

563. *Localised Molecular Orbitals in Self-consistent Field Wave Functions. Part VI.* Bond Energies, Atomisation Energies, and their Relationships with Ionisation Energies.*

By DAVID PETERS.

It is shown that the atomisation energy of a molecule may be written as a sum over the bond energies of localised bonds. These bond energies are determined by three main factors, two of which we can calculate easily while the third is intractable at the moment. The first factor is twice the difference between the ionisation energy of the bond and an average of the ionisation energies of the two atomic orbitals which form the bond, plus a correction factor. The second factor is concerned with the polarity of the bond and is the reason why heteropolar bonds are stronger than the average of the two homopolar counterparts. The third, intractable, factor is the main Coulomb term which is estimated by assuming that the theory is correct and taking the difference between this and the experimental numbers.

THE work in Part IV * shows how the ionisation energies of the lone pairs and localised bonds can be derived from the computed ionisation energies of the delocalised molecular orbitals. Part V shows how to break down the ionisation energies of the lone pairs and bonds into simple physical quantities. Now we use these results to derive expressions for the atomisation and bond energies of these molecules.

* Parts IV and V, preceding Papers.

The formal computation of the complete wave function of a molecule¹ gives the atomisation energy. This is the energy required to disrupt the molecule into its constituent atoms in their ground states. So far, the computed values of this quantity have been inaccurate (*ca.* 30% of the experimental values) but there are signs² that more accurate values will soon be obtained. Even when we have such values, however, we will not have reached the final goal because this is the individual bond energies rather than their sum, the atomisation energy. We now show how to get the bond energies themselves from the results of the formal computations, using the ionisation energies as intermediates. We have seen that there is a rough connection between certain ionisation energy quantities and bond energies (Part IV) and we now explore the various inter-relationships between bond energies, atomisation energies, and ionisation energies. We thus get a quite detailed and clear picture of the formation of localised bonds. Two things must be stressed. First, this picture is not definitive because the energy quantities are not yet established with certainty. Secondly, it is indisputable that *some* electron delocalisation always occurs. The intention of this work is to push the idea of localised bonds as far as possible in an attempt to reach the upper limits of the genuine delocalisation effects.

The notation used was explained in Part V. Atomic units (unit of energy, 27.21 eV, unit of length, 0.529 Å) are used except in the Table.

Theory.—We take the hydrogen molecule as a first example, although, as we see later, this molecule is in one way quite atypical of the general two-electron bond. The total energy of this molecule, within the Hartree–Fock approximation, is given by

$$E(\text{H}_2) = 2e^\mu - J(\mu, \mu) + 1/R \quad (1)$$

where $J(\mu, \mu)$ is the self-energy of the molecular orbital and R is the internuclear distance. The atomisation energy is then given by

$$\Delta E(\text{H}_2) = 2[(-e^\mu) - (-e)] + J(\mu, \mu) - 1/R \quad (2)$$

$$= 2[16.9 - 13.6] + 15.35 - 19.40 = 2.55 \text{ eV} \quad (3)$$

The sign convention is that used in the two preceding Papers and the atomisation energy, written as in (2), is positive. This equation, in fact, contains much of the essentials of the present work, at least as far as non-polar bonds are concerned. It shows that only if the electron repulsion and the nuclear repulsion terms cancel will the bond strength be twice the difference between the ionisation energy of the bond and the average of the two atomic orbital ionisation energies. The numerical results³ for the equilibrium internuclear distance (3) show that this does not happen in this example and later on it is shown that this cancelling is not accurate to more than several eV in the general case.

We want to find for the general localised bond an expression for its bond energy which is as close to (2) as possible. The expression will necessarily be more complicated than (2) because several new factors are present. Both the bond itself and the other bonds in the molecule may be polar. There may also be lone pairs in the molecule and there is also the general problem of the promotion energy of multivalent and hybridised atoms. Finally, and most important, the bond energy is no longer the same thing as the atomisation energy. The formal treatment required to systematise these effects is as follows.

The total energy, E , of a polyatomic molecule which is built from localised bonds and lone pairs is written down in terms of the ionisation energies of these bonds and lone pairs. The expression is^{4,5} (including nuclear repulsion)

$$E = 2\sum e^{\lambda_j} + 2\sum e^{\mu_{jg}} - \sum\sum 2G(\lambda_f, \lambda_j) - \sum\sum 4G(\lambda_f, \mu_{jk}) \\ - \sum\sum 2G(\mu_{jg}, \mu_{jk}) + \sum(\text{pairs})Z_f Z_j / R_{fj} \quad (4)$$

¹ See ref. 7, Part I, *J.*, 1963, 2003, and ref. 6 of Part V (preceding Paper).

² Ref. 3 of Part V, Allen and Karo, *J. Phys. Chem.*, 1962, **66**, 2331.

³ Mulliken, *J. Chim. phys.*, 1949, **46**, 675.

⁴ Roothaan, *Rev. Mod. Phys.*, 1951, **23**, 69.

⁵ Kotani, Ohno, and Kayama, "Handbuch der Physik," Vol. 37/2, Springer, Berlin, 1961.

The first two sums run over all the lone pairs and bonds, respectively, in the molecule. In the first and third double summations, both sums go over all the lone pairs or bonds separately. The total energy, E , is a negative quantity when written in this way. The ionisation energies are both negative and, in their combined sums, the positive total electron interaction energy occurs twice so it is necessary to subtract the latter once to get the total electronic energy. Adding the total nuclear repulsion energy gives the total energy.

The electron interaction terms are now simplified by the same approximation as in Part V. This gives

$$\begin{aligned} 4G(\lambda_j, \mu_{jk}) &= 2l(jk, j)2G(\lambda_f, \nu_j) + 2l(jk, k)2G(\lambda_f, \nu_k) \\ &= 2G(\lambda, \nu_j) + 2G(\lambda_f, \nu_k) - q(jk, j)2G(\lambda_f, \nu_j) - q(jk, k)2G(\lambda_f, \nu_k) \end{aligned}$$

and

$$\begin{aligned} 2G(\mu_{fg}, \mu_{jk}) &= \\ &[1 - q(jk, j) - q(fg, f)]G(\nu_f, \nu_j)/2 + [1 - q(jk, j) - q(fg, g)]G(\nu_j, \nu_g)/2 \\ &+ [1 - q(jk, k) - q(fg, f)]G(\nu_k, \nu_f)/2 + [1 - q(jk, k) - q(fg, g)]G(\nu_k, \nu_g)/2 \quad (5) \end{aligned}$$

The total energy is now given by

$$\begin{aligned} E &= 2\sum e^{\lambda_f} + 2\sum e^{\mu_{fg}} - \sum_{\mu_{fg}} J(\mu_{fg}, \mu_{fg}) - \left\{ \sum_{\lambda_f} \sum_{\lambda_j} 2G(\lambda_f, \lambda_j) \right. \\ &+ \sum_{\lambda_f} \sum_{\nu_j} 2G(\lambda_f, \nu_j) + \sum_{\nu_f \neq \nu_j} \sum_{\nu_f} (1/2)G(\nu_f, \nu_j) - \sum (\text{pairs}) Z_f Z_j / R_{fj} \left. \right\} \\ &+ \left\{ \sum_{\mu_{jk}} \sum_{\lambda_f} q(jk, j)2O_{jk}(\lambda_f) + \sum_{\mu_{fg} \neq \mu_{jk}} \sum_{\lambda_f} (1/2)q(jk, j)[O_{jk}(\nu_f) + O_{jk}(\nu_g)] \right\} \quad (6) \end{aligned}$$

In all the double summations, both sums run over all the lone pairs or over all the valence atomic orbitals in the molecule. The terms in the second braces $\{\}$ arise from the polarity of the bonds.

The terms in the first $\{\}$ are divided into one and two-centre terms. The one-centre ones are just those which occur in the expression below for the total energy of an atom and, in the atomisation energy, the two sets of terms will cancel out. The two centre terms on atoms g and k , say, are those in the expression

$$\underline{C}_{gk} = \sum_{\lambda_g} \sum_{\lambda_k} 4G(\lambda_g, \lambda_k) + \sum_{\lambda_g} \sum_{\nu_k} 2G(\lambda_g, \nu_k) + \sum_{\nu_g} \sum_{\nu_k} G(\nu_g, \nu_k) - Z_g Z_k / R_{gk} \quad (7)$$

The double sums here go over all the lone pairs or valence atomic orbitals on atoms g and k . This quantity \underline{C}_{gk} is called the main Coulomb term between atoms g and k . When g and k are far apart, it is zero. When g and k are bonded, then one term—the interaction between the two valence electrons forming the bond—is missing from the third term on the right of (7). To balance this, we remove $1/R_{gk}$ from the nuclear repulsion term in (7) and then write the main Coulomb term between bonded atoms as \underline{C}_{fg}^+ , etc.

The polarity terms contained in the second $\{\}$ of (6) can also be simplified by separating out those which belong to two bonded atoms *only* from all others. These terms are

$$\sum_{\mu_{jk}} q(jk, j) \left\{ \sum_{\lambda_j} 2O_{jk}(\lambda_j) + \sum_{\lambda_k} 2O_{jk}(\lambda_k) + \sum_{\nu_j} O_{jk}(\nu_j) + \sum_{\nu_k} O_{jk}(\nu_k) \right\} \quad (8)$$

From the sums over ν_j and ν_k , the valence orbitals forming the bond μ_{jk} are omitted. The terms in $\{\}$ are independent of the polarity of any bond in the molecule and are written as Γ_{jk} . The expression (8) is then given by

$$\sum q(jk, j) \Gamma_{jk} \quad (9)$$

The remaining terms from the second $\{\}$ of (6) describe the interactions between non-bonded atoms which form polar bonds. These terms do present some difficulties and a detailed

study of them in relation to the small delocalisation effect is required. This will be reported elsewhere and for now we simply drop them from the expression for the total energy of the molecule.

We now have the total energy of the molecule in a suitable form. The total energy of all the atoms, in terms of the ionisation energies of the atomic orbitals, is given by

$$\sum\{2\sum e_f + \sum \dot{e}_f - \sum J(\lambda_f, \lambda_f) - \sum(\text{pairs})4G(\lambda_f, \lambda_f') - \sum(\text{pairs})2G(\lambda_f, \nu_f) - \sum(\text{pairs})G(\nu_f, \nu_f')\} \quad (10)$$

The first and third summations in the $\{\}$ go over all the lone pairs in the atom, the second over all the valence atomic orbitals. A prime is used to distinguish a second lone-pair or valence atomic orbital of the same atom. This equation is essentially a definition of the atom in the molecule and if there are hybrid atomic orbitals in the molecule, then the atomic orbitals of (10) must be hybridised in the same way. It is assumed that the molecule is electrically neutral and that the atomisation is to neutral atoms.

Subtracting the expression for the total energy of the molecule from (10) gives the atomisation energy as a positive quantity and referred to the atom in the molecule, not to the ground states of the atoms. This is

$$\Delta E = \sum_{\mu_{fg}} \{2(-\delta e^{\mu_{fg}}) + [J(\mu_{fg}, \mu_{fg}) - 1/R] + q(fg, f)\Gamma_{fg} + \underline{C}_{fg}^+\} + 2\sum(-\delta^{\lambda e}) + \sum(\text{pairs})\underline{C}_{fg} \quad (11)$$

The summation over $(-\delta e^{\lambda})$ goes over all the lone pairs in the molecule and that over \underline{C}_{fg} over all the pairs of non-bonded atoms in the molecule.

This equation is the generalisation of (2) to the localised bond in a polyatomic molecule and it is the important one of this work because it shows that, in order to relate bond ionisation energies to bond energies, five other factors must be considered. Three of these belong to the individual bonds and, of the remaining two, one is known to be small (see below) and the other is probably small. Assuming these two terms to be unimportant, we can write for the bond energy of a localised bond between atoms f and g the expression

$$E_{fg}^{\mu} = 2(-\delta e^{\mu}) + [J(\mu, \mu) - 1/R] + q(fg, f)\Gamma_{fg} + \underline{C}_{fg}^+ \quad (12)$$

The second term on the right of (12) is the balancing of a small part of the nuclear repulsion with the electron repulsion which is internal to the bond. This term as a whole is called the "internal Coulomb term." The third term on the right of (12) is a polarity term and deals with the internal polarity of the bond μ_{fg} , not with the polarity of other bonds. It is called the "internal polarity term" and is quite distinct from the other, external, polarity terms such as that in Part V. The last term on the right of (12) is the main Coulomb term of the bond and it is the difference between almost all the nuclear repulsion and almost all the electron-electron interaction between the two atoms f and g . Note that it refers to *neutral* atoms because the polarity term has been removed from this main Coulomb term. It turns out that we have no choice but to neglect the main Coulomb term in the first instance. This is commonly done but we cannot determine yet whether this procedure is really justified. The point is taken up in the Discussion.

The evaluation of the terms in (12) is carried out in the same way as in Part V. The main Coulomb term, \underline{C}_{fg}^+ , has been evaluated in a few simple cases, using the idealised hybridisations. In evaluating the polarity term, the same approximations were used as in Part V. The delocalised π bonds are a problem because we do not know yet how they contribute to the bonding. This will be examined later: we simply write $(+\pi)$ in the calculated atomisation energies.

DISCUSSION

We first compare the calculated with experimental atomisation energies. This is done in the right-hand columns of the Table, the main Coulomb term being left out.

Broadly, agreement is good with the small molecules and poor with the large ones. In the small molecules, the difference between theory and experiment is 1–2 eV, or some 50% of the experimental value, but in the larger molecules the calculated atomisation energies are too large by a factor of two or three.

It is noteworthy that the values of the atomisation energy calculated here are consistently too large (apart from the hydrogen, lithium, and lithium hydride molecules) while those from the formal computations are consistently too small. We have left out of the present work an important factor whose sign and magnitude are such as to reduce substantially the calculated atomisation energies of this work. There is little doubt that this is the main Coulomb term, \underline{C}_{fg}^+ , of eqn. (12). It first makes itself clearly felt in the nitrogen and carbon dioxide molecules and these are the first examples of a short bond between two many electron atoms.

A related point is that the calculated values for the main Coulomb term in the small molecules must be too large. Were we to include these, the calculated atomisation energy would be negative. These Coulomb terms were calculated using the idealised hybridisations and the numerical value of \underline{C}_{fg}^+ must obviously be very sensitive to the hybridisations (and the forms) of the atomic orbitals. This suggests that this term must be important in determining hybridisations and the usual assumption that the valence electrons only determine the hybridisations must be a serious oversimplification. This result agrees with some recent work on Coulomb energy in valency-bond theory.⁶ Fraga and Mulliken showed that this can vary wildly with the hybridisations in the atomic orbitals of the molecule, a result which led them to pessimistic conclusions about the value of semi-empirical valence-bond theory. We are on safer ground in the molecular orbital work because we know that the hybridisations are only large in the polyvalent situation (Part I). Consequently, although the main Coulomb term is large, it is not absurdly so and is in fact about the same size as the ionisation energy term. There seems to be no real reason why we should not calculate this in a straightforward fashion once the hybridisations are accurately known. We now ignore it, bearing in mind that if we get useless results, this neglect of the main Coulomb term will probably be responsible.

The results for the terms which we can calculate are given in the Table. Of these, the lone-pair term can be disposed of immediately since it is small. Notice that this is only true when the atomisation energy is referred to the atom in the molecule (Part IV).

This leaves two main terms both of which belong to individual bonds. The first is the internal Coulomb term, $[J(\mu, \mu) - 1/R]$, and this is commonly several eV. In many cases, it is roughly proportional to the ionisation energy term and can be grouped together with it. One striking exception to this generalisation is the fluorine molecule, where the internal Coulomb term is very large (~9 eV). In this molecule, the electron repulsion term, $J(\mu, \mu)$, is large and because this is included twice in the ionisation energy term, the latter is negative. This is then corrected by the large positive $[J(\mu, \mu) - 1/R]$ term. This molecule is an extreme case, but it warns us that in exceptional circumstances there may be no connection between the ionisation energies and the bond strengths.

Apart from this example, there are many cases, as we saw earlier, in which the $(-\delta e^{\mu})$ term is proportional to the bond strength. We also know that strongly polar bonds do not obey this generalisation and the reason is clear from the results in the Table. These show that, although the polarity term, $q(fg, f)\Gamma_{fg}$, is often unimportant, in the strongly polar diatomic hydrides OH and FH it is important. Only by including the polarity term can we reproduce the increasing bond energies from BH to FH. This is the result which Pauling⁷ explained with the idea of ionic-covalent resonance and it is pleasing to find a parallel explanation in this molecular orbital work because it is a very common result that the heteropolar bond is stronger than the average of the two homopolar analogues. The alkali-metal hydrides do not obey this rule and it is noteworthy that lithium hydride is the

⁶ Fraga and Mulliken, *Rev. Mod. Phys.*, 1960, **32**, 254.

⁷ Pauling, "Nature of the Chemical Bond," Cornell Univ. Press, Ithaca, New York, 1960.

Factors determining the energies of localised bonds (ev).*

Molecule	Bond	Bond terms		Calculated bond energy	$2\Sigma(-\delta e^A)$	Calculated atomisation energy	Promotion energy	Calculated atomisation energy (G.S.)	Experimental atomisation energy	Main Coulomb term, c^+	
		$2(-\delta e\mu)$	$[J(\mu, \mu) - 1/R]$							Calc.	Difference
H ₂	1s _H -1s _H	6.6	-4.0	2.6	—	2.6	—	2.6	4.7	—	—
	s _{PH} -1s _H	-2.0	3.6	1.6	—	1.6	—	1.6	2.5	—	—
LiH	2p _{Li} -1s _H	3.9	0.8	7.1	-1.0	7.1	—	7.1	3.0?	—	(-4.1)
	2p _{OB} -1s _H	5.0	1.4	6.4	-1.0	5.4	0.3	5.1	3.6	—	(-1.5)
CH	2p _{OC} -1s _H	4.5	2.2	7.8	-1.0	6.8	0.5	6.3	4.0	—	(-2.3)
	2p _{ON} -1s _H	2.5	2.9	7.8	-1.0	6.8	0.5	6.3	4.6	—	(-1.7)
OH	2p _{OC} -1s _H	1.0	3.5	8.0	-1.0	7.0	0.0	7.0	6.0	—	(-1.0)
	2p _{OF} -1s _H	-1.0	0.1	-0.9	—	-0.9	0.0	-0.9	1.0	—	(-1.0)
Li ₂	2s _{Li} -2s _{Li}	28.0	4.4	32.4	-4.0	44.0	—	40.0	9.8	—	(-30)
	2p _{ON} -2p _{ON}	5.0	2.9	7.9	—	—	—	—	—	—	—
N ₂	2p _{MN} -2p _{MN}	-9.0	9.5	0.5	-2.0	-1.5	0.0	-1.5	1.5	—	—
	2p _{OF} -2p _{OF}	25.0	6.2	38.8	-4.0	36.0	4.0?	32.0	11.1	—	(-21)
CO	2p _{OC} -2p _{OC}	4.5	2.5	0.5	—	—	—	—	—	—	—
	2p _{OC} -2p _{NO}	13.0	5.6	18.9	-1.5	36.0	8.0	28.0	?	—	—
C ₃	2p _{OC} -sp _{OC}	13.0	5.4	18.3	-1.5	(+π)	16.0	(+π)	?	—	—
	2p _{OC} -sp _{OC}	20.0	7.8	27.8	—	(+π)	—	(+π)	—	—	—
C ₄	sp _{OC} -sp _{OC}	20.0	7.3	27.3	—	74.0	16.0	58.0	17.2	—	(-40)
	sp _{OC} -sp _{OC}	13.0	3.7	19.0	—	—	—	—	—	—	—
C ₂ H ₂	sp _{OC} -1s _H	2.5	1.8	4.3	—	—	—	—	—	—	—
	2p _{OC} -2p _{OC}	19.0	6.0	26.0	-0.5	53.7	8.0	45.7	13.3	—	(-32)
HCN	sp _{OC} -2p _{ON}	13.0	3.8	19.6	—	—	—	—	—	—	—
	sp _{OC} -1s _H	3.0	2.3	4.3	—	—	—	—	—	—	—
C ₂ N ₂	2p _{OC} -2p _{MN}	20.0	8.2	28.2	-0.5	95.3	16.0	79.3	21.2	—	(-58)
	sp _{OC} -sp _{OC}	19.5	6.0	26.4	—	—	—	—	—	—	—
CO ₂	sp _{OC} -2p _{MN}	3.0	2.3	3.7	—	—	—	—	—	—	—
	sp _{OC} -2p _{OC}	18.0	7.4	27.1	2.0	56.2	8.0	48.2	16.7	—	(-31.5)
COS	sp _{OC} -2p _{OC}	19.0	7.6	29.3	2.0	(+π)	—	(+π)	—	—	—
	sp _{OC} -2p _{OC}	13.0	7.5	23.7	-5.0	48.8	8.0	40.8	15.8	—	(-25)
CH ₂ O	sp _{OC} -1s _H	9.0	3.3	14.8	—	—	—	—	—	—	—
	2p _{OC} -2p _{NO}	-2.0	3.6	0.5	—	—	—	—	—	—	—

