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562. *Localised Molecular Orbitals in Self-consistent Field Wave Functions. Part V.* Relationships between Atomic and Molecular Ionisation Energies.*

By David Peters.

A theory is developed to explain the observed relationships between atomic and molecular ionisation energies. This shows in physical terms (*a*) why lone-pair ionisation energies are close to those of the atom in the molecule and (*b*) why bond ionisation energies are larger than the average of the ionisation energies of the two atomic orbitals which form the bond. The results imply that σ bonds are independent of their environment while π bonds are sensitive to this.

The objective is to see the physical reasons why (*a*) the ionisation energy of a molecular lone pair is close to that of the same electron of the " atom in the molecule " and (*b*) the ionisation energy of a two-electron bond is generally larger, by some 1—10 ev, than an average of the ionisation energies of the two atomic orbitals which form the bond. For example, we want to know why the polarity of adjacent bonds does not seriously affect the ionisation energy of a lone pair or a σ bond.

To answer such questions, we have to establish a connection between the theoretical expressions for the ionisation energy of the lone pair or bond and the ionisation energy of the appropriate electrons of the atom. This is done in this Paper. We use a complete quantum mechanical formulation for all intra-atomic and intrabond quantities because we know that quantum effects matter very much for these. On the other hand, when working with non-bonded interactions and other long-distance effects, we use simple classical arguments as much as possible. The basis for such assumptions is the observed constancy of bond strengths and lengths in many molecules and it turns out that this is about the right level of approximation to use.

Since the work is based on the Hartree–Fock method [1-4] for atoms and molecules, the conclusions depend on its general validity. Some of the electron-interaction integrals which arise in this theory have been approximated in ways suggested by the results of Part IV and by the Mulliken approximations for the many-centre integrals.[5] Some of these approximations could be removed by computational methods but some are an intrinsic part of the theory of this Paper.

Notation and Terminology.—Atomic units [6] ($e=m=\hbar=1$, energy in units of 27·21 ev, distances in units of 0·529 Å) are used except in the Tables. The nuclei are labelled *a*,*b* . . *f*,*g* . . and the same label is used for the atom in the molecule. Nuclear charges, in units of minus the electronic charge, are written Z_a, etc. Internuclear distances are written R_{ab}, inter-electronic distances r_{12}, and electron–nucleus separations either as r_{1a} or simply r_a.

The normalised molecular orbital of a lone pair is written λ_a and that of a localised bond μ_{ab} where

$$\mu_{ab} = p_a\nu_a + p_b\nu_b$$

and ν_a and ν_b are the normalised and in general hybridised atomic orbitals of atoms *a* and *b*. The p_a and p_b are the linear coefficients of the atomic orbitals in the molecular orbital. The population of ν_a is defined as

$$l(ab,a) = p_a^2 + p_a p_b S(\nu_a\nu_b)$$

* Part IV, preceding Paper.

[1] Roothaan, *Rev. Mod. Phys.*, 1951, **23**, 69.
[2] See ref. 7 of Part I (*J.*, 1963, 2003).
[3] Clementi, *J. Chem. Phys.*, 1962, **36**, 33; Nesbet, *ibid.*, 1962, **36**, 1518; Krauss, *ibid.*, 1963, **38**, 564.
[4] Mulliken, *J. Chem. Phys.*, 1962, **36**, 3428.
[5] Mulliken, *J. Chim. Phys.*, 1949, **46**, 675.
[6] Kotani, Ohno, and Kayama, " Handbuch der Physik," Vol. 37/2, Springer, Berlin, 1961.

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where $S(\nu_a\nu_b)$ is the overlap integral between the atomic orbitals ν_a and ν_b. The differential charge in the atomic orbital ν_a is written

$$q(ab,a) = 1 - 2l(ab,a)$$

(Note that the 2 was omitted from eqn. 14 of Part II.)

The quantities $(-e^{\lambda}{}_a)$ and $(-e^{\mu}{}_{ab})$ are the calculated ionisation energies of the lone pairs and the two-electron bonds. The symbol $(-e_a)$ denotes the ionisation energy of a doubly occupied atomic orbital of the atom and $(-\bar{e}_a)$ that of a singly occupied valence atomic orbital of the atom.

