

561. Localised Molecular Orbitals in Self-consistent Field Wave Functions. Part IV.¹ Ionisation Energies of Lone Pairs and Two-electron Bonds.

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Some further numerical evidence for the existence of lone pairs and localised two-electron bonds in some small molecules is provided by their calculated ionisation energies. These are generally characteristic of a particular lone pair or two-electron bond and independent of the nature of the rest of the molecule.

The ionisation energy of a lone pair is very close to that of the same electron of the "atom in the molecule." The ionisation energy of a localised bond is generally greater than the simple average of the ionisation energies of the two atomic orbitals which form the bond and larger by an amount comparable with the bond energy.

Introduction to Parts IV—VI.—ONE aim is to translate the results² of self-consistent field wave function computations into a language which is familiar to the chemist. It was shown* that a linear transformation³ of the set of occupied delocalised molecular orbitals of a molecule gives a set of localised molecular orbitals which correspond to the two-electron bonds and lone pairs of chemical valence theory, so providing evidence for their existence in the molecules studied. The ground states of many stable molecules cannot be represented in this way, but we are concerned with those molecules for which such a representation gives a useful approximation.

G. N. Lewis⁴ first formulated the idea of the two-electron bond and lone pair and Pauling⁵ used both in developing his partly quantum mechanical, partly empirical,

* In Part I, Table 4, there is an error in BMO_{ab} in the wave function of C_4 . The term $-0.4256(2p_{0b})$ should be replaced by $-0.0701(2s_d)$. In Part II, eqn. 14 should read $q(j;a) = 1 - 2l(j;a)$. In Part II, a footnote to Fig. 3 was omitted. The reported π charges are the total charges, not the charges per dimension. The reported π charges for the molecules N_3^- and NO_2^+ are relative to the molecules with the charges

-1.0	1.0	-1.0	0.0	1.0	0.0
N	N	N	O	N	O

In fact, it is best with these charged molecules to report the total π atomic populations and not the charges. The total π populations are

2.74	2.52	2.74	2.92	2.16	2.92
N	N	N	O	N	O

I regret that the name of Professor H. Shull was mis-spelt throughout Part III.

¹ Parts I, II, III, *J.*, 1963, 2003, 2015, 4017.

² Kotani, Ohno, and Kayama, "Handbuch der Physik," Vol. 37/2, Springer, Berlin, 1961; ref. 7 of Part I.

³ Lennard-Jones, *Proc. Roy. Soc.*, 1949, 198A, 1, 14; Hall and Lennard-Jones, *ibid.*, 1950, 202A, 155; Lennard-Jones and Pople, *ibid.*, 1950, 200A, 166; Hurley, Lennard-Jones, and Pople, *ibid.*, 1953, 220A, 446.

⁴ G. N. Lewis, *J. Amer. Chem. Soc.*, 1916, 38, 762.

⁵ Pauling, "The Nature of the Chemical Bond," Cornell Univ. Press, Ithaca, New York, 1960.

valence-bond scheme of molecular structure. Now it is possible to show in a purely quantum mechanical way that localised two-electron bonds and lone pairs do exist and hence to understand quite thoroughly their nature. Of course, no bond in a polyatomic molecule is ever *perfectly* localised and this point will be examined later.

In Parts I—III,* the hybridisations in the hybrid atomic orbitals forming the bonds and lone pairs were calculated together with the populations and electronic charges in these hybrid atomic orbitals and on the atom in the molecule as a whole. This was done for some twenty di-, tri-, and tetra-atomic molecules and the results agreed with many of the ideas of chemical valence theory.

Now we examine the various energy quantities of the lone pairs and bonds. The most interesting of these is the bond energy of the individual bonds. The energy quantities in the literature are the ionisation energies of the delocalised molecular orbitals. We have to connect the ionisation energies with the bond energies of the localised bonds. This is done in three steps. First, in this Paper, we convert the ionisation energies of the delocalised molecular orbitals into the ionisation energies of the lone pairs and localised bonds. Secondly, in Part V, these ionisation energies are broken into a sum over simple integrals to see why they show the regularities found in this Paper. Thirdly, in Part VI, the atomisation energy is formulated as a sum over bond energies which are themselves obtained from the ionisation energies of the localised bonds.

This approach, despite difficulties, gives a good insight into the nature of localised bonds and particularly those σ bonds which underlie π bonds. Our lack of understanding of these bonds is the major defect⁶ in our understanding of multiple bonds and it seems that our best chance of learning something about them is by formal quantum mechanical computation. This work in many ways develops Mulliken's re-examination⁷ of the semi-empirical molecular orbital method although the emphasis differs because we are not concerned with the semi-empirical methods.

