, 882 ; 1937, **59**, 1200, 1400, 2434.

[11] According to Sutton and Brockway, *J. Am. Chem. Soc.*, 1935, **57**, 473, the dipole moments of the C—Cl linkages in CH_2Cl_2 (1·35 D) and $CHCl_3$ (1·28 D) are considerably reduced as compared with CH_3Cl(1·85 D).

[12] Rossini, *Bureau of Standards*, 1934, **12**, 735 ; **13**, 21 ; Knowlton and R., *ibid.*, 1939, **22**, 415.

[13] Wheland and Pinkston, jr., *J. Chem. Physics*, 1944, **12**, 69.

[16] Kistiakowsky *et al.*, *J. Am. Chem. Soc.*, 1935, **57**, 65, 876 ; 1936, **58**, 137, 146 ; 1937, **59**, 831 ; 1938, **60**, 440, 2764.

[17] Corresponding changes of dipole moments are also reported.

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TABLE II.[14]—Bond Distances in A.

Substance.	C—H.	C—C.	C=C.	C≡C.	C≡N.	C=O.
CH_4 . . .	1·093	—	—	—	—	—
$H_3C—CH_3$ . .	1·09	1·55	—	—	—	—
$H_2C=CH_2$ . .	1·087	—	1·34	—	—	—
	1·071	—	1·358	—	—	—[15]
$H_2C=O$ . . .	1·09	—	—	—	—	1·21
$HC\equiv CH$ . . .	1·057	—	—	1·204	—	—
$HC\equiv N$ . . .	1·06	—	—	—	1·154	—
$Me_2C=CMe_2$ . .	—	1·54	1·34	—	—	—
$MeCH=O$ . .	—	1·50	—	—	—	1·22
$MeC\equiv CH$ . .	—	1·46	—	1·20	—	—
$MeC\equiv CMe$ . .	—	1·47	—	—	—	—
$MeC\equiv N$ . . .	—	1·49	—	—	1·16	—
$H_2C=CH—CH=CH_2$	—	1·46	1·35	—	—	—
$Ph—Ph$ . .	—	1·48	—	—	—	—
$Ph—C_6H_4—Ph$.	—	1·48	—	—	—	—
$O=CH—CH=O$.	—	1·47	—	—	—	1·20
$HC\equiv C—C\equiv CH$.	—	1·36	—	1·19	—	—
$N\equiv C—C\equiv N$.	—	1·37	—	—	1·16	—
$Ph—CH=CH—Ph$.	—	1·44	1·33	—	—	—
$Ph—C\equiv C—Ph$.	—	1·40	—	1·19	—	—

[14] For original literature, cf. Pauling,[1] Maxwell, J. Optical Soc. Am., 1940, **30**, 375 ; Annual Reports, 1940, **37**, 76.
[15] Thompson, Trans. Faraday Soc., 1939, **35**, 697 ; Gallaway and Barker, J. Chem. Physics, 1942, **10**, 88.

strong polarizability. It will correspond to a decreased electron density at these atoms, allowing an increased hold (attraction) on the electrons of the other linkages. The replacement of electrons forming a single linkage by such relatively weakly held electrons will, therefore, have a similar, but much greater effect than the withdrawal of electrons by an inductive mechanism. Atoms belonging to multiple linkages will behave as if they have a smaller atomic radius. This effect should increase in the order C=C, C=O, C≡C, C≡N, i.e. with increasing polarizability or polar character and correspond to an increasing electron affinity of the C atoms in this order. This is in agreement with the increasing acidity of the corresponding hydrogen compounds.

2. Steric repulsive interaction of the atomic orbitals.—The C atoms in ethane, ethylene, and acetylene derivatives are surrounded by a decreasing number of substituents allowing a closer approach of substituents to the C atoms. The importance of this effect has been already emphasised by Conn, Kistiakowsky and Smith.[18] For the same reason,

TABLE III.[14]—Bond Distances in A.

Substance.	C—Hlg.
$H_3C—F$ . .	1·42
$C_6H_5—F$ . .	1·34
$H_3C—Cl$ . .	1·77
$C_6H_5—Cl$ . .	1·69
$H_2C=CH—Cl$.	1·69
$HC\equiv C—Cl$.	1·68
$N\equiv C—Cl$.	1·67
$H_3C—Br$ . .	1·91
$C_6H_4Br_2—p$.	1·88
$H_2C=CH—Br$.	1·86
$HC\equiv CBr$ . .	1·80
$N\equiv C—Br$ . .	1·79
H_2CI_2 . .	2·12
HCI_3 . .	2·12
$C_6H_4I_2—p$.	2·05
$H_2C=CH—I$.	2·03
$I—C\equiv C—I$.	2·03

[18] J. Am. Chem. Soc., 1939, **61**, 1868 ; cf. also J. Physic. Chem., 1937, **41**, 78.
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the size of the *substituents* should also be a factor in determining the degree of shortening, since steric interaction of any atomic orbitals should restrict the contraction made possible by the decreased effective size of the atoms belonging to the multiple linkages. This is confirmed by observations.