The bracket notation is used for all integrals so that a two-electron integral is written

$$\int A(1)B(1)(r_{12})^{-1}C(2)D(2)\mathrm{d}v_{1,2} = \langle AB\,|\,CD\rangle = \langle BA\,|\,CD\rangle, \text{ etc.}$$

where A,B,C, and D stand for the space parts of atomic or molecular orbitals. The positions of the electron labels will always be held fixed. The integrals

$$\langle AA\,|\,BB\rangle = J(A,B) \quad \langle AB\,|\,AB\rangle = K(A,B)$$

occur so often that they are given the special symbol shown. The combination of integrals

$$J(A,B) - (1/2)K(A,B) = G(A,B)$$

and

$$\langle AB\,|\,CC\rangle - (1/2)\langle AC\,|\,BC\rangle = G(AB,C)$$

also occur frequently and are given the special symbols shown. We *define*

$$G(AB,CD) = \langle AB\,|\,CD\rangle - (1/4)\,\langle AC\,|\,BD\rangle - (1/4)\,\langle AD\,|\,BC\rangle$$

Such expressions as $J(A,\ )$, $G(A,\ )$ etc., are, then operators.

Summary of Procedure.—We write down first the expression for the ionisation energy of the electron of the molecule, simplify this until it matches that of the same electron of the atom as closely as possible and then subtract the expression for the ionisation energy of the atom. The bulk of the work lies in the simplification of the expression for the molecular ionisation energy.

Theory.—We consider a molecule with a ground state built from a closed shell of $2n$ electrons which inhabit a total of n lone pairs and localised bonds. The wave function of the molecule is [1]

$$\Phi = (2n!)^{-1/2}\,|\,1s_a\alpha\,.\,1s_a\beta\,.\,.\,.\,.\,\lambda_a\alpha\;\lambda_a\beta\,.\,.\,.\,.\,\mu_{ab}\alpha\,.\,\mu_{ab}\beta\,.\,.\,.\,.\,| \qquad (1)$$

The ionisation energies of the lone pairs and bonds are

$$e^{\lambda}{}_a = \langle\lambda_a\,|\,\mathrm{F}\,|\,\lambda_a\rangle \quad \mathrm{e}^{\mu}{}_{ab} = \langle\mu_{ab}\,|\,\mathrm{F}\,|\,\mu_{ab}\rangle \qquad (2)$$

where F is the Hartree–Fock operator of the molecule (Part IV). We take the lone pairs first because they are easier to handle than the bonds.

Lone pairs. Writing out the Hartree–Fock operator in the expression for $e^{\lambda}{}_a$ we obtain

$$e^{\lambda}{}_a = \langle\lambda_a| - (1/2)\nabla^2 - \sum_f Z_f/r_f + \sum_{\lambda} 2G(\lambda_f,\ ) + \sum_{\mu fg} 2G(\mu_{fg},\ )|\lambda_a\rangle \qquad (3)$$

The three summations go over all the nuclei, all the lone pairs (including λ_a itself), and all the bonds in the molecule. We replace the operator $G(\mu_{fg},\ )$ by a simpler expression in the following way. Consider $J(\mu_{fg},\ )$. This is given by

$$J(\mu_{fg},\ ) = \langle p_f{}^2\nu_f{}^2 + p_g{}^2\nu_g{}^2 + 2p_fp_g\nu_f\nu_g|\quad\rangle \qquad (4)$$

Writing the overlap charge $\nu_f\nu_g$ as [5] $0{\cdot}5\mathrm{S}(\nu_f\nu_g)(\nu_f{}^2 + \nu_g{}^2)$ we obtain

$$J(\mu_{fg},\ ) = l(fg,f)J(\nu_f,\ ) + l(fg,g)J(\nu_g,\ ) \qquad (5)$$

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The exchange integral $K(\mu_{fg},\ )$ is

$$K(\mu_{fg},\ ) = \langle(p_f\nu_f + p_g\nu_g) \quad |(p_f\nu_f + p_g\nu_g) \quad \rangle \tag{6}$$

$$= p_f{}^2\langle\nu_f \ |\nu_f \ \rangle + p_g{}^2\langle\nu_g \ |\nu_g \ \rangle + 2p_fp_g\langle\nu_f \ |\nu_g \ \rangle \tag{7}$$