In this Paper, the ionisation energies of the lone pairs and two-electron bonds are obtained from those of the delocalised molecular orbitals. The latter correspond⁷ quite closely with the observable ionisation potentials of the molecules. The ionisation energies of the lone pairs and bond are *not* observables but they are the only well defined one-electron energies in molecules (or atoms) and, as we insist that all energies be well defined, we use these as the one-electron energies. Moreover, since ionisation energies are useful for grouping together into a single quantity the very large number of integrals over atomic orbitals which occur in the energy expressions for molecules, we have to work with these non-observables.⁸ The theory of the conversion of the computed ionisation energies of the delocalised molecular orbitals into the ionisation energies of the lone pairs and localised bonds is set out in the next section.

Theory.—The reported self-consistent field wave function of a $2n$ electron closed shell molecule consists of a single determinant of delocalised molecular orbitals ($\phi_1 \dots \phi_n$). Each molecular orbital has one energy parameter ($\epsilon_1 \dots \epsilon_n$) associated with it. The ϕ are the eigenfunctions and the ϵ are the eigenvalues of the simplest form of the Hartree-Fock equation

$$F\phi_k = \epsilon_k\phi_k \quad (1a)$$

F is the Hartree-Fock operator of the molecule and in it the true time-dependent electron-electron interaction is replaced by an averaged time-independent interaction. This is the characteristic feature of the Hartree method. The complete formulation of this operator is discussed elsewhere.⁹ In matrix notation, equation (1a) is

$$F\varphi = \varphi\epsilon \quad (1b)$$

* Moskowitz and Barnett, Quart. Progress Reports No. 49, July 1963, Solid State and Molecular Theory Group, Massachusetts Institute of Technology, Cambridge, Mass.

⁷ Mulliken, *J. Chim. phys.*, 1949, **46**, 675 *et seq.*; Lorquet, *Rev. Mod. Phys.*, 1960, **32**, 312.

⁸ Platt, "Handbuch der Physik," Vol. 37/2, Springer, Berlin, 1961, p. 173.

⁹ Roothaan, *Rev. Mod. Phys.*, 1951, **23**, 69.

where φ is the n dimensional row vector of the occupied molecular orbitals and ϵ is a diagonal matrix with the ϵ_k as its elements.

The linear transformation of the row of occupied molecular orbitals (Part I) is

$$\varphi' = \varphi A \quad A\tilde{A} = E \quad (2)$$

and this gives the localised molecular orbitals, ϕ_k' . A is an $n \times n$ orthogonal matrix and E is the unit matrix. Each of the localised molecular orbitals is either a lone pair (λ) or a two-electron bond (μ). The λ carry one label ($a, b \dots$) to denote the atom to which they belong and the μ carry two labels ($ab, ac \dots$) to denote the two atoms which they join together. Then

$$\phi_1' \dots \phi_n' \equiv \lambda_a, \lambda_b \dots \mu_{ab}, \mu_{ac} \dots \quad (3)$$

The localised molecular orbitals satisfy, not equation (1), but a transformed equation in which the diagonal matrix ϵ has been replaced by a real symmetric but non-diagonal matrix e . This is related to ϵ by a similarity transformation with the matrix A

$$e = \tilde{A}\epsilon A \quad (4)$$

where \tilde{A} is the transpose of A ($\tilde{A}_{kj} = A_{jk}$). The Hartree-Fock equation is now

$$F\varphi' = \varphi e \quad (5a)$$

or without matrix notation

$$F\phi_k' = \sum_{j=1}^n \phi_j' e_{jk} \quad (5b)$$

Taking scalar products of (5b) gives

$$e_{kk} = \langle \phi_k' | F | \phi_k' \rangle \quad e_{jk} = e_{kj} = \langle \phi_j' | F | \phi_k' \rangle \quad (6)$$

since the ϕ_k' are an orthonormal set. The operator F is invariant under the transformation.⁹ The symbol ϵ will always be used for the energy parameter of the delocalised molecular orbitals and the symbol e for that of the localised lone pairs and bonds. A systematic notation for the diagonal elements of the e matrix is e_a for the lone pair and e_{ab} for the bond.

It remains to show that the e_a and the e_{ab} are the amounts of energy required to remove one electron from the lone pair and from the bond. This follows easily if one writes

$$E^{\lambda a}_{\text{ion}} - E_{\text{molecule}} = \langle \lambda_a | F | \lambda_a \rangle = -e_a \quad (7a)$$

$$E^{\mu ab}_{\text{ion}} - E_{\text{molecule}} = \langle \mu_{ab} | F | \mu_{ab} \rangle = -e_{ab} \quad (7b)$$

The details are given elsewhere.⁹ Written thus, the ionisation energy is positive and this is given by $-e_a$ and $-e_{ab}$. The essential assumption involved in these equations is that the same molecular orbitals will serve for the positive ion as for the neutral molecule and this is Koopmans's theorem.

The off-diagonal elements of the e matrix do not have any clear physical significance although they are usually thought of as representing the interaction between the localised bonds and lone pairs. It is unfortunate that these quantities are not better defined because they do show marked regularities from molecule to molecule.

General Procedure.—From equation (4), the A matrices from the earlier work, and the ϵ matrices from the literature, the e matrices have been evaluated for all the molecules of this set. The results are shown in the Tables. Those for the water and ammonia molecules are too inaccurate to be useful for present purposes.

These numbers can be used in several ways. First, it can be shown that the ionisation

energy of a given lone pair is the same in different molecules and this can then be compared with the ionisation energy of the same electron of the free atom and the "atom in the molecule." The ionisation energy of a localised bond is compared with the ionisation energies of the valence atomic orbitals of the "atom in the molecule" to show that the electron is more tightly bound in the bond than in the atomic orbitals of the atoms. The increased binding of the electron is then compared with the bond energies.

Finally, we must decide just what "atomic ionisation energy" to use in comparing the atomic and molecular ionisation energies. To do this, we have to adopt a model for the "atom in the molecule" and two possibilities have been considered. The first is the usual van Vleck valence state¹⁰ on which Hinze and Jaffé¹¹ have recently reported some detailed computations. The second is the "configuration atom" discussed by Slater¹² and whose energy he writes E_{av} . This is obtained by taking a simple average over the observed energy levels, of given L and S , which arise from a given configuration of the atom. This is the energy which the atom would have if there were no coupling between the spin angular momenta of the various electrons or between the orbital angular momenta of the electrons. The van Vleck and the Slater "atom in molecule" differ only slightly

TABLE 1a.
Ionisation energies of molecular lone pairs ($-e^{\lambda}_a$) and of the free atom and the "atom in the molecule" lone pairs ($-e_a$)*.

Atom	Molecule	Lone pair	Atomic charge	$(-e^{\lambda}_a)$	Atomic ionisation energy ($-e_a$)			
					Average of ($-e^{\lambda}_a$)	Free atom	Slater	Hinze-Jaffé
Boron	BH	0.93 $2s_B$	0.12	13.2	13.2	12.9	14.0	14.0
Carbon	CH	0.97 $2s_C$	0.00	18.8	18.5	16.6	19.45	19.4
	CO	0.85 $2s_C$	0.10	16.0/17.8				
	C ₃	0.93 $2s_C$	0.20	18.8				
	C ₄	0.97 $2s_C$	-0.02	18.8				
Nitrogen	N ₃	0.86 $2s_N$	0.00	23.3	24.5	20.4	25.6	25.6
	NH	0.98 $2s_N$	-0.08	24.9				
	HCN	0.92 $2s_N$	-0.08	25.3				
	C ₂ N ₂	0.92 $2s_N$	-0.02	25.9				
	N ₃ ⁻	0.92 $2s_N$	—	14.7				
Oxygen	OH	0.99 $2s_O$	-0.13	31.4	32.0	28.5	32.4	32.3
	CO	0.90 $2s_O$	-0.10	29.3/32.8				
	CO ₂	0.97 $2s_O$	-0.21	33.7				
	COS	0.96 $2s_O$	-0.10	34.4				
	CH ₂ O	0.94 $2s_O$	-0.12	29.3/31.2				
	CH ₂ O	1.00 $2p_O$	-0.12	11.9				
	NO ₂ ⁺	0.98 $2s_O$	—	46.7				
Fluorine	F ₂	0.99 $2s_F$	0.00	38.6	38.5	37.9	40.1	39.4
	HF	0.99 $2s_F$	-0.15	38.4				
	HF	1.00 $2p_F$	-0.15	12.6				
Sulphur	COS	0.92 $2s_S$	0.10	21.0	21.0	20.2	20.95	21.1

