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Quantum Mechanical Guides to the Potential Energy Curves of Some Simple Molecules

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The molecular orbital expression for the bond energy of a chemical bond is used to obtain some insight into the factors which produce the potential energy curves of a number of simple bonds. The resulting picture of bond formation and the potential energy curve is an electrostatic one and it depicts the potential energy curve as the sum of a long range attractive curve and a short range repulsive one. Broadly speaking, that part of the curve to the long bond length side of the minimum is determined essentially by the two electrons which form the bond and, in particular, by the 'binding energy' of these two electrons. The position of the minimum and the shape of the short bond length side of the curve do depend in general on the other valence electrons of the two atoms. The long range attractive curve is easily calculated but it is difficult to get the short range repulsive curve accurately. The results may prove useful in the construction of potential energy surfaces where the long bond length side of the potential energy curve is the important part.

Der MO-Ausdruck für die Bindungsenergie wird bei der Betrachtung von Potentialkurven einer Anzahl kleiner einfacher Bindungen benutzt. Bindungsbildung und Potentialkurve ergeben sich aus einem elektrostatischem Bild; die Potentialkurve enthält einen anziehenden Anteil großer Reichweite und einen abstoßenden kleiner. Die Seite langer Bindungslängen wird durch die beiden bindenden Elektronen bestimmt, das Minimum und die Seite kurzer Bindungslängen durch die anderen Valenzelektronen. Der anziehende Anteil der Potentialkurve läßt sich im Gegensatz zum abstoßenden leicht berechnen. Die Ergebnisse könnten sich bei der Konstruktion von Potentialkurven, bei denen der Anteil großer Reichweite von Bedeutung ist, als nützlich erweisen.

On utilise l'expression de l'énergie d'une liaison chimique dans la méthode des orbitales moléculaires afin d'obtenir des éclaircissements sur les facteurs déterminant les courbes d'énergie potentielle d'un certain nombre de liaisons simples. La représentation résultante pour la formation de la liaison et pour la courbe d'énergie potentielle est électrostatique; elle décrit la courbe d'énergie potentielle comme la somme d'une courbe d'attraction à longue portée et d'une courbe de répulsion à courte portée. D'une manière générale, la partie de la courbe située par rapport au minimum du coté des grandes longueurs de liaison est essentiellement déterminée par les deux électrons qui forment la liaison et en partie par leur énergie de liaison. La position du minimum et la forme de la courbe du côté des longueurs de liaison courtes dépend en général des autres électrons de valence des deux atomes. La courbe d'attraction à longue portée est facilement calculée mais il est difficile d'obtenir avec précision la courbe de répulsion à courte portée. Les résultats peuvent s'avérer utiles pour la construction de surfaces d'énergie potentielle où la partie de la courbe d'énergie potentielle correspondant aux liaisons longues est la plus importante.

Introduction

There is at present no reasonably simple theoretical method of calculating the potential energy curve of a chemical bond. It is true that the rigorous theoretical methods are now beginning to give accurate potential energy curves [3], and this is a most encouraging result, but these methods are very complicated indeed and very much divorced from the type of physical insight which is so useful in qualitative discussion and in extrapolating the results from one molecule to another. For example, in the nitrogen molecule the formal theory implies that the potential energy curve is determined by the behaviour of all fourteen electrons in the molecule. Such a description is not easy to visualise. No doubt all fourteen electrons do play *some* part in determining the potential energy curve but it is natural to hope that at least the qualitative form of this curve is determined by the six electrons which we commonly suppose to form the triple bond in this molecule.

One major simplification which is often thought to be true of potential energy curves is that they are essentially the sum of an attractive curve and a repulsive curve and that the repulsive curve is steeper at short bond lengths but dies away faster at long bond lenghts. This is just the way in which a Morse curve is built up [2] and the present theory is arranged so as to build up such a picture. There is an attractive curve which is a long range one and this is determined by the two electrons of the bond. The other valence electrons on both atoms are important in determining the repulsive curve and the position of the minimum in the potential energy curve.

The present theory [6] already contains the rudiments of an attractive and a repulsive curve since the bond energy appears as a difference of two positive terms (small terms aside). This work is now extended to provide at least a qualitative picture of how the potential energy curves of some simple bonds arise.

One difficulty which confronts us in this work is that the entire theory is a molecular orbital one and it is one of the major shortcommings of molecular orbital wave functions that they exagerate the importance of ionic terms and so are quite wrong at long bond lengths. This is why valence bond theory is ordinarily used in discussing long bond situations [1]. It turns out, however, that if we take the original expression for the bond energy and modify it slightly, the resulting expression does describe the dissociation of the bond correctly. This amounts to forgetting about the wave function and working with the energy expression alone.

Theory

To begin with a simple example, consider the isolated homonuclear bond such as that in the hydrogen molecule. This is a two electron problem and we can work out the potential energy curve quite easily. The complete wave function for the molecule is

$$\Psi_{\mathrm{MO}} = |\mu\,\bar{\mu}| \tag{1}$$

where the molecular orbital μ is given by

$$\mu = p_a \nu_a + p_b \nu_b \qquad p_a = p_b = [2 + 2\,S(\nu_a\,\nu_b)]^{-\frac{1}{2}} \tag{2}$$

and ν_a and ν_b are the normalised valence atomic orbitals which form the bond. $S(\nu_a\,\nu_b)$ is the overlap integral between these two atomic orbitals. The total energy of the molecule is given by

$$E_{\mathrm{molecule}} = 2e^{\mu} - J(\mu,\mu) + 1/R \tag{3}$$

where e^{μ} is the eigenvalue of the Hartree-Fock equation and is also (approximately) the ionisation energy of the molecular orbital. $J(\mu,\mu)$ is the self-energy of the molecular orbital (the mutual repulsion of the two electrons in the molecular orbital) and R is the internuclear distance. Atomic units (unit of energy, 27.21 eV: unit of length, 0.529 Å) are used unless otherwise specified. The atomisation energy, ΔE, is then given as a positive quantity, by

$$\Delta E = E_{\text{atoms}} - E_{\text{molecule}} = 2\,[(-e^{\mu}) - (-\bar{e})] - [1/R - J(\mu, \mu)] \tag{4}$$

where $\bar{e}$ is the ionisation energy of the atom ($\bar{e}$ itself is negative) and the quantity $[1/R - J(\mu, \mu)]$ is the internal coulomb term [*6f*]. Notice that the sign convention has been changed from that used in reference [*6f*]. If we introduce the quantity $(-\delta e^{\mu})$ which is now called the binding energy [*6h*] of the electron or of the molecular orbital and is defined by

$$(-\delta e^{\mu}) = (-e^{\mu}) - (-\bar{e}) \tag{5}$$

then the atomisation energy is given by

$$\Delta E = 2(-\delta e^{\mu}) - [1/R - J(\mu, \mu)] \tag{6}$$

In this simple example, this is the bond energy. Both terms are positive so the bond energy appears as the difference of the two. Up to this point, it is only the grouping of the terms which is at all novel.

One might now try to use this equation to calculate potential energy curves by evaluating e^{μ} for various bond lengths. This cannot be successful for long bond lengths since e^{μ} contains within it $J(\mu, \mu)$ and this is a completely incorrect measure of the electron interaction at long bond lengths. An alternative procedure is to expand $(-\delta e^{\mu})$ as in the earlier work [*6e*] giving

$$e^{\mu} = \langle \mu \mid F \mid \mu \rangle = 0.5\,(\bar{e}) + 0.5\,(\bar{e}) - p_a^2\,\omega_{aa}\,(b) - p_b^2\,\omega_{bb}\,(a) - p_a\,p_b\,\omega_{ab}\,(a+b) + {} + J(\mu, \mu) \tag{7}$$

where, for example,

$$\omega_{aa}\,(b) = \langle \nu_a \mid 1/r_b \mid \nu_a \rangle \text{ and } \omega_{ab}\,(a+b) = \langle \nu_a \mid 1/r_a + 1/r_b \mid \nu_b \rangle\,. \tag{8}$$

The binding energy is given by

$$(-\delta e^{\mu}) = p_a^2\,\omega_{aa}\,(b) + p_b^2\,\omega_{bb}\,(a) + p_a\,p_b\,\omega_{ab}\,(a+b) - J(\mu, \mu) = \omega - J(\mu, \mu) \tag{9}$$

and the atomisation energy by

$$\Delta E = 2\,[\omega - J(\mu, \mu)] - [1/R - J(\mu, \mu)] \tag{10}$$

This is close to the basic equation of this work and it represents the atomisation energy as a difference of two positive quantities. The equation could obviously be contracted further but it is convenient to leave it as it is.

Now we know that (10) cannot give a correct value of zero for the bond energy at infinite bond length because, although the quantities ω and $1/R$ vanish at infinite bond length, $J(\mu, \mu)$ does not. At long bond lengths, we must obviously replace $J(\mu, \mu)$ by $J\,(\nu_a\,\nu_b)$ to get the correct answer. This has been done at all bond lengths since various more complicated procedures for approximating $J(\mu, \mu)$ at finite bond lengths gave no improvement over this simple approximation.

The modified expression for the bond energy is then

$$\Delta E = 2\,[\omega_{ab} - J(\nu_a\,\nu_b)] - [1/R_{ab} - J(\nu_a\,\nu_b)] \tag{11}$$

and there is no obvious reason why this should not give a useful estimate of the potential energy curve of a simple bond. That it does do so for the examples of the hydrogen, lithium and lithium hydride molecules is shown in Figs. 1, 2 and 3. These results will be discussed further below but it is important to notice now that it is these results which convince us that the theory is really meaningful. This is because, in the more complicated bonds, there are additional uncertainties which make it difficult to get a clear comparison with experiment.

Going on to the general case now, we assume for simplicity that there are no lone pairs in the molecule. This does simplify the expressions without causing any real loss of generality. The total energy of the molecule which is built from localised bonds is written as

$$E_{\text{molecule}} = 2 \sum_i e_i - \sum_i J(\mu_i, \mu_i) - \sum_{i \neq j} \sum 2\, G(\mu_i, \mu_j) + \sum (\text{pairs})\, Z_a Z_b / R_{ab} \quad (12)$$

where e_i is the eigenvalue of the i^{th} bond (molecular orbital), the second term is the total self-energy of all the molecular orbitals, the third term is the total electron interaction energy between electrons in different molecular orbitals and the last term is the total nuclear repulsion energy. If there are n-bonds and $2n$-electrons the sums over i and j run over 1 through n.

The total energy of the atoms is given by

$$E_{\text{atoms}} = \sum (\text{atoms}) \left\{ \sum_p \bar{e}_{ap} - \sum_{p \neq q} \sum G(\nu_{ap}, \nu_{aq}) \right\} \quad (13)$$

where p, q ... distinguish the different atomic orbitals of atom a. Remember that there are no lone pairs present, so that all the atomic orbitals are singly occupied valence atomic orbitals. If the atom in the molecule is promoted, this must be allowed for in writing out (13). The bar in $\bar{e}_{ap}$, for example, denotes that this is the ionisation energy of a singly occupied atomic orbital. This is the Van Vleck atom in the molecule in which the interaction between the pair of valence electrons in the atomic orbitals ν_{ap} and ν_{aq} is written

$$J(\nu_{ap}, \nu_{aq}) - (\tfrac{1}{2})\, K(\nu_{ap}, \nu_{aq}) \,.$$

Suppose next that all the bonds of the molecule are non-polar. We know [*6i*] that this will cause only a small error in the atomisation energy. Suppose that the molecular orbital μ_i is the bond between atoms a and b while μ_j is that between atoms a and c. These molecular orbitals are given by

$$\mu_i = (\nu_{ap} + \nu_{bq})\,(2 + 2\,S_i)^{-\frac{1}{2}} \qquad \mu_j = (\nu_{ar} + \nu_{cs})\,(2 + 2\,S_j)^{-\frac{1}{2}} \,. \quad (14)$$

The coulomb integral is expanded as

$$4\, J(\mu_i, \mu_j) = J(\nu_{ap}, \nu_{ar}) + J(\nu_{ap}, \nu_{cs}) + J(\nu_{bq}, \nu_{ar}) + J(\nu_{bq}, \nu_{cs}) \,. \quad (15)$$

The matching expansion of the exchange integral is given by

$$4\, K(\mu_i, \mu_j) = K(\nu_{ap}, \nu_{ar}) + K(\nu_{ap}, \nu_{cs}) + K(\nu_{bq}, \nu_{ar}) + K(\nu_{bq}, \nu_{cs}) \,. \quad (16)$$

The coulomb integral expansion is MULLIKEN'S [*4*] and the matching expansion of the exchange integrals was suggested earlier [*6e*]. The question of the reliability of this expansion for the exchange integrals requires further study but the essential motivation for the use of (16) is that it leads to the cancelling of the G-integrals of (13) from the expression for the atomisation energy. If one does not use this expansion for the exchange energy, there is no simple expression for the bond energy and further progress is difficult.

The expansions (15) and (16) are used for all the G-integrals of (12) and then the atomisation energy is written down as a positive quantity by subtracting the energy of the molecule from that of the atoms. The result is

$$E = \sum_{i=l}^{n} E^i \tag{17}$$

where i labels the bond and E^i is the bond energy given by

$$E^i = 2\,(-\delta e_i) - [1/R_i - J(\mu_i, \mu_i)] - C_i\,. \tag{18}$$

The first term is the binding energy again and is dealt with below, the second term is the internal coulomb term [6f] and the last term is the main coulomb term [6f] defined by

$$C_i = (Z_a\,Z_b - 1)/R_{ab} - \sum_{p,q}\sum G(\nu_{ap}, \nu_{bq}) \tag{19}$$

where the sums run over all the valence atomic orbitals of atoms a and b, omitting from the double sum only that pair which forms the bond. Remember that the i^{th} molecular orbital joins atoms a and b and notice that the sign convention has been changed as compared with reference [6f]. Experience shows that this main coulomb term is too repulsive and so the natural thing do do is to omit the exchange terms and use instead the expression

$$C_i = (Z_a\,Z_b - 1)/R_{ab} - \sum_{p,q}\sum J(\nu_{ap}, \nu_{bq})\,. \tag{19'}$$

There are certain other small terms which have been omitted from these equations [6f].

We are going to use the same sort of simplification as in the simple bonds. That is, we expand the binding energy as

$$(-\delta e_i) = (-e_i) - (\tfrac{1}{2})\,[(-\bar{e}_{ap}) + (-\bar{e}_{bq})] = \omega_{ab} - J(\mu_i, \mu_j) \tag{20}$$

and ω_{ab} is given as before by

$$\omega_{ab} = p_a^2\,\omega_{aa}\,(b) + p_b^2\,\omega_{bb}\,(a) + p_a\,p_b\,\omega_{ab}\,(a+b)\,. \tag{21}$$

The difference from the isolated two electron bond case lies in the definitions of the operator which appears in the $\omega_{aa}\,(b)$ *etc.* This is now the operator Ω_a, say, which is given by

$$\Omega_a = Z_a/r_a - \sum G(\nu_a, \;) \tag{22}$$

where Z_a is the charge, in atomic units, on nucleus a and the sum runs over all the other valence electrons of atom a. Since we are supposing that the atom in the molecule is electrically neutral and that dissociation of the molecule gives neutral atoms, this operator is roughly equal to $1/r_a$. Then the integrals in (21) are given by

$$\omega_{aa}\,(b) = \langle \nu_a \,|\, \Omega_b \,|\, \nu_a \rangle \qquad \omega_{ab}\,(a+b) = \langle \nu_a \,|\, \Omega_a + \Omega_b \,|\, \nu_b \rangle\,. \tag{23}$$

We will also use the approximation of replacing $J(\mu, \mu)$ by $J(\nu_a, \nu_b)$ as for the simpler bonds.

The final expression for the bond energy of the i^{th} bond in the general case is

$$E^i = 2\,[\omega_i - J_i] - [1/R_i - J_i] - C_i \tag{24}$$

where ω_i has been written in place of ω_{ab}. Remember that the i^{th} bond joins atoms a and b.

The working equation is that given in (24). As it stands, however, this is not sufficiently accurate to be useful. One difficulty is that, in approximating the two electron integrals, we have lost too much numerical accuracy for the main coulomb term C_i to give good results in all cases. We know the qualitative form of this curve: it vanishes at infinite bond length and is positive (in the sense that it represents a repulsion) at finite bond lengths. What we have done is to derive both the calculated form of the main coulomb term from Eq. (19) and, if necessary, an empirical form C_{emp}, which would lead to exact agreement with experiment. Another difficulty with Eq. (24) is the calculation of the integrals in the Ω operator. Previous experience with this operator [*6e, f*] has shown that it tends to be about $1.5/r$ at short bond lengths and we know that it tends to $1/r$ at infinite bond length. What we have done for the moment is to use $1/r$ for this operator for all bond lengths. This may prove to be a serious source of trouble but, like the approximation used for the main coulomb term, further work may show that it does represent the Ω operator reasonably well. It is, of course, possible to improve on both of these approximations in an effort to achieve closer agreement with experiment.

The calculations on which Figs. 1 to 7 are based are those of Eq. (24) modified as in the above paragraph. The experimental potential energy curves are Morse curves drawn from the values of $\overline{\omega}_e$, D_e and r_e given by HERZBERG [*2*].

Discussion

The important result of this work is the physical picture of bond formation as the balancing of the attractive curve $2(\omega - J)$, called the binding energy of the electrons, and the two repulsive coulomb terms. Moreover, it is shown below and in the figures that the attractive term alone is enough to reproduce much of the long bond length side of the potential energy curve. The calculation of the position of the minimum is much more difficult because it involves the main coulomb term in the general case. This term is difficult to calculate accurately although the results in Figs. 5, 6 and 7 show that the calculated and empirical forms are similar. It is certainly reasonable to suppose that, even if we cannot calculate the whole of the potential energy curve in detail, the general physical picture is correct. Perhaps we should look for more semi-empirical formulations of the repulsive curves, or perhaps we should try the use of more accurate expansions for the two electron integrals.

One attractive feature of this method is that it gives a purely electrostatic picture of bond formation. Both the kinetic energy of the electrons and the exchange energy between the pair of electrons which form the bond have been absorbed into the background leaving just the electrostatic interactions between the electron clouds and the nuclei to determine the bond energy and the potential energy curve. It should be appreciated, of course, that this result is not so clear-cut as this statement suggests. The electron kinetic energy must change on molecule formation and this point requires further study.

Taking the individual molecules now, the hydrogen, lithium and lithium hydride molecules are two electron problems with no main coulomb term to

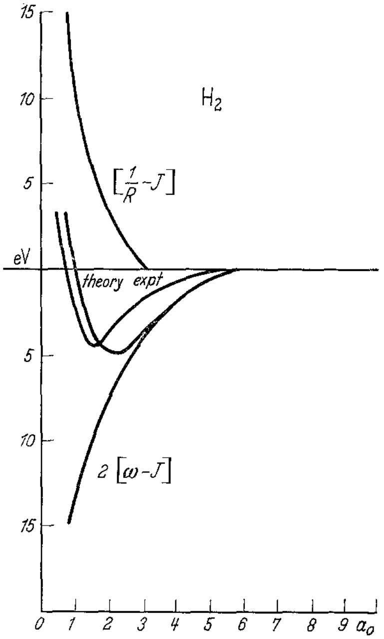

Fig. 1

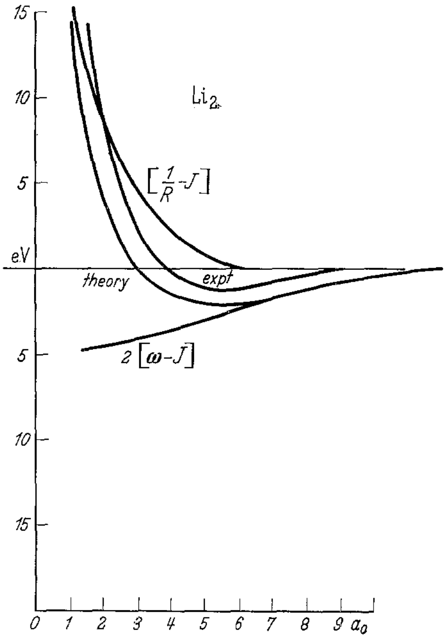

Fig. 2

Fig. 1—7. In order to give the usual appearance to the potential energy curve, positive values of $2(\omega - J)$ are plotted below the line and positive values of the coulomb terms above the line. Internuclear distances in Bohr radii (0.529 Å). The curve is drawn from Eqs. (11) and (24)