The third term on the right of (7) is expanded by writing [7]

$$\nu_f = S(\nu_f\nu_g)\nu_g + \ldots.$$

$$\nu_g = S(\nu_f\nu_g)\nu_f + \ldots. \tag{8}$$

and then

$$K(\mu_{fg},\ ) = l(fg,f)K(\nu_f,\ ) + l(fg,g)K(\nu_g,\ ) \tag{9}$$

This expansion of the exchange integral is chosen to match the expansion of the Coulomb integral and is an important part of this work. We now have

$$2G(\mu_{fg},\ ) = 2l(fg,f)G(\nu_f,\ ) + 2l(fg,g)G(\nu_g,\ ) \tag{10}$$

$$= G(\nu_f,\ ) + G(\nu_g,\ ) - q(fg,f)O_{fg}(\ ) \tag{11}$$

where $O_{fg}(\ )$ is an operator related to the bond μ_{fg} and is defined by

$$O_{fg}(\ ) = G(\nu_f,\ ) - G(\nu_g,\ ) \tag{12}$$

The above integral approximations are the essential ones of this work because they break up the Hartree–Fock operator into a sum of terms each of which belongs to an "atom in the molecule." If we write

$$\Omega_f = Z_f/r_f - \sum_{\lambda f} 2G(\lambda_f,\ ) - \sum_{\nu f} G(\nu_f,\ ) \tag{13}$$

and define the atomic ionisation energy by

$$e_a = \langle\lambda_a| - (1/2)\nabla^2 - Z_a/r_a + \sum_{\lambda'_a} 2G(\lambda'_a,\ ) + \sum_{\mu_{ab}} G(\nu_a,\ )|\lambda_a\rangle \tag{14}$$

then it is easy to show that

$$e^{\lambda}{}_a = e_a - \sum_{f\neq a} \Omega_f(\lambda_a) - \sum_{\mu fg} q(fg,f)O_{fg}(\lambda_a) \tag{15}$$

As in Part IV, we define

$$(-\delta e^{\lambda}{}_a) = (-e^{\lambda}{}_a) - (-e_a) \tag{16}$$

then

$$(-\delta e^{\lambda}{}_a) = \sum_{f\neq a} \Omega_f(\lambda_a) + \sum_{\mu fg} q(fg,f)O_{fg}(\lambda_a) \tag{17}$$

This is the important equation for the lone-pair ionisation energies. It shows that the modification of the ionisation energy of the lone-pair electron on molecule formation is due to two terms, the first of which is the penetration of the lone-pair electron into the *neutral* atoms and the second the effect of the polarity of all the bonds in the molecule.

The evaluation of the terms in eqn. (17) requires the q from Part II and certain integrals. The penetration integrals are difficult to evaluate accurately and, since some rough estimates show them to be small, they have not been worked out in detail. The J and K integrals which occur in the polarity term were evaluated by using the idealised hybridisations. The G integrals for non-neighbour atoms are approximated as the inverse distance between the two nuclei.

To get some idea of the effect of hybridisation on the lone-pair ionisation energies, the result of including 10% of the $2p$ atomic orbital in the lone pair's $2s$ atomic orbital has been estimated by taking an average of the Slater ionisation energies of the $2s$ and $2p$ atomic orbitals in the ratio 9 : 1. This almost certainly exaggerates the importance of

[7] Reudenberg, *J. Chem. Phys.*, 1951, **19**, 1433.

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the hybridisation effect on the lone-pair ionisation energies so the numbers are an upper limit to this. The results are shown in Table 1.

Localised bonds. Before dealing with the general case, it is helpful to think of a simple example, such as the bond in HeH^+. In this case, $\varepsilon^\mu = e^\mu$ and by assuming that ν_a is an

TABLE 1.

Effect of bond polarity on the ionisation energies of lone pairs (ev).*

Atom	Molecule	Lone pair	Polarity effect $(-\delta e^\lambda)$	$(-\delta e^\lambda)_{hybn.}$	Atom	Molecule	Lone pair	Polarity effect $(-\delta e^\lambda)$	$(-\delta e^\lambda)_{hybn.}$
Boron	BH	0·93 $2s_B$	0·4	−0·8	Oxygen	OH	0·99 $2s_O$	−1·2	−1·6
Carbon	CH	0·97 $2s_C$	0·0	−0·9		CO	0·90 $2s_O$	−0·9	
	CO	0·85 $2s_C$	0·2			CO_2	0·97 $2s_O$	−0·4	
	C_3	0·93 $2s_C$	−0·3			COS	0·96 $2s_O$	−1·7	
	C_4	0·97 $2s_C$	−0·1			CH_2O	0·94 $2s_O$	−2·2	
Nitrogen	N_2	0·86 $2s_N$	0·0	−1·3		NO_2^+	0·98 $2s_O$	15·0	
	NH	0·98 $2s_N$	−0·6			CH_2O	1·00 $2p_O$	−1·8	
	HCN	0·92 $2s_N$	−2·0		Fluorine	F_2	0·99 $2s_F$	0·0	−2·2
	C_2N_2	0·92 $2s_N$	0·1			HF	0·99 $2s_F$	−1·8	
	N_3^-	0·92 $2s_N$	−12·2			HF	1·00 $2p_F$	−1·6	

* See eqn. (17). A positive value of $(-\delta e^\lambda)$ denotes an increase in the ionisation energy of the lone pair on molecule formation. All lone pairs but two are taken as pure $2s$ atomic orbitals and the atomic orbitals forming the bonds from the end atoms are taken as pure $2p\sigma$ or $2p\pi$. See footnote in Part IV concerning the atomic charges of NO_2^+ and N_3^-. In the molecules with delocalised π bonds covering three atoms (C_3, CO_2, COS, NO_2^+, N_3^-), the π charge on the central atom is divided into two, and one half assigned to psuedo-localised π bonds on each side. The same method was used for C_4 but the π charges for C_2N_2 were assumed to come from localised π bonds.

eigenfunction of $[-(1/2)\nabla^2 - Z_a/r_a]$ with eigenvalue e_a and similarly for ν_b, it is easy to show that

$$(-\delta e^\mu) = (-e^\mu) - [l(ab,a)(-\bar{e}_a) + l(ab,b)(-\bar{e}_b)] = \{-J(\mu,\mu) + p_a{}^2\Omega_b{}^+(\nu_a) + p_a{}^2\Omega_a{}^+(\nu_b) + p_a p_b[\Omega_a{}^+(\nu_a\nu_b) + \Omega_b{}^+(\nu_a\nu_b)]\} \quad (18)$$

where $\Omega_a{}^+(\ ) = Z_a/r_a$, etc. Notice that Ω^+ refers to the positively charged atom, not to the neutral atom as does Ω itself.

The terms on the right-hand side of eqn. (18) will be referred to as the "internal terms" because they concern only the two atomic orbitals and the two electrons which form the bond. The physical meaning of the terms on the right of eqn. (18) is as follows. The first term, $J(\mu,\mu)$, is the mutual repulsion of the two electrons which form the bond. The other three terms are attraction terms of the two electrons to the nuclei. The first two of these are the attraction of an electron in ν_a for nucleus b and that of an electron in ν_b for nucleus a, respectively. The third is the attraction of the overlap charge cloud, $\nu_a\nu_b$, to both nuclei. The latter term is interesting because it is the best simple measure of the strength of a bond. This will be shown elsewhere. For the moment, the important point about eqn. (18) is that the nuclear attraction terms must together outweigh the electron repulsion term before the bond ionisation energy is greater than the average of the two atomic orbital ionisation energies. Notice that there is no direct mention of the exchange energy in eqn. (18), all the terms being those of simple electrostatics.

There are many additional factors to deal with in the general heteronuclear localised bond. For example, not only is the bond itself polar but there will be polar neighbouring bonds and there may also be extensive hybridisation in the atomic orbitals which form all the bonds. This work follows much the same lines as that for the lone pairs and will be given in a more compact form.

The ionisation energy of the general two electron bond is given by

$$e^\mu{}_{ab} = \langle\mu_{ab}|\,F\,|\mu_{ab}\rangle = \langle\mu_{ab}|\,-(1/2)\nabla^2 - \sum Z_f/r_f + \sum_{\lambda f} 2G(\lambda_f,\ ) + \Big\{\sum_{\mu_{fg}\neq\mu_{ab}} 2G(\mu_{fg},\ )\Big\} + 2G(\mu_{ab},\ )\,|\,\mu_{ab}\rangle \quad (19)$$

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By simplifying $G(\mu_{fg},\ )$as before, this reduces to

$$e^{\mu}_{ab} = \langle \mu_{ab}| - (1/2)\nabla^2 - \Omega_a{}^+ - \Omega_b{}^+ |\mu_{ab}\rangle + J(\mu,\mu) - \sum_{f\neq a,b} \Omega_f(\mu_{ab}) - \Big\{ \sum_{\mu_{fg}\neq\mu_{ab}} q(fg,f) O_{fg}(\mu_{ab}) \Big\} \quad (20)$$

where

$$\Omega_f = Z_f/r_f - \sum_{\lambda_f} 2G(\lambda_f,\ ) - \sum_{\mu_{fg}} G(\nu_f,\ ) \quad (21)$$

and this is *roughly* equal to $1/r_f$.

The terms enclosed by $\langle\ \rangle$ in eqn. (20) easily reduce to

$$\{l(ab,a)(\bar{e}_a) + l(ab,b)(\bar{e}_b)\} + p_a{}^2\Omega_b{}^+(\nu_a) + p_b{}^2\Omega_a{}^+(\nu_b) + p_a p_b[\Omega_a(\nu_a\nu_b) + \Omega_b(\nu_a\nu_b)] \quad (22)$$

and the final expression for $(-\delta e^{\mu})$ is

$$(-\delta e^{\mu}) = (-e^{\mu}) - [l(ab,a)(-\bar{e}_a) + l(ab,b)(-\bar{e}_b)] = \{-J(\mu,\mu) + p_a{}^2\Omega_b{}^+(\nu_a) + p_b{}^2\Omega_a{}^+(\nu_b) + p_a p_b[\Omega_a{}^+(\nu_a\nu_b) + \Omega_b{}^+(\nu_a\nu_b)]\} + \Big\{ \sum_{f\neq a,b} \Omega_f(\mu_{ab}) + \sum_{\mu_{fg}\neq\mu_{ab}} q(fg,f) O_{fg}(\mu_{ab}) \Big\} \quad (23)$$

We now have the expression for the increase in ionisation energy on bond formation in a very similar form to that for the isolated bond (18). The terms in the first curly brace { } of (23) are called the " internal terms " as before, although the Ω^+ operators do introduce other electrons into this term. This is written $(-\delta e^{\mu}$ int). The terms in the second curly brace of (23) are the " exterior terms " and they are written $(-\delta e^{\mu}$ ext). These describe the effect of the environment on the ionisation energy of the localised bond.

The evaluation of the terms in (23) is carried out as follows. First, the penetration integrals of neutral atoms have been dropped out as before. Secondly, the terms in $q(fg,f)$ are small and so the integrals $O_{fg}(\mu_{ab})$ have been approximated by writing

$$2O_{fg}(\mu_{ab}) = 2G(\nu_f,\mu_{ab}) - 2G(\nu_g,\mu_{ab}) = G(\nu_f,\nu_a) + G(\nu_f,\nu_b) - G(\nu_g,\nu_a) - G(\nu_g,\nu_b) \quad (24)$$

Then the neighbouring-atom G integrals are evaluated using Mulliken's approximation [5] for the exchange integrals. The G integrals for non-neighbouring atoms are replaced by the inverse distance.

The internal terms of eqn. (23) are large and must be evaluated as accurately as possible. Before this was realised, the approximation of replacing the operators Ω_a, etc., by $1/r_a$ was tried. This is an exact identity at infinite bond length and corresponds to the simple picture of bond formation which would say that the electrons of atom b which are not involved directly in forming the bond to a do nothing but shield off perfectly all but one of the nuclear charges of atom b. This is not a bad approximation when one of the atoms forming the bond is hydrogen but, when neither atom is hydrogen, it is very bad indeed and often produces errors of 10 ev. Consequently, all the electron interaction integrals in the internal terms must be evaluated explicitly. In doing this, we have approximated the exchange and hybrid integrals by the Mulliken approximations and this *may* be a serious source of error, particularly when π atomic orbitals are involved.

The integral $J(\mu,\mu)$ has also been approximated by writing it as

$$J(\mu,\mu) = l^2(ab,a)J(\nu_a,\nu_a) + l^2(ab,b)J(\nu_b,\nu_b) + 2l(ab,a)l(ab,b)J(\nu_a,\nu_b) \quad (25)$$

This approximation, like those above, has been checked against literature values where possible with the results shown in Table 2*b*. All the results for the bonds are reported in Tables 2*a* and 2*b* and those for the internal terms are reported in some detail in preparation for future work.

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TABLE 2*a*.*

Effect of the internal terms on the bond ionisation energy (ev).

σ Bond			Nuclear attraction terms			Electron repulsion term,		
		Molecule	p_ap_b factor	p_a^2,p_b^2 factor	Total	$-J(\mu,\mu)$	$[-\delta e\mu$ (int.)]	$(-\delta e\mu)$ †
H	H		9·2	9·5	18·7	−15·35	3·35	3·3
1*s*	1*s*							
Li	H		5·1	5·9	11·0	−13·0	−2·0	−1·0
s^2p	1*s*							
B	H		7·3	10·5	17·8	−13·55	4·25	3·5
2*p*	1*s*		(7·5)	(10·6)	(18·1)	(−15·1)		
C	H		7·9	11·9	19·8	−14·2	5·6	2·5
2*p*	1*s*							
N	H		8·1	13·3	21·4	−16·1	5·3	2·5
2*p*	1*s*		(8·7)	(13·6)	(22·3)	(−17·6)		
O	H		8·2	14·5	22·7	−17·7	5·0	1·5
2*p*	1*s*							
F	H		8·1	15·7	23·8	−19·2	4·6	1·0
2*p*	1*s*							
Li	Li		2·7	3·2	5·9	−5·5	0·4	−0·5
2*s*	2*s*							
N	N		15·1	19·9	35·0	−17·6	17·4	14·0
2*p*	2*p*		(12·6)	(21·7)	(34·3)	(−17·85)		
F	F		5·3	11·1	16·4	−19·6	−3·2	−4·5
2*p*	2*p*							
C	C	C_3	15·9	16·6	32·5	−16·85	15·6	6·5
sp	2*p*							
		C_4 (1 : 2)	15·9	16·1	32·0	−16·6	15·4	6·5
C	C	C_4 (2 : 3)	19·2	15·3	34·5	−19·0	15·5	10·0
sp	*sp*							
		C_2H_2	17·5	15·7	33·2	−19·3	13·9	10·0
		C_2N_2	14·2	13·0	27·2	−18·6	8·6	10·0
C	H	HCN	10·25	11·6	21·85	−17·4	4·4	6·5
sp	1*s*							
		C_2H_2	10·0	11·5	21·5	−17·3	4·2	6·5
		CH_2O	10·6	11·7	22·3	−16·9	5·4	4·5
C	N	HCN	15·6	19·1	34·7	−18·5	16·2	9·5
sp	2*p*							
		C_2N_2	15·7	19·2	34·9	−18·5	16·5	9·5
C	O	CO	12·5	18·55	31·0	−19·0	12·0	12·5
2*p*	2*p*							
C	O	CO_2	15·1	19·3	34·4	−19·8	14·6	9·0
sp	2*p*							
		COS	14·9	19·0	33.9	−20·0	13·9	9·0
		CH_2O	14·0	18·2	32·2	−19·3	12·9	6·5
N	N	N_3^-	15·2	18·2	33·4	−20·4	13·0	?
sp	2*p*							
N	O	NO_2^+	15·7	19·1	34·8	−20·8	14·0	22·0
sp	2*p*							
π Bond								
C	C	C_2H_2	5·25	8·4	13·6	−13·7	−0·1	1·0
2*p*π	2*p*π							
C	N	HCN	4·8	9·1	13·9	−14·7	−0·8	1·5
2*p*π	2*p*π							
C	O	CO	4·8	9·85	14·6	−15·3	−0·7	2·0
2*p*π	2*p*π							
		CH_2O	5·3	9·6	14·9	−15·5	−0·6	−1·0
N	N	N_2	5·7	9·9	15·6	−16·1	−0·5	2·5
2*p*π	2*p*π							

* See eqn. (23). The numbers are generally rounded to 0·1 ev. Where there is no entry in the column headed " molecule," the latter is the diatomic given under " bond." In all molecules save LiH and CH_2O, the ideal hybridisations were used, as shown in the column headed " bond." The bracketed values are the accurate values from the literature [11] for the numbers immediately above them. In evaluating the nuclear attraction terms, it is necessary to renormalise the p_a and p_b values in Part I, using the condition that the hybrids are the ideal ones. In the N_3^- and NO_2^+ results, the two atoms forming the bonds are given their normal number of electrons. That is, the central nitrogen is assumed sp^4 and the end nitrogen and oxygen atoms are assumed s^2p^3 and s^2p^4, respectively.

† Part IV.

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TABLE 2*b*.

Effect of the polarity of other bonds on the bond ionisation energy (ev).*

σ Bond	Molecule	Polarity effect ($-\delta e\mu$ ext.)	σ Bond	Molecule	Polarity effect ($-\delta e\mu$ ext.)
CH	HCN	0·1	CO	CO_2	0·4
	C_2H_2	−0·4		CH_2O	−0·7
	CH_2O	−0·4	NN	N_3^-	−11·5
CC	C_3	−1·0	NO	NO_2^+	17·9
	C_4 (1 : 2)	0·0	π Bond		
	C_4 (2 : 3)	0·2	CC	C_2H_2	−1·1
	C_2N_2	−0·3	CN	HCN	−0·7
	C_2H_2	−2·1	CO	CH_2O	−1·1
CN	HCN	−0·6			
	C_2N_2	0·4			

* See eqn. (23). A positive value of ($-\delta e\mu$ ext.) denotes an increase in the bond ionisation energy. Only localised π bonds are dealt with here. In the molecules C_3, CO_2, N_3^-, and NO_2^+, one-half of the π charge on the central atom was assigned to pseudo-localised π bonds on each side. The same method was used for C_4 but the π charges of C_2N_2 were assumed to come from localised bonds. For the two charged molecules, the expression in eqn. (17) was used with the π charges (*a*) for N_3^- : $N_1 = -0{\cdot}24$, $N_2 = 0{\cdot}48$ and (*b*) for NO_2^+ : O = 0·08; N = −0·16. To these results were added the effects of an additional 0·5 electrons on both end nitrogens (of N_3^-) and a single unit positive charge on the nitrogen of NO_2^+. This second term is the large one for these two molecules. The idealised hybridisations were used for all molecules save CH_2O; in this molecule, the carbon hybrid atomic orbital forming the bond to hydrogen was assumed to be sp^2 (see Part III).

DISCUSSION

We take the lone pairs first and then the bonds. It must be remembered that the numbers of interest here must be about the same size as the inherent error in the theory and in the computations on which the work is based so that only the consistent behaviour of the whole set of molecules should be considered significant.

Lone Pairs.—The results in Table 1 tell us two further things about the lone pairs. First, the polarity of the bonds has only a small effect (~0·5 ev) on the ionisation energy of the lone pair electron, in agreement with the Part IV result. This is true even for the molecules with delocalised π bonds where the present theory does not strictly apply. The second is that the introduction of a few percent. of the 2*p* atomic orbital into the lone pair's atomic orbital reduces the ionisation energy by some 1—2 ev. It is not yet possible to be more precise.

There are some interesting points concerning individual molecules. The first concerns hydrogen fluoride where it has been felt [8] that the amount of charge transfer from hydrogen to fluorine is much larger than the present value of 0·15 electrons. The result in Table 1 shows that, in terms of energies, a small amount of charge transfer has a comparatively large effect in reducing the ionisation energy of the 2*s*-like lone pair. Thus, in going from NH to FH, the amount of charge transfered doubles but the reduction of the ionisation energy of the 2*s*-like lone pair is trebled. It has been suggested [9] that small amounts of charge transfer do indeed affect energy quantities quite strongly when the receiving atom is fluorine.

The ($-\delta e^{\lambda}$) values for the two molecules with formal charges are very different from those of the neutral molecules, as was found in Part IV, and there is good agreement between the present numbers and those of Part IV.

This completes the study of the lone pairs and it is convenient to summarise all the information about them obtained in this work. This is put in the form of a series of statements about what happens to the lone pair as the atom becomes part of the molecule. (1) The ionisation energy of the lone pair is modified by the changes which occur in the coupling of the spin and orbital angular momeda of the valence electrons. This is sometimes a substantial effect (several eV) and it *increases* the ionisation energy of the lone-pair

[8] See ref. 4, p. 3436.
[9] Peters, *J. Chem. Phys.*, 1963, **38**, 561.

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electron. (2) The 2*s* atomic orbital is modified by the inclusion of some 5—10% of the 2*p* atomic orbital. The sign of this is such as to concentrate the lone-pair electrons outside the binding region. This decreases the ionisation energy of the lone pair by some 1 ev. (3) The ionisation energy of the lone-pair electron is modified by the polarity of adjacent bonds by a relatively small (~0·5 ev) amount.

The main reservation on these results is that all delocalisation effect have been excluded and this will be examined in the future. The lone-pair work is useful in confirming that the approximations used in the present theory are reasonably accurate. The advantage of this is that, when we deal with the bonds, the situation is so complicated that no direct check on the approximations is possible.

Localised Bonds.—These results are divided into those for the internal and the external terms of eqn. (23).

Internal terms (*Table* 2*a*). These results show that the $(-\delta e^{\mu})$ values of Part IV are determined by the internal nature of the bond. This result completes the demonstration that a σ bond is comparatively independent of its environment. This is not true for the π bonds whose internal terms are quite small.

The present theory reproduces the Part IV results satisfactorily. For example, two of the three negative $(-\delta e^{\mu})$ values of Part IV are reproduced clearly. Furthermore, the large $(-\delta e^{\mu})$ values of the bonds which are built from hybridised atomic orbitals are reproduced correctly. The present values tend to be larger than those in Part IV and the latter set of values is the more accurate because it includes the detailed hybridisations and the accurate integral values.

The breakdown of the $(-\delta e^{\mu})$ values in terms of integrals over atomic orbitals (Table 2*a*) establishes several points. First, the self-energy of the bond, $J(\mu,\mu)$, is quite constant in this set of molecules. Only in the extreme case of the lithium molecule does it depart greatly from 15—17 ev. Secondly, of the two types of nuclear attraction term, the ones in p_a^2 and p_b^2 are rather more variable than is the $J(\mu,\mu)$ term but these are by no means so variable as the overlap term in $p_a p_b$. The latter varies from 5 to 20 ev in the different bonds of this set of molecules and it is much more sensitive to the particular type of bond than is either of the other two terms. This overlap nuclear attraction term is small in π bonds (4—5 ev), somewhat larger (7—9 ev) in bonds formed from one hydrogen, atom and considerably larger (15—20 ev) in bonds formed from *sp* hybrid atomic orbitals. It is easy to show that this variation in the $p_a p_b$ term comes from the values of the integrals: the $p_a p_b$ factor is quite constant in these bonds.

This is an interesting result because this overlap nuclear attraction term has much in common with the overlap integral so the result confirms our general feeling that the best simple picture of bond formation that can be given is an accumulation of electronic charge in the binding or overlap region.[10] It will be shown elsewhere that the $p_a p_b$ term alone does in fact give a good guide to bond strengths.

The present results for the π bonds also reproduce the Part IV results quite well although the present numbers are systematically about 2 ev lower than those in Part IV. This discrepancy is due to our neglecting the σ–π exchange integrals in the present results. This is clear from the published accurate values for these integrals. The results in Table 2*a* certainly support the contention that the $(-\delta e^{\mu})$ values for π bonds are much smaller than those for σ bonds and the reason for this is nothing more than the geometry of the atomic orbitals. The opposite nucleus is well shielded from a π electron but not from a σ electron so the σ bond is the stronger of the two. This also explains why the σ electrons obey the electronegativity rules while the π electrons do not. The argument that the

[10] Pauling, " The Nature of the Chemical Bond," Cornell Univ. Press, Ithaca, New York, 1960, ch. 1. Coulson and Lewis in " Quantum Theory," ed. Bates, Pure and Applied Physics Series, Academic Press, New York, 1962, p. 189. Slater, " Quantum Theory of Molecules and Solids," McGraw-Hill, New York, 1963, vol. 1, ch. 1.

[11] Ohno, *J. Phys. Soc. Japan*, 1957, **12**, 938 (BH); Boyd, *J. Chem. Phys.*, 1958, **29**, 109 (NH); Scherr, *ibid.*, 1955, **23**, 569(N_2).

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π electrons are the more polarisable so that the π bonds should be more polarised in the molecule is misleading because it presupposes that both the σ and the π electrons experience similar electric fields in the molecule. The present results show that this is quite untrue.

External terms. The results are in Table 2*b*. These are very like the lone-pair results in that the total effect of the polarity of adjacent bonds is small in comparison with the internal terms. We have to exempt the π bonds from this generalisation because their internal terms are no larger than their external ones. The present theory again seems to work for molecules with delocalised π bonds. The two molecules with formal charges, NO_2^+ and N_3^-, have very large external terms ($\sim$15 ev). This agrees with the result in Part IV for NO_2^+ while the earlier result for N_3^- is suspect.

Quite drastic approximations have been made in evaluating the external terms of the bonds and before significance is attached to the individual numbers they must be re-evaluated accurately first.

Delocalisation Effects.—No explicit mention of these has yet been made but the Part IV results do contain delocalisation effects because the lone pairs and bonds are not perfectly localised (Part I). The results in Part V, on the other hand, necessarily refer to perfectly localised bonds and lone pairs. Insofar as the two sets of results agree, it is clear that whatever the delocalisation effects may be they are not large enough to upset the agreement. To put the point formally, we can say that there is no clear numerical evidence that delocalisation effects are of *major* importance in determining the energetics of the ground states of these molecules (apart from the molecules with delocalised three centre π bonds).

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