* The experimental atomisation energies are from Cottrell's book.⁸ The promotion energies are from Pritchard and Skinner.⁹ The $(-\delta e^A)$ values are from Part IV and are an average of the Slater and Hinze-Jaffe numbers. The π bonds of C₂N₂ are assumed localised, using the Part II charges. The large $(-\delta e^A)$ values of the 2p_{OC} lone pairs of the fluorine atom of HF have been omitted because their inclusion gives nonsensical results. The numbers in column 10 which is headed "calculated atomisation energy (G.S.)" refer to the ground-state atoms. They are the numbers in column 8 minus those in column 9. The two charged molecules have been omitted here.

⁸ Cottrell, "The Strengths of Chemical Bonds," Butterworths Scientific Publications, 2nd edn., London, 1958.

⁹ Pritchard and Skinner, *Chem. Revs.*, 1955, **55**, 782.

only diatomic hydride in which there is significant hybridisation in the atomic orbitals. Just how this is connected with the breakdown of Pauling's rule is not clear but it does suggest that there may be important qualitative differences between the valence in the alkali metal compounds and that in other compounds.

As far as the σ bonds are concerned, then, we have an interesting picture of bond formation. Providing the bond is not too polar, the important factor in determining the bond energy is the ionisation energy terms ($-\delta e^u$) and since this is sensitive to the electronegativities of the atomic orbitals forming the bond (Part V), the forms of the σ bonds are also sensitive to these electronegativities.

The π bonds are less easy to understand. This is partly because we have only a few examples of localised π bonds so it is difficult to pick out informative trends. We already know that the π bonds do not obey the usual electronegativity rules and that their atomic charges are smaller than those for the σ bonds. Moreover, their ionisation energy terms are small (~ 1 eV). From the work in this Paper, we see that their polarity terms are quite large. The final result is that no one term dominates the π bond strengths as the ionisation energy term does for the σ bonds. One thing that does seem certain is that the π bond energies are small compared with the σ bond energies but further than this it is difficult to go for now.

General Survey of Results.—The main achievement of this work is to show that the localised two-electron bond and lone pair do exist in the molecules of this set. To put this more precisely, one can say that the representation of the molecular wave function in terms of localised bonds and lone pairs will give an estimate of the various energy quantities which is accurate enough to provide useful chemical information. The importance of using a well defined one electron energy has been stressed and this must be the ionisation energy. If, instead of using these as the one electron quantity, one uses intuitively defined one electron energies then all contact with the formal theory of molecular structure is rapidly lost.

To summarise what the theory can do, suppose we are given the SCF LCAOMO wave function, in the Roothaan approximation, for a molecule. Providing only that the molecular orbitals are localisable, we can then derive the bond energies of the individual bonds in the molecule. The conversion of the theory into a practical tool is seriously hampered by the problem of the main Coulomb term but we can still find many useful results and there is every reason to hope that the main Coulomb term will be calculable soon. If we do not have the SCF computation, it is a good deal more difficult to derive bond energies but the work in Part V suggests a way of doing this.

There are several other points which require comment. The first is the question of what has become of the exchange energy which plays such an important part in the valence bond theory. It is still there, of course, but we are not picking it out as that part of the total energy which corresponds to the bond energy. Which particular fraction of the total energy one equates with the bond energy is arbitrary and there is an advantage in avoiding the use of the conceptually difficult exchange energy for this. There is also the important question of the accuracy of the approximation we have used for some integrals. An accurate computation of these is desirable. Finally, there is a number of important questions which have been mentioned only briefly or not at all. One of these is the general problem of the nature of the atom in the molecule and the related problem of electronegativities. Then there is the question of electron delocalisation and how important this really is. This problem is closely linked with the general basis of π electron theories and it is hoped that some further analysis of these wave functions will give us some information about these and other problems.