The exceptionally small shortening of the C—H linkage (none in benzene and ethylene outside experimental error [19]) and very little in acetylene and hydrogen cyanide, 0·035 A., should be connected with the shortness of the linkage. A repulsion of the nuclei will counteract further contraction. The qualitative nature of the present discussion dealing only with the *variations* in the bond properties may justify the neglect of such forces in the case of linkages not involving a H atom. Repulsion of the nuclei will play an important part in the mechanism of the transmission of a polar effect within a chain of atoms X—C—C'—C"—. The decreased effective size of the atom C due to a withdrawal of electrons by X will be responsible for an attraction of the electrons shared with C', but also of the nucleus C' since the latter would not necessarily weaken its hold on the shared electrons. This, however, is required for the transmission of the effect to atom C", and is accounted for by an increased repulsion of the nuclei C and C' owing to the increased positive charge on C and the shortened distance C—C'. The attraction of the electrons by C will be, therefore, greater than that of the nucleus C'.

The negligible decrease of the C—C distances in the methyl ethylenes and methyl benzenes is due to the large size of the methyl group, since the shortening is considerable in methyl- and dimethyl-acetylene (0·085 A.), methyl-cyanide (0·06 A.) and acetaldehyde (0·05 A.), where no steric inter-action of the atomic orbitals, or a smaller one, is possible. This inter-pretation is also supported by the following facts : The C—C distances in butadiene (0·09 A.) and diphenyl (0·06 A.) are shorter by much more than twice the decreases in the methyl-ethylenes and methyl-benzenes (<0·02 A.), since the second C atom also belongs to a smaller group, thus reducing steric repulsive interaction. On the other hand, the shortening in di-acetylene (0·19 A.) and cyanogen (0·18 A.) is only *slightly greater* than twice the contraction in methyl- and dimethyl-acetylene and methyl-cyanide, where steric interaction is much smaller or negligible.

Again, the smaller size of the halogen atoms accounts for the consider-able contraction of the C—Hlg linkages and (only a slight steric inter-action, or none, being possible) for the very small variations in the shorten-ing of all the C—Hlg distances of the benzene, vinyl, acetylene or cyano halides. Any steric interaction would show itself in a decrease of the shortening in the order C—F > C—Cl > C—Br > C—I within the same series, and, especially, in an increasing difference between the vinyl or benzene halides and the acetylene or cyano halides in the same order of linkages. There are, indeed, indications of such an effect (*cf.* Table III). However, the known distances are not equally reliable, and may require further confirmation.

Other linkages involving atoms with unshared electrons behave simi-larly to the halogen atoms, steric interaction being again negligible. Thus, the C—N distance in urea and acetamide is found to be 1·37 and 1·38 A. respectively, *i.e.* considerably shorter than that of a normal C—N distance (1·47 A.). The bond energy is also increased in acetamide (by 21 k. cal.) and urea (by 18·5 k. cal. per linkage).[1]

Moreover, excluding the exceptional C—H linkage, in contrast to the benzene and ethylene derivatives, the contractions in the acetylene de-

[19] The C—H linkages in ethylene and benzene absorb at shorter wavelengths (3·28 ; 3·25 μ) than those in aliphatic hydrocarbons (ca. 3·4 μ), indicating an increased bond energy [20] and most probably shorter C—H distances.

[20] *Cf.* Bonino, *Trans. Faraday Soc.*, 1929, **25**, 879 ; Ellis, *ibid.*, p. 894 ; Brackett, *Proc. Nat. Acad. Sci.*, 1928, **14**, 857 ; Fox and Martin, *Proc. Roy. Soc.*, A, 1940, **175**, 208.

rivatives vary only slightly, when X is methyl, vinyl, phenyl, acetylenyl or halogen (0·09-0·11 A.), indicating that the C atom behaves as having an almost constant radius, since steric interaction is negligible.

Variations due to Changes in Valency.