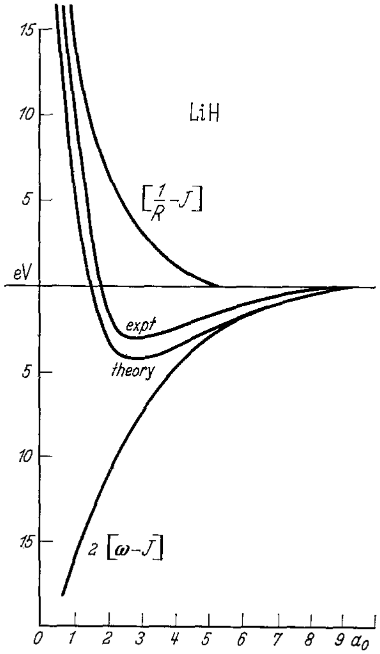

Fig. 3

complicate matters. These are simple molecules but they do differ in that the hydrogen molecule has a short strong bond, the lithium molecule has a long weak bond and the lithium hydride molecule is intermediate between the two. This work easily reproduces these differences. This result is a confirmation of the use of $J(\nu_a \nu_b)$ in place of $J(\mu, \mu)$ for all bond lengths. It is true that the calculated curves do lie somewhat below the experimental ones on the long bond length side and this may be a result of using $J(\nu_a \nu_b)$ in place of $J(\mu, \mu)$ because the latter is commonly 1 to 2 eV larger at the equilibrium internuclear distance and this is about right to explain the discrepancy. Notice that the variation theorem does not apply here because the integrals are being approximated.

The result for the hydrogen molecule is interesting because the original theory

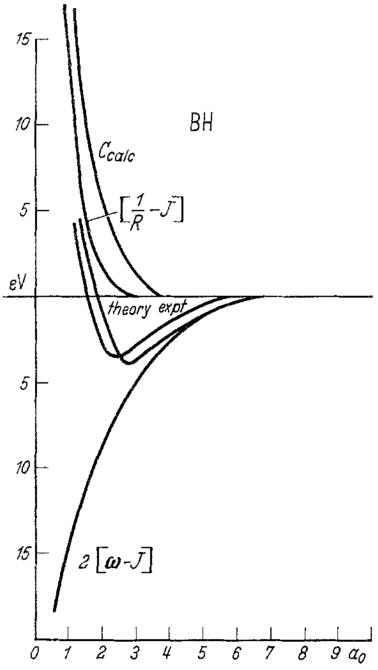

Fig. 4

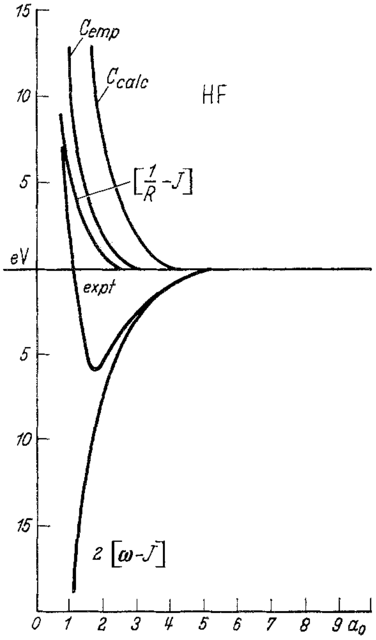

Fig. 5

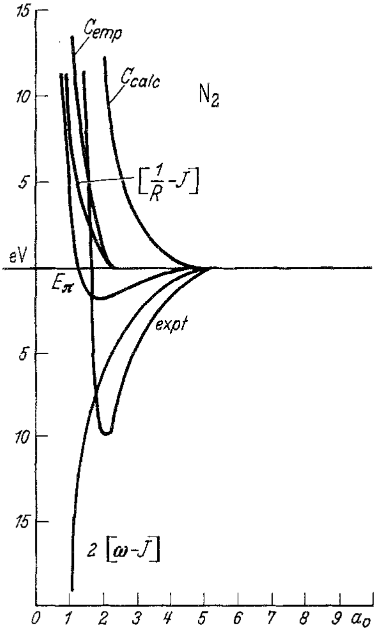

Fig. 6

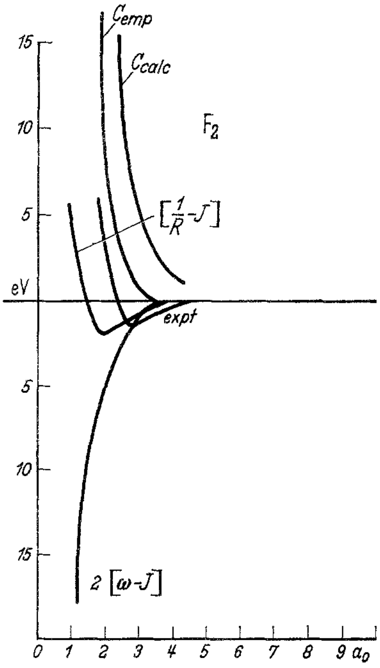

Fig. 7

gives about 2.5 eV for the bond energy at the equilibrium internuclear distance. This represents an error of about 2 eV, one half of which is the correlation error and the other half comes from the use of an approximate form for the molecular orbital. It seems that when we replace $J(\mu, \mu)$ by $J(\nu_a \nu_b)$ we recover not only the correlation error but also the error which comes from the use of an approximate form for the molecular orbital. This result seems fortuitous but it may be possible to exploit it constructively in the future if it proves to be general.

The lithium hydride result is interesting in another way. The result in Fig. 3 was obtained while ignoring both the polarity of the bond and any hybridisation in the lithium valence atomic orbital. Evidently these two factors do not play a *large* part in determining the bond energy and the potential energy curve. This is consistent with other findings [*6i*].

The BH molecule in Fig. 4 is the first example in which the main coulomb term is present and it is also the first case in which we use the $1/r$ approximation in place of the Ω operator. The explicit form of the main coulomb term in this case is

$$C = 2/R - 2\,J(1s_{\mathrm{H}}, 2s_{\mathrm{B}})\,.$$

The agreement between the experimental and calculated potential energy curves is so good that both approximations are surely working well here. The figure shows the three separate terms which enter the bond energy and it is easy to see by inspection that if one were to leave out the main coulomb term C the resulting bond would be about twice too strong and much too short. It seems that already in this case the other electrons of the two atoms are important in determining the bond strength and the bond length. We have again ignored the fact that the bond in the BH molecule is slightly polar and that there might be some hybridisation in the valence atomic orbital which the boron atom uses to form the bond. It is clear that any effects form these two sources are not very large.

The results for the hydrogen fluoride molecule take us one step further and show what happens when more electrons contribute to the main coulomb term. The latter is now given by

$$C = 6/R - 2\,J(1s_{\mathrm{H}}, 2s_{\mathrm{F}}) - 4\,J(1s_{\mathrm{H}}, 2p\pi_{\mathrm{F}})$$

and it is clear from the figure that this term is too repulsive. This is the first case in which we derive an empirical main coulomb term by taking the difference between the other two terms and the experimental result. It is clear that the empirical main coulomb term is very like the calculated one but shifted along the axis. It is also clear that the part of the experimental potential energy curve to the long bond length side of about 2.5 a_0 is determined by the attractive curve alone. So even if we cannot find the whole curve, we can find a substantial part of it.

The nitrogen molecule results are more complicated in that there is a triple bond and, although each bond has its own internal coulomb term, there is only one main coulomb term. It turns out that it is best to take the π bond with its internal coulomb term and define

$$E_\pi = 2\,[\omega_\pi - J_\pi] - [1/R - J_\pi]\ .$$

This function has the simple behaviour shown in the figure. Interestingly enough, there is a minimum in this curve at just the correct point and this result should be explored further. As to the σ bond of the nitrogen molecule, this behaves rather like that of the hydrogen fluoride molecule, the calculated form of the main coulomb term being clearly too repulsive. So again we find an empirical main coulomb term as in the figure, although that part of the potential energy curve to the right of the minimum is again largely determined by the attractive curves.

The results for the fluorine molecule in Fig. 7 are included to show that matters are not always as simple as in the earlier examples. The results are consistent with the others in that the calculated main coulomb term is too repulsive and that the attractive curve is quite close to the experimental curve at long bond lengths. It does seem odd, however, that the internal coulomb term should be attractive while in all the other examples it is negative or repulsive.

Conclusions

The point of this work is to get as close as possible to the experimental facts without introducing ill-defined quantities into the theory (coulomb integrals, resonance integrals, electronegativity etc.) but without resorting to the use of elaborate wave functions and extensive computations. In some senses, the work is intermediate between the elaborate methods and the use of such devices as MULLIKEN's magic formula [5]. The results are disappointing in that we cannot get the whole of the potential energy curve and perhaps a semi-empirical formulation of the main coulomb term is required. On the other hand, we can get the long bond length side of the potential energy curve and this is the part that matters as far as potential energy surfaces are converned, so perhaps this method will prove helpful for the chemical reactivity problem. Another problem which we may study is the nature of the carbon-hydrogen bond and why it is that the bond energy of this bond is variable. Finally, it is important to see how it is that the bond energy can be given by twice the binding energy of a molecular orbital, as we commonly suppose, and the present results show this result reasonably clearly.

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