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A New Approach to the Molecular Orbital Theory of Bonding

By

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The Moffitt 'Atoms in Molecules' approach [8] and the Mulliken approximation [11] to two-centre integrals have been applied to M. O. Theory to give a simple equation for the energy of a diatomic molecule in terms of atomic spectral parameters and nuclear attraction integrals.

The equation has been used to calculate the potential energy curves of 24 electronic states of the diatomic hydrides of second row elements and 24 states of the corresponding iso-electronic singly charged positive molecular ions. The agreement between the calculated and experimental values of the energies, the equilibrium internuclear separations, the force constants and the dipole moments is satisfactory.

L'approximation de Moffitt «atomes en molécules» [8] et l'approximation de Mulliken pour les intégrales bicentriques [11] sont utilisées dans la méthode des O. M. pour obtenir une équation simple pour l'énergie d'une molécule diatomique, contenant des termes en fonction de données de spectroscopie atomique et des intégrales d'attraction nucléaire.

Cette équation est utilisée pour l'évaluation des courbes d'énergie potentielle pour 24 états électroniques des hydrures diatomiques des éléments de la deuxième période et de 24 états des mono-cations moléculaires correspondants isoélectroniques. L'agrément est satisfaisant entre les résultats calculés et les données expérimentales de l'énergie, des distances internucléaires d'equilibre, des constantes de force et des moments dipolaires.

Die Moffittsche Näherung der „Atome in Molekülen“ [8] und die Mullikensche Näherung für Zweizentrenintegrale [11] wurden auf die MO-Theorie angewandt, um eine einfache Gleichung für die Energie eines zweiatomigen Moleküls mit Termen aus atomaren Spektralparametern sowie Kernwechselwirkungsintegralen zu erhalten.

Diese Gleichung wurde benutzt, um Potentialkurven für 24 elektronische Zustände zweiatomarer Hydride von Elementen der zweiten Hauptreihe zu berechnen sowie 24 Zustände der korrespondierenden isoelektronischen, positiv einfach geladenen Ionenmoleküle zu bestimmen. Die Übereinstimmung zwischen berechneten und experimentellen Werten der Energie, der Gleichgewichtsabstände, der Kraftkonstanten und der Dipolmomente ist befriedigend.

I. Introduction

In spite of the considerable improvements in high speed computing techniques in recent years, there is still a need for calculations of molecular properties by semi-empirical methods which involve less computational effort than the more rigorous approaches. For example, Moffitt's 'Atoms in Molecules' method [8], which regards bonding as a perturbation of the atoms forming the molecule, has been used very successfully in modified forms (see Parr [13]).

This paper describes an attempt to simplify the L. C. A. O. molecular orbital approach to bonding by relating the one-centre integrals to the energies of *atomic orbitals*, and by introducing certain approximations to some of the more complex multi-centre integrals. This procedure gives a simple equation for the energy of a molecule in terms of the atomic energy levels of the constituent atoms (or ions) and the coulombic interaction between these atoms (or ions).

The general method is outlined for diatomic molecules, and we give the results of calculations on some of the spectroscopic states of the diatomic hydrides of second row elements, and the corresponding positively charged molecular ions.

Later papers will discuss the application of the method to polyatomic molecules.

II. Diatomic Molecules

1. Energy Equation

Consider the diatomic molecule formed from atoms X and Y by placing one electron from X and one electron from Y in a bonding molecular orbital of the form

$$(aA + bB)/(a^2 + b^2 + 2\,abS)^{\frac{1}{2}} \tag{1}$$

where A and B are normalised atomic orbitals (possibly hybrid) of atoms X and Y respectively, and S is their overlap integral. a and b are undetermined coefficients.

Suppose that atom X has a set of non-bonding atomic orbitals $C_1, C_2, C_3 \ldots C_k \ldots$ If we are to relate the orbitals A, C_1, C_2, $C_3 \ldots C_k \ldots$ to the eigenfunctions of atom X, they must form an orthonormal set. Similarly, the atom Y is considered to have an orthonormal set of non-bonding atomic orbitals D_1, D_2, $D_3 \ldots D_m \ldots$ which are orthogonal to atomic orbital B. The non-bonding orbitals are not necessarily orthogonal to the molecular orbital, nor are any of the C_k orbitals necessarily orthogonal to any of the D_m orbitals. The effects of lack of orthogonality are considered in section II 3 and in Appendix 4.

If two electrons occupy the molecular orbital, the wave function for the molecule can be assumed to be formed from linear combinations of determinantal functions of the form

$$\Psi = det\,[(aA + bB)(1)s_1 \quad (aA + bB)(2)s_2 \quad C_1(3)s_3 \ldots C_k\,(i)\,s_i \ldots D_m\,(N)\,s_N]/d\,.\,\sqrt{N!} \tag{2}$$

where N is the number of electrons, d is equal to $a^2 + b^2 + 2\,abS$, *det* signifies a determinantal function, and s_i indicates electron spin + or $-\frac{1}{2}\cdot h/2\,\pi$. The wave function will have to be an eigenfunction of the spin and angular momentum of the molecule.

The above type of wave function gives an equation for the energy of the molecule consisting of four sets of integrals as shown in Appendix 1.

The Hamiltonian operator is subdivided as follows:

$$H = H_X + H_Y + H' + H'' \tag{3}$$

where H_X and H_Y are the Hamiltonian operators for the electrons in the *isolated* atoms X and Y respectively. H' is the operator for interaction between the ions X^+ and Y^+, where X^+ and Y^+ are formed by loss of electrons from atomic orbitals A and B respectively, H'' is the operator for all other interactions.

The one-centre integrals derived from H_X and H_Y are identified with the energies of the atomic orbitals of atoms X and Y (Appendix 2), and approximations similar to those devised by MULLIKEN [*11*] are introduced for some of the two-centre integrals (Appendix 3) to give the following equation for the energy of the molecule:

$$E = E\,(X^+) + E\,(Y^+) + E_{rep}\,(X^+\,Y^+) \tag{4a}$$

$$+ 2\,\varrho_A\,E\,(A) + 2\,\varrho_B\,E\,(B) \tag{4b}$$

$$
\begin{aligned}
&+ 2\,\varrho_A\,[- \mid Z_Y \mid AA \mid + \sum_m (\mid AA \mid D_m\,D_m \mid - \tfrac{1}{2} \mid AD_m \mid AD_m \mid)] \\
&+ 2\,\varrho_B\,[- \mid Z_X \mid BB \mid + \sum_k (\mid BB \mid C_k\,C_k \mid - \tfrac{1}{2} \mid BC_k \mid BC_k \mid)] && \text{(4c)} \\
&+ \varrho_A^2 \mid AA \mid AA \mid + \varrho_B^2 \mid BB \mid BB \mid && \text{(4d)} \\
&+ 2\,\varrho_A\,\varrho_B \mid AA \mid BB \mid && \text{(4e)} \\
&+ \frac{abS}{d}[- \mid Z_X \mid AA \mid + \sum_k (\mid AA \mid C_k\,C_k \mid - \tfrac{1}{2} \mid AC_k \mid AC_k \mid) \\
&- \mid Z_Y \mid BB \mid + \sum_m (\mid BB \mid D_m\,D_m \mid - \tfrac{1}{2} \mid BD_m \mid BD_m \mid) \\
&+ \varrho_A \mid AA \mid AA \mid + \varrho_B \mid BB \mid BB \mid && \text{(4f)} \\
&+ \mid Z_Y \mid AA \mid - \sum_m (\mid AA \mid D_m \mid D_m \mid - \tfrac{1}{2} \mid AD_m \mid AD_m \mid) \\
&+ \mid Z_X \mid BB \mid - \sum_k (\mid BB \mid C_k\,C_k \mid - \tfrac{1}{2} \mid BC_k \mid BC_k \mid) \\
&- \mid AA \mid BB \mid]
\end{aligned}
$$

where

$$\varrho_A = (a^2 + abS)/d \qquad \text{and} \qquad \varrho_B = (b^2 + abS)/d = 1 - \varrho_A\ . \tag{5}$$

The integrals in equation (4) are of three types:

Nuclear attraction integrals e. g. $\mid Z_Y \mid AA \mid$ representing the potential energy of attraction of an electron in A to the nuclear charge Z_Y.

Coulombic repulsion integrals between electrons in specified orbitals e. g. $\mid AA \mid AA \mid$, $\mid AA \mid D_m\,D_m \mid$.

Exchange integrals involving specified orbitals e. g. $\mid AD_m \mid AD_m \mid$, $\mid AC_k \mid AC_k \mid$.

$E\,(X^+)$ and $E\,(Y^+)$ are the energies of the isolated ions X^+ and Y^+ formed by removing electrons from orbitals A and B respectively, and $E_{rep}\,(X^+\,Y^+)$ is the potential energy of repulsion involved when the ions approach each other.

$E\,(A)$ and $E\,(B)$ are the 'energies' of the atomic orbitals A and B respectively i. e. the difference in energy between X and X^+ and between Y and Y^+.

2. 'Model' for Bonding

The energy equation (4) is *mathematically* equivalent to that for the following hypothetical model for the formation of a single bond.

The energy associated with the ions X^+ and Y^+ at a given internuclear separation is given by section (4a). The formation of the bond can be regarded as being equivalent to placing an amount of charge $2\,\varrho_A$ in *atomic orbital* A, and an amount of charge $2\,\varrho_B$ in *atomic orbital* B as shown diagrammatically in Fig. 1. The density in each orbital is equally distributed between spin α and spin β i. e. corresponds to randomised spin. The terms (4b) correspond to the energies of the charge densities $2\,\varrho_A$ and $2\,\varrho_B$ in their respective *atomic orbitals*, and section (4c) gives the potential energies of attraction of charge density $2\,\varrho_A$ to the ion Y^+ and of charge density $2\,\varrho_B$ to the ion X^+.

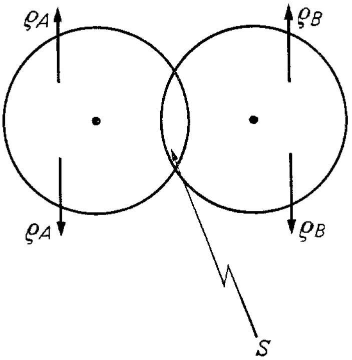


Fig. 1. "Model" for Bonding

The terms (4d) and (4e) correspond to the energy of repulsion between two electrons with opposed spin 'shared' between the two atomic orbitals as shown in Fig. 1.

The terms (4f) can be compared to a '*bonding*' or '*antibonding*' term arising from the overlap S between the atomic orbitals A and B. If abS/d is positive section (4f) produces stabilisation (*bonding*) and if it is negative it will produce destabilisation (*antibonding*).

For the model to be valid ϱ_A (and ϱ_B) must be restricted to the range 0 to 1 and the values of a and b must correspond to this situation.

It is not proposed that the above model has any physical reality, but, if the approximations to molecular orbital theory are reasonable, then the model can be said to be approximately equivalent energetically to the molecular orbital model of the chemical bond.

3. Orthogonality Correction

The non-bonding orbitals C_k are not necessarily orthogonal to the molecular orbital, the deviation from orthogonality being dependent on the overlap integral S' between orbitals B and C_k. If we have a pair of electrons in C_k, then the correction term required is (see Appendix 4)

$$a'\,b'\,S'\,[I]/(a'^2 + b'^2 + 2\,a'\,b'\,S') \tag{6}$$

with

$$b'/a' = -\,bS'/(b + aS) \tag{7}$$

$[I]$ is of the same form as the term in braces in section (4f) of the energy equation.

The correction embodied in equations (6) and (7) is adequate, provided S' is less than 0.3 which is, fortunately, the case for all the molecules treated so far by this method. If S' is greater than 0.3 other correction terms must be added if serious errors are to be avoided.

The correction must be applied for all orbitals C_k and D_m which are not orthogonal to the molecular orbital (the correction involving D_m will include the overlap integral for A and D_m), and a correction is also required for lack of orthogonