555. *Localised Molecular Orbitals in Self-consistent Field Wave Functions. Part VII.*[1] *Electron Delocalisation and "Sigmaconjugation"*

By David Peters

The small amounts of electron delocalisation which occur in the "localised" lone pairs and two-electron bonds of some small molecules generally lead to energy changes which are *small* compared with bond and atomisation energies. These delocalisation effects are a generalised hyperconjugation involving the σ electrons. This is called "sigmaconjugation."

This work concludes the proof that localised lone pairs and two-electron bonds are a valid approximate description of the electron organisation in these molecules. It is also a step towards a thorough evaluation of all the various effects of conjugation in large molecules.

In much chemical thinking about the structures of large molecules, two ideas are particularly important. The first is the idea of conjugation or electron delocalisation, and the second is the idea of bond polarity with the associated ideas of dipole–dipole interaction and the inductive effect. The work in the previous Parts of this Series[1] may be used to put these ideas on to a firmer footing. In this Paper, we deal with conjugation in a general way.

The theoretical work is based on the self-consistent field molecular orbital method,[2] which has the important advantage that all energy quantities in the work are well defined. It must not be concluded from this that the numbers obtained are definitive or final but, because the theory is rigorous, it is easy to see how to improve on them. This work has already served to clarify some of the ideas of chemical valence theory.[1]

The work in Parts V and VI[1] led to a general expression for the energy of the chemical bond. There is, however, one deficiency in that work, namely, the neglect of the effects of the small amounts of delocalisation of the electrons; it was supposed there that all the lone pairs and bonds are perfectly localised, but this is not quite true. The lone pairs and

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[1] D. Peters, *J.*, 1963, 2003, 2015, 4017 (Parts I—III); 1964, 2901, 2908, 2916 (Parts IV—VI).

[2] C. C. J. Roothaan, *Rev. Mod. Phys.*, 1951, **23**, 69.

bonds do generally contain a small amount of atomic orbitals of atoms other than those of the bond or lone pair, and this is a generalised hyperconjugation effect which involves σ rather than π electrons (or π-type electrons). A self explanatory name for this effect is " sigmaconjugation." The term " sigmahyperconjugation " is more precise but more clumsy.

We must establish quantitatively how these small amounts of electron delocalisation affect the atomisation and bond energies of a molecule. Since we can show that the changes in energy which result from the electron delocalisation are small compared with typical bond energies, we can say that the valence in these molecules is represented, to a specified accuracy, by the localised bonds and lone pairs. This is done in the present Paper.

A related problem is that of the delocalised π bonds which some of these molecules contain. In this case, the delocalisation energy is large compared with the typical π-bond energies, and it is convenient to take this case separately.

To see what the energetic consequences of the electron delocalisation are, we simply write down the energy quantities both with and without the delocalisation in the wave functions. The difference is the " delocalisation energy " or " sigmaconjugation energy." The fact that the amount of delocalisation is small means that we can use simpler mathematical techniques than for the general problem where the delocalisation energy is large.

Theory.—The notation is the same as that used in the earlier Parts,[1] and detailed definitions of the terms can be found there. It is assumed that there are no extensively delocalised molecular orbitals in the molecule. All quantities relating to the exact, slightly delocalised molecular orbitals are written with a prime (′) and those which refer to the approximate, perfectly localised molecular orbitals are written without a prime. Thus, the exact ionisation energy of a lone pair is written ($-e^{\lambda'}$) while the approximate ionisation energy based on the perfectly localised lone pair is written ($-e^{\lambda}$). The label which identifies a particular lone pair or bond is not usually needed in this work.

If both λ and λ' are normalised, we write

$$\lambda' = k\lambda + d\tau, \qquad (1)$$

where k and d are numbers, k being approximately unity and d being generally less than 0·1. The quantity τ is the collection of the atomic orbitals of " foreign " atoms which occur in the exact wave function of the lone pair. This function is normalised as written. The overlap integral, $S(\lambda', \lambda)$, between λ' and λ is then

$$S(\lambda', \lambda) = k + dS(\lambda, \tau) \qquad (2)$$

These overlap integrals, $S(\lambda', \lambda)$, are given in Table 1, and they are a useful rough guide to how well localised are the lone pairs.

The ionisation energy of the exact lone pair is given by [1,2]

$$e^{\lambda'} = \langle\lambda'|\mathrm{F}'|\lambda'\rangle \qquad (3)$$

where F′ is the Hartree–Fock operator whose electron interaction part is built from the exact molecular orbitals. The $\langle\,\rangle$ sign denotes an integral over the space part of λ'. We may write the operator F′ as

$$\mathrm{F}' = \mathrm{F} + g \qquad (4)$$

where g is given by

$$g = \sum_i\{2G(\phi_i',\quad) - 2G(\phi_i,\quad)\} \qquad (5)$$

where F (without prime) is the Hartree–Fock operator whose electron interaction part is built from the perfectly localised molecular orbitals. In equation (5), ϕ_i and ϕ_i' denote either a lone pair (λ) or a bond (μ), and the sum runs over all the molecular orbitals in the molecule. The operator G is defined by

$$2G(\phi,\quad) = 2J(\phi,\quad) - K(\phi,\quad) \qquad (6)$$

TABLE 1

Localisation overlap integrals of lone pairs and bonds *

Molecule	Lone pair	$S(\lambda', \lambda)$	Bond	$S(\mu', \mu)$	Average *
N_2	$2s_N$	99·8	$2p\sigma_N$–$2p\sigma_N$	100·0	99·9
CO	$2s_C$	A 100·0	$2p\sigma_C$–$2p\sigma_O$	A 100·0	A 99·7
		B 99·0		B 100·0	B 99·7
	$2s_O$	A 99·1			
		B 100·0			
F_2	$2s_F$	99·9	$2p\sigma_F$–$2p\sigma_F$	100·0	99·9
CO_2	$2s_O$	99·7	$2p\sigma_O$–$sp\sigma_C$	99·6	99·7
C_3	$2s_C$	99·9	$2p\sigma_C$–$sp\sigma_C$	98·6	99·3
C_4	$2s_C$	99·9	(ab) $2p\sigma_C$–$sp\sigma_C$	97·8	99·1
			(bc) $sp\sigma_C$–$sp\sigma_C$	100·0	
N_3^-	$2s_N$	99·8	$2p\sigma_N$–$sp\sigma_N$	99·5	99·7
NO_2^+	$2s_O$	99·7	$2p\sigma_O$–$sp\sigma_N$	99·4	99·6
HCN	$2s_N$	99·8	$1s_H$–$sp\sigma_C$	99·7	99·8
			$2p\sigma_N$–$sp\sigma_C$	99·8	
C_2N_2	$2s_N$	99·8	$2p\sigma_N$–$sp\sigma_C$	99·8	99·8
			$sp\sigma_C$–$sp\sigma_C$	100·0	
C_2H_2	—	—	$1s_H$–$sp\sigma_C$	A 99·9	A 99·9
				B, C 100·0	B, C 99·8
				D 99·7	D 99·3
			$sp\sigma_C$–$sp\sigma_C$	A 100·0	
				B, C 99·5	
				D 98·6	
H_2O	$2s_O$	A 100·0	OH	A 98·1	A 98·7
		B 95·9		B 97·2	B 96·8
NH_3	$2s_N$–sp_N	A 100·0	NH	A 99·1	A 99·3
		B 99·3		B 99·1	B 99·1
		C 100·0		C 98·7	C 99·0
		D 98·3		D 98·4	D 98·4
CH_2O	$2p_O$	A 98·2	CH	A 98·8	A 99·2
		B 98·2		B 99·7	B 99·5
	$2s_O$	A 100·0	CO	A 100·0	
		B 99·7		B 100·0	

* Cf. equations (2) and (9). A, B, etc., refer to the localisation routes reported in Parts I and III. The hybridisations implied in $2s_N$, etc., are the ideal ones (Part I). For the detailed hybridisations of H_2O, NH_3, and CH_2O, see Part III. The average is the arithmetic mean of the S values for all the lone pairs and bonds in the molecule.

where J and K are the usual coulomb and exchange operators.[1,2] It follows that the ionisation energies of the exact and the perfectly localised lone pairs are related by

$$e^{\lambda'} = k^2 e^{\lambda} + \langle\lambda|g|\lambda\rangle + 2d\langle\lambda|\mathrm{F}|\tau\rangle \qquad (7)$$

to first order in the small quantity d. Higher terms are negligible. The numerical results from this equation are reported in Table 2 in terms of the quantity $(-\delta e^{\lambda}{}_{\text{del}})$ which is given by

$$(-\delta e^{\lambda}{}_{\text{del}}) = (-e^{\lambda'}) - (-e^{\lambda}) = (k^2 - 1)(-e^{\lambda}) - \langle\lambda|g|\lambda\rangle - 2d\langle\lambda|\mathrm{F}|t\rangle \qquad (8)$$

Written in this way, $(-\delta e^{\lambda}{}_{\text{del}})$ is a positive quantity if the effect of the delocalisation is to *increase* the absolute magnitude of the ionisation energy of the electron.

The bonds are dealt with in a similar way. The exact but slightly delocalised molecular orbital which represents the bond is written μ' and that for the perfectly localised counterpart is written μ. Then μ' is given by

$$\mu' = k\mu + d\tau \qquad (9)$$

where k is approximately unity and d is generally less than 0·1. The expression for the overlap integral between μ' and μ is then

$$S(\mu', \mu) = k + dS(\mu, \tau) \qquad (10)$$

The numerical values of $S(\mu', \mu)$ are given in Table 1.

TABLE 2

Delocalisation or sigmaconjugation energies (ev) *

Molecule	Lone pair	$(-\delta e^{\lambda}{}_{\rm del})$	Bond	$(-\delta e^{\mu}{}_{\rm del})$	Total	Two-electron term	$\Delta E_{\rm del}$
N_2	$2s_N$	0·5	$2p\sigma_N$–$2p\sigma_N$	0·3	3·8	−1·6	2·2
			$2p\pi_N$–$2p\pi_N$	0·3			
CO	$2s_O$	A 1·4	$2p\sigma_O$–$2p\sigma_C$	A 0·3	A 5·1	A −2·4	A 2·6
		B 0·4		B 0·65	B 5·0	B −5·0	B 0·1
	$2s_C$	A 0·2	$2p\pi_O$–$2p\pi_C$	A 0·3			
		B 0·2		B 0·6			
F_2	$2s_F$	0·2	$2p\sigma_F$–$2p\sigma_F$	0·2	1·2	−0·3	0·9
CO_2	$2s_O$	−0·3	$2p\sigma_O$–$sp\sigma_C$	0·4	0·4	−2·0	−1·6
C_3	$2s_C$	0·3	$2p\sigma_C$–$sp\sigma_C$	1·5	7·2	−7·1	0·1
C_4	$2s_C$	2·1	$2p\sigma_C$–$sp\sigma_C$	1·0	16·8	−16·3	0·5
			$sp\sigma_C$–$sp\sigma_C$	2·2			
N_3^-	$2s_N$	−0·2	$2p\sigma_N$–$sp\sigma_N$	0·5	1·2	−3·7	−2·5
NO_2^+	$2s_O$	0·5	$2p\sigma_O$–$sp\sigma_N$	0·7	4·8	−5·9	−1·1
HCN	$2s_N$	0·4	$1s_H$–$sp\sigma_C$	0·2	3·8	−3·6	0·2
			$2p\sigma_N$–$sp\sigma_C$	0·5			
			$2p\pi_N$–$2p\pi_C$	0·4			
C_2N_2	$2s_N$	0·1	$2p\sigma_N$–$sp\sigma_C$	0·5	2·8	−2·5	0·3
			$sp\sigma_C$–$sp\sigma_C$	0·2			
C_2H_2	—	—	$1s_H$–$sp\sigma_C$	A 0·4	A 4·4	A −3·2	A 1·2
				B, C 0·4	B, C 8·2	B, C −2·6	B, C 5·6
				D −0·2	D 2·8	D −3·5	D −0·7
			$sp\sigma_C$–$sp\sigma_C$	A 0·6			
				B, C 2·5			
				D 0·4			
			$2p\pi_C$–$2p\pi_C$	A 0·4			
				B, C 0·4			
				D 0·7			

* Cf. equations (8), (11), (14), and footnote to Table 1. The columns headed $(-\delta e^{\lambda}{}_{\rm del})$ and $(\delta e^{\mu}{}_{\rm del})$ refer to one lone pair or bond. The column headed " total " is *twice* the sum of these two quantities over all the lone pairs and bonds in the molecule. The delocalised π bonds are omitted from CO_2, N_3^-, NO_2^+, C_3, and C_4. The column headed " two-electron term " contains the G terms from equation (14).