* Energies in ev. Atomic charges (see Part II) are the total atomic charges of the lone pair's atom and are in fractions of the electronic charge: a positive sign for the atomic charge denotes that there is a deficit of electrons on the atom in the molecule as compared with the free atom. Hybridisations (see Parts I and III), written as 0.93 $2s_B$, denote that the lone pair is formed from a hybrid atomic orbital which is 93% $2s$ of boron. The average value of ($-e^{\lambda}_a$) is taken to nearest 0.5 ev. Other energies are to nearest 0.1 ev. The ionisation energies of the free atoms are from ref. 13, as are the Slater atom ionisation energies. The Hinze and Jaffé numbers are from ref. 12. Where two values are given for ($-e^{\lambda}_a$), they refer to two different localisation routes (see Part I).

¹⁰ van Vleck, *J. Chem. Phys.*, 1933, **1**, 177, 219; 1934, **2**, 20, 297.

¹¹ Hinze and Jaffé, *J. Amer. Chem. Soc.*, 1962, **84**, 540 and the extended version of this work mentioned in footnote 39 of the Paper.

¹² J. C. Slater, "Quantum Theory of Atomic Structure," Vol. 1, ch. 14, McGraw-Hill, New York, 1960.

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TABLE 1b.

Ionisation energies of two-electron bonds ($-e\mu_{ab}$), of the atomic orbitals $[(-\bar{e}_a \bar{e}_b)/2]$ and the difference, $(-\delta e\mu_{ab})$.*

σ Bond	Molecule	Bond atomic orbitals		$(-e\mu_{ab})$	Average atomic ionisation energy		$(-\delta e\mu_{ab})$		
					Slater	Hinze-	Slater	Jaffé	
H-H	H ₂	1.00 1s _H	1.00 1s _H	16.9	13.6	13.6	3.5	3.5	
Li-Li	Li ₂	0.95 2s _{Li}	0.95 2s _{Li}	4.9	5.4	5.4	-0.5	-0.5	
N-N	N ₂	0.99 2p _N	0.99 2p _N	27.6	12.9	13.95	14.5	13.5	
	N ₃ ⁻	0.46 2p _N	0.87 2p _N	18.9	16.1	18.0	3.0	1.0	
F-F	F ₂	1.00 2p _F	1.00 2p _F	15.4	18.6	20.9	-3.0	-5.5	
Li-H	LiH	0.34 2p _{Li}	1.00 1s _H	8.3	—	9.2	—	-1.0	
B-H	BH	0.94 2p _B	1.00 1s _H	13.8	9.65	10.95	4.0	3.0	
C-H	CH	0.91 2p _C	1.00 1s _H	14.7	12.2	12.3	2.5	2.4	
	HCN	0.47 2p _C	1.00 1s _H	21.8	14.35	15.5	7.0	6.0	
	C ₂ H ₂	0.62 2p _C	1.00 1s _H	21.1					
	CH ₂ O	0.63 2p _C	1.00 1s _H	19.0/20.2	14.35	15.5	5.0	4.0	
N-H	NH	0.91 2p _N	1.00 1s _H	15.6	13.3	13.8	2.5	2.0	
O-H	OH	0.92 2p _O	1.00 1s _H	16.4	14.75	15.45	1.5	1.0	
F-H	FH	0.92 2p _F	1.00 1s _H	17.2	16.1	17.2	1.0	0.0	
C-C	C ₃	0.37 2p _C	0.94 2p _C	19.9	12.9	14.2	7.0	6.0	
	C ₄ (1:2)	0.39 2p _C	0.75 2p _C	16.1					
	C ₄ (2:3)	0.28 2p _C	0.28 2p _C	26.9	15.1	17.4	11.0	9.0	
	C ₃ N ₂	0.51 2p _C	0.51 2p _C	27.0					
	C ₂ H ₂	0.39 2p _C	0.39 2p _C	25.7					
C-N	HCN	0.48 2p _C	0.98 2p _N	24.0	14.0	15.7	10.5	9.0	
	C ₂ N ₂	0.50 2p _C	0.98 2p _N	25.4					
C-O	CO	0.98 2p _C	0.98 2p _O	25.0/26.7	13.3	14.1	13.5	12.0	
	CO ₂	0.44 2p _C	0.92 2p _O	25.1					
	COS	0.43 2p _C	0.96 2p _O	26.0	15.5	17.35	10.0	8.0	
	CH ₂ O	0.50 2p _C	0.98 2p _O	22.6/23.2					
C-S	COS	0.43 2p _C	0.91 3p _S	23.2	13.4	14.9	10.0	8.0	
N-O	NO ₂ ⁺	0.40 2p _N	0.81 2p _O	41.0	17.6	20.1	23.5	21.0	
π Bond									
N-N	N ₂	1.0 2p π _N	1.0 2p π _N	15.8	12.9	13.9	3.0	2.0	
C-N	HCN	1.0 2p π _N	1.0 2p π _C	13.8	11.8	12.6	2.0	1.0	
C-C	C ₂ H ₂	1.0 2p π _C	1.0 2p π _C	12.0	10.7	11.2	1.5	1.0	
C-O	CO	1.0 2p π _C	1.0 2p π _O	15.9	13.3	14.1	2.5	2.0	
C-O	CH ₂ O	1.0 2p π _C	1.0 2p π _O	12.8	13.3	14.1	-0.5	-1.5	

* Energies in ev. The hybridisation notation is explained in the footnote to Table 1a. The $(-\delta e\mu)$ values (eqn. 9) are to nearest 0.5 ev; other energies to nearest 0.1 ev. Where two values are given for the bond ionisation energy $(-e\mu_{ab})$, these correspond to different localisations (see Part I).

and we have considered both to see whether there is any profit at present in using the more elaborate van Vleck model. In fact, we have gone further and used the experimental ionisation energies of the free atom itself to see how necessary it is to bother with models for the "atom in the molecule." It turns out that it is essential to use some model for it: the free atom is certainly not good enough.

Earlier Work.—The formal theory used here is well established. It was developed extensively by Lennard-Jones, Hall, Pople, and others^{3,13} and used by Hall in setting up a semi-empirical theory of molecular ionisation energies. Both Hall and Franklin¹³ reported good results with this method and the present work helps to justify their semi-empirical method.

DISCUSSION

It is convenient to take first the ionisation energies of the lone pairs, then those of the bonds, and finally some general points.

¹³ Hall, *Trans. Faraday Soc.*, 1953, **49**, 113; Franklin, *J. Chem. Phys.*, 1954, **22**, 1304.

Ionisation Energies of Lone Pairs (Table 1a).—The hybridisations in the hybrid atomic orbitals are not reliable to better than about $\pm 5\%$ (Part I) so it is sufficient to think of all the lone pairs as being formed from pure $2s$ ($3s$ for sulphur) atomic orbitals. The numbers in Table 1a show that the ionisation energy of a given lone pair is effectively constant from molecule to molecule and this shows again that the lone pairs do exist effectively unchanged in different molecules. There does not seem to be any general connection between the ionisation energy and either the hybridisation in the atomic orbital or the total charge on the atom. Such connections are expected (see following Paper) and are expected to appear with more accurate wave functions.

The calculated ionisation energies of the lone pairs do not agree with the experimental ionisation energies of the same electron of the free atom. This is particularly so for carbon, nitrogen, and oxygen atoms. This important result shows that the “atom in the molecule” really does differ from the free atom. The ionisation energies of the lone pairs agree well with those of either the van Vleck or the Slater “atom in molecule.” Moreover, the ionisation energy of the lone pair is always about 1 eV smaller than the “atom in molecule” one and this is just what we would expect if there were a few percent of the $2p$ atomic orbital in all the lone pairs.

There are some interesting points about the ionisation energies of individual lone pairs. The $2p$ -like lone pairs in the hydrogen fluoride and the formaldehyde molecules have lower ionisation energies than do the same electrons of the “atom in the molecule.” The reason is not clear and we will have to wait for more computations on such systems. The results for the nitrogen and carbon monoxide molecules are interesting because their lone pairs seem to contain a relatively large amount of the $2p$ atomic orbital (Part I). This fits with the present result that their lone-pair ionisation energies are some 2 eV lower than those of the same lone pairs in other molecules. This is not the whole story, however, because their bond ionisation energies are unusually large and it will be shown that there is a failure of the localisation in these two molecules so that the present results for them may be partly spurious.

The two molecules with formal charges, NO_2^+ and N_3^- , have, respectively, lone-pair much larger and smaller ionisation energies than expected in a neutral molecule. This is as expected, and further computations on these charged species would be most useful.

This completes the present results for the lone pairs and the overall impression is that the $2s$ -like lone pairs behave quite simply. This may *not* be the case for the $2p$ -like lone pairs but we cannot settle this yet.

Ionisation Energies of Two-electron Bonds (Table 1b). We take the σ bonds first since they are easier to understand than the π bonds. The situation with the bonds is less simple than with lone pairs because we have fewer sets of apparently identical bonds from which to show that the ionisation energies of such bonds are constant. Moreover, the comparison with atomic ionisation energies is less direct.

The bond ionisation energy depends strongly on the hybridisation in the atomic orbitals which form the bond. There are examples of this among the carbon-carbon and the carbon-hydrogen bonds. The effect of the hybridisation is large (several eV) and of the expected sign. This fits well with the result in Part II that the population of a hybrid atomic orbital depends on its hybridisation, and with Hinze and Jaffé's finding that the electronegativity of a hybrid atomic orbital depends strongly on its hybridisation.

The next step is to compare the bond ionisation energies with those of the atomic orbitals which form the bond. Unfortunately, some arbitrary decisions have first to be made. The hybridisations have again been idealised so that a hybrid atomic orbital which is close to a $2p$ atomic orbital has been taken as such. Then we have to average the ionisation energies of the two atomic orbitals forming the bond. Although there is something to be said for weighting this average according to the populations of the atomic orbitals, this makes little difference and the arithmetic mean has been used.

The results are given in columns 6 and 7 of Table 1b. In columns 8 and 9 are given the

quantities $(-\delta e^\mu)$ which are the differences between the bond ionisation energies (column 5) and the two sets of averaged atomic ionisation energies. The formal definition is

$$(-\delta e^\mu) = (-e^\mu) - 0.5\{(-\bar{e}_a) + (-\bar{e}_b)\} \quad (8)$$

where the bar over e_a and e_b denotes that it is the ionisation energy of a *singly* occupied atomic orbital. So defined, $(-\delta e^\mu)$ is *positive* if the ionisation energy of the bond is *greater* than the average of the two atomic orbital ionisation energies. This is nearly always the case.

Now we look empirically at the connection between these $(-\delta e^\mu)$ values and the bond energies, leaving the formal theory for the following Papers. The four homonuclear diatomic molecules, hydrogen, lithium, nitrogen, and fluorine, are the simplest to understand and the $(-\delta e^\mu)$ values clearly reproduce the sequence of bond strengths. Thus, the lithium and fluorine molecules have weak bonds, the hydrogen molecule has a stronger bond, and the nitrogen σ bond is (probably) very strong, and this sequence is reproduced in $(-\delta e^\mu)$. The reason for the negative $(-\delta e^\mu)$ value for the fluorine molecule is given in Part VI. This is a pleasing result because these four molecules are very different in their general nature and to find reasonable agreement with them suggests that the theory is really useful.

The simplest heteropolar bonds are those of the diatomic hydrides, lithium hydride to hydrogen fluoride inclusive. In all except lithium hydride, $(-\delta e^\mu)$ is positive and about 1–4 eV. This is about right for the bond energies of these molecules, but there is no agreement with individual bond strengths within the set. Thus, hydrogen fluoride with the strongest bond has the smallest $(-\delta e^\mu)$. This result is explained in Part I.

The group of carbon–hydrogen bonds exemplifies the effect of hybridisation on the bond ionisation energy. As the carbon hybrid changes from pure $2p$ to sp the bond ionisation energy increases by about 7 eV and $(-\delta e^\mu)$ also increases in the same sense. This fits with our idea that the sp hybrid atomic orbitals form stronger bonds than do $2p$ atomic orbitals but the promotion energy of the atom is also involved here (see Part VI).

The next group of bonds, carbon–carbon, carbon–nitrogen, and carbon–oxygen, are particularly important because the numbers in Table 1*b* really give us our only substantial information about these σ bonds which underlie π bonds. The hybridisation effect again shows up clearly in the carbon–carbon bonds. The result is that the $(-\delta e^\mu)$ value is larger for the sp – sp bond than for the $2p$ – sp bond and this again fits our idea that this bond is stronger than the $2p$ – sp one.

The molecule NO_2^+ behaves as expected in having a very large bond ionisation energy but the N_3^- result is anomalous. It seems certain that at some stage an error has occurred in the numbers for this molecule.

The π bonds all have small $(-\delta e^\mu)$ values and, bearing in mind that those of the underlying σ bonds are very large, we infer that π bonds are much weaker than σ bonds. It is true that there are some complicated questions here about how to divide up the promotion energies but the present result agrees with chemical ideas.

I thank Professor H. H. Jaffé for information on atomic ionisation energies (see ref. 12).

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