Considerable variations of bond distances and bond energies are also observed, if the valency of atoms is changed. The C=O distance and energy in carbon monoxide are, respectively, 1·13 A. and 210 k. cal., but in formaldehyde [1] 1·21 A. and 142 k. cal. Again, this is due to the replacement of shared electrons of single linkages by more weakly held (unshared) electrons responsible for a decreased effective size and increased electron attraction of the C atom. The negligible dipole moment (0·1 D.) is also accounted for.[21]

The *effect of a trivalent C atom* is similar. It is comparable with that of a C atom belonging to a multiple linkage. As in butadiene, diacetylene or styrene, substitution by a C atom belonging to a multiple linkage is accompanied by a considerable increase in the C—C bond energy. This accounts partly for the great stability of triphenylmethyl and allied radicals. The bond energy and dissociation energy of the C—C linkage in hexaphenylethane being about 54·0 [22] and 11·5 k. cal.[23] respectively, each C (phenyl)—C(methyl) linkage in the radical is stronger by about 7 k. cal. than in the undissociated hexaphenylethane. This is comparable with the increase of the C—C energy in butadiene and styrene as compared with ethylethylene and ethylbenzene (4-6 k. cal.). Space does not allow to multiply these typical examples.

Variations due to a + St Effect.

The considerable bearing of steric interaction of atomic orbitals on bond properties should lead us to expect that in certain conditions replacement of smaller atoms, in particular the H atom, by atoms or groups of larger size should owing to steric interaction lengthen bond distances, decrease bond energies and cause corresponding changes of other bond properties. This is confirmed by numerous observations, such as the reduced C—C energy in hexaphenylethane [22] and the increased C—C distance in hexamethyl-ethane and dibenzyl [24] (1·58 A.). For the same reason, the shortening of the C—Cl distances in chlorobenzene and chloroethylene (1·69 A.) is reduced in poly-chlorobenzenes and poly-chloroethylenes (1·71-1·73 A.) containing Cl atoms at adjacent C atoms,[25] as well as in isocrotylchloride Me$_2$C=CHCl (1·72 A.).[26] Similarly, corresponding changes in the dipole moments [27] have also been reported.

The *quantitative* prediction or treatment of the constitutive changes of a linkage within polyatomic molecules will require the consideration of the mentioned effects between all the nuclei and electrons within a molecule. Such a treatment does not appear to be possible (as yet). The analysis of the constitutive structural changes given in this paper has only a qualitative or semi-quantitative significance showing the *nature* of and the most important *factors* responsible for these changes. In contrast to resonance among several valence bond structures, the theory advanced

[21] *Cf.* also the views of Lessheim and Samuel, *Proc. Physic. Soc.*, 1934, **46**, 523 ; Hunter and Samuel, *Chem. and Ind.*, 1935, **54**, 31, 635, whose views the author shares.

[22] Bent *et al.*, *J. Am. Chem. Soc.*, 1935, **57**, 1242 ; 1936, **58**, 165, 170.

[23] Ziegler and Ewald, *Annalen*, 1929, **473**, 163.

[24] Bauer and Beach, *J. Am. Chem. Soc.*, 1942, **64**, 1142 ; Robertson, *Proc. Roy. Soc.*, A, 1935, **150**, 348.

[25] Brockway *et al.*, *J. Am. Chem. Soc.*, 1935, **57**, 2693 ; 1937, **59**, 2181.

[26] Beach and Stevenson, *ibid.*, 1939, **61**, 2643.

[27] Hampson *et al.*, *J.C.S.*, 1937, 10 ; 1939, 981.

not only accounts fully for the variations of the bond distances and energies, but, as will be shown elsewhere, for the facts related to the dipole moments, dissociation constants, chemical properties and light absorption of organic compounds. It has been arrived at by the consideration of all known facts. Like nature, it is not concerned, whether the present mathematical methods allow of its quantitative treatment.

Summary.

Deformation effects contribute considerably to the physical properties of H_2 and other covalent linkages. In this paper, the constitutive changes of covalent linkages within polyatomic molecules are analysed. They are accounted for by corresponding, although more complicated deformation effects. Their nature is discussed. The introduction of the hypothesis of resonance among several (idealised) valence bond structures, a speculative application of the quantum-mechanical principle of resonance, is unnecessary and in disagreement with numerous facts.

Added in Proof.

In two most important papers just appeared, Samuel[28] has analysed the changes of physical properties which accompany changes in the valency state of atoms. He has convincingly shown that the classical conceptions of the chemical linkages are justified from the point of view of wave-mechanical theory and, indeed, for many reasons preferable to the conceptions generally identified with the postulate of resonance among several valence bond structures. Atoms in a different valency state behave like different atoms and, consequently, are responsible for quantitative, but not qualitative, changes of linkages. In the unabbreviated paper the author had also discussed numerous structures treated by Samuel, e.g. Co, N_2O, NO, PCl_5 and has arrived at almost identical conclusions, although often by different argument.

[28] Samuel, *J. Chem. Physics*, 1944, **12**, 167, 180.