It then follows, in the same way as for the lone pairs, that

$$(-\delta e^{\mu}{}_{\rm del}) = (-e^{\mu'}) - (-e^{\mu}) = (k^2 - 1)(-e^{\mu}) - \langle\mu|g|\mu\rangle - 2d\langle\mu|\mathrm{F}|\tau\rangle \qquad (11)$$

and this represents the change in the ionisation energy of a bond electron with the delocalisation. It is positive if the delocalisation *increases* the absolute magnitude of the ionisation energy of the electron. The numerical results for $(-\delta e^{\mu}{}_{\rm del})$ are given in Table 2. Notice that, even if the lone pair or bond is itself perfectly localised, there is still the term $\langle\mu|g|\mu\rangle$ or $\langle\lambda|g|\lambda\rangle$ which will arise if there are one or more delocalised lone pairs or bonds in the molecule. This is an example of how subtle the effects which arise from electron interaction can be.

Now we need the expression for the atomisation energies. The total energy of a molecule which is built from the exact, slightly delocalised molecular orbitals is

$$E' = 2\sum e^{\lambda'} + 2\sum e^{\mu'} - \sum_i\sum_j 2G(\phi_i', \phi_j') + \sum(\text{pairs})\, Z_sZ_t/R_{st} \qquad (12)$$

where the first summation goes over all the lone pairs and the second goes over all the bonds in the molecule. The terms in the double summation run separately over all the molecular orbitals in the molecule, lone pairs plus bonds. The last term in equation (12) is the total nuclear repulsion.

The expression for the total energy of the same molecule built from the perfectly localised molecular orbitals is

$$E = 2\sum e^{\lambda} + 2\sum e^{\mu} - \sum_i\sum_j 2G(\phi_i, \phi_j) + \sum(\text{pairs})\, Z_sZ_t/R_{st} \qquad (13)$$

As it is written in equations (12) and (13), the total energy is a negative quantity. The effect of the electron delocalisation on the total energy is the same as its effect on the atomisation energy, ΔE, and is given by

$$\Delta E_{\text{del}} = (-E') - (-E) = (-\Delta E') - (-\Delta E) = \\ \{2\sum(-\delta e^{\lambda}{}_{\text{del}}) + 2\sum(-\delta e^{\mu}{}_{\text{del}})\} + \sum_{i}\sum_{j}\{2G(\phi_i', \phi_j') - 2G(\phi_i, \phi_j)\} \quad (14)$$

Written in this way, ΔE_{del} is a positive quantity if the total effect of the delocalisation is to *increase* the atomisation energy, as it is expected to do. The terms within the first braces of equation (14) are called the "one-electron terms" and those in the second are called the "two-electron terms." This terminology is not precise because even the terms within the first braces of equation (14) contain electron-interaction integrals, but it seems to be a helpful division. The numerical results from equation (14) are reported in Table 2.

This theory establishes the energetic consequences of the electron delocalisation in these molecules. It is rigorous apart from the assumption that the perfectly localised molecular orbitals are exactly orthogonal so that the expressions for e^{λ} and e^{μ} are the simple ones of equation (3) and its analogue for e^{μ}. In fact, the perfectly localised molecular orbitals are slightly non-orthogonal, but attempts to allow for this led into excessively complicated energy expressions. Since we get sensible answers by ignoring this complication, no further attention has been given to it. It is also true that the localisation routes reported in Part I were chosen by inspection and not by a rigorous criterion. This means that there is some arbitrariness in the localised molecular orbitals, and they are not necessarily those localised molecular orbitals which minimise the delocalisation energy. So our estimates of the delocalisation energy are an upper limit to the true delocalisation energy. In fact, the present work provides a formal criterion for choosing the localisation route.

Calculations.—The k and d values of equations (1) and (9) are read directly from the wave functions reported in Part I (cf. errata in Part IV).[1] It is necessary for present purposes to renormalise these wave functions accurately. The G integrals are mostly available from the earlier work, as are the e^{λ} and e^{μ} values. The latter are in fact the $e^{\lambda'}$ and $e^{\mu'}$ but the difference is negligible in the context of equations (7) and (11). Many of the matrix elements of the Hartree–Fock operator are available from Part IV (the interaction elements of that work) and the remainder are easily calculated or estimated.

DISCUSSION

It is true of this work, as of the earlier work, that we are dealing with energy quantities whose size is uncomfortably close to the inherent error in the original computations. In these circumstances, it is best to accept only those results which are large or are shown by several of the molecules, and to ignore small or isolated results.

(a) *Localisation Overlap Integrals.*—These are the overlap integrals between the perfectly localised and the near localised lone pairs and bonds. They are reported in Table 1 (as percentages) and they give us a rough guide as to how well localised are the molecular orbitals of the bonds and lone pairs. Most of these integrals are greater than 99·0%. The notable exceptions are the water, ammonia, C_3, and C_4 molecules and this suggests that the localisation in these molecules is poor. This agrees with the earlier work on the wave functions and energy quantities of these molecules, the results of which seemed unreliable. The general inference from these results is that the localisation overlap integrals should be greater than about 99·5% before the lone pairs and bonds are thought of as being genuinely localised.

(b) *Delocalisation Energies.*—We have defined these as the amounts by which the atomisation energy is changed by the sigmaconjugation. They are reported in Table 2. The important thing about them is that they are generally small as compared with bond and atomisation energies. This result completes the proof that the localised lone pairs and bonds do give an accurate picture of the electron organisation in these molecules. To be more precise, we can say that the localised bonding gives a picture of the valence which is accurate enough to explain the constancy of bond properties in different molecules. It is true of course that we still have to show that dipole–dipole and induction energies are not large enough to affect the constancy of bond properties to a large extent. This will be done later.

It is also true that all the delocalisation energies should be positive. Were they genuinely negative, the delocalisation of the electrons would destabilise the molecule and so would simply not occur. It is pleasing to find that all but four of the small numbers reported in Table 2 are positive and that three of the four negative numbers occur in molecules (CO_2, N_3^-, and NO_2^+) which have heavily delocalised π bonds and so are not formally within the scope of the present theory. We could, quite legitimately, leave out these three examples. It is the fact that all but one of the other delocalisation energies are positive which justifies our neglect of the non-orthogonality of the perfectly localised molecular orbitals.

No significance should be attached to the delocalisation energies for individual molecules. It must be remembered also that these numbers are an upper limit to the sigmaconjugation energies. The true values may be much lower.

It is interesting to notice that the small total change in the atomisation energy which is caused by the electron delocalisation is made up of two larger effects of opposite sign. The first is positive and represents an increase in the ionisation energy of the electron. This is the one electron term of equation (14) and it is the kind of term which is calculated by the independent-electron or semi-empirical theories. The second is the two electron term of equation (14) and this is negative. This term is neglected in the independent-electron theories. In this circumstance, it is unfortunately true that we cannot expect independent-electron theories to give a realistic account of this sigmaconjugation effect.

It is perhaps helpful, for qualitative discussion, to restate these results in valence-bond language. Briefly, the effect of this kind of electron delocalisation is to include in the wave function both long bonded structures and their associated ionic structures. Taking hydrogen cyanide as an example, the simplest wave function from a valence-bond point of view is that of the perfectly paired structure (I). The next more complicated wave function is the perfectly localised molecular orbital one which, when expanded into valence bond structures, includes such ionic structures as (II) but does not include any of the covalent or ionic long bonded structures such as (III) and (IV). It is only when one admits the small amounts of sigmaconjugation discussed in the present Paper that these latter structures are included.

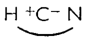
H–C–N

(I)

$H^+\ {}^-C–N$

(II)

(III)



(IV)

(c) *General Conclusions.*—In Part VI,[1] we wrote down an expression for the atomisation energy of a molecule which is built from localised bonds and lone pairs. This expression is a sum over the bonds, and each term in it is a bond energy. We now have to add to this expression for the atomisation energy an extra term for the delocalisation energy of the molecule. This new term does not yet appear as a sum over bonds. If one tries to make is do so, the results are very sensitive to the exact choice of localisation route (see below). For now, we can say that the delocalisation energy or sigmaconjugation energy is small compared with the two large terms, the one-electron term, and the main coulomb term (Part VI), which together determine bond strengths. These two large terms are both of the order of 10 ev. The polarity term of the bond-energy expression, on the other hand, is about the same size as the delocalisation energy (~1 ev), and these are the two terms which are either identical with, or at least closely related to, the familiar inductive and conjugative effects of large molecule theory. In other words, we have analytical expressions for the inductive and conjugative effects of large-molecule theory (or certain types of these) although it is not yet possible to calculate these quantities with high accuracy.

There is one other more technical point. The present work provides us with a criterion for choosing the optimum localised molecular orbitals, a problem which has been discussed by other workers.[3] The obvious way to do this is to impose, on the localisation route, the condition that the delocalisation energy as defined in this Paper be a minimum. Exploratory calculations have shown that this requires more elaborate calculations than those needed for the present work so the matter will be taken up later.

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[3] C. Edmiston and K. Ruedenberg, *Rev. Mod. Phys.*, **1963**, **35**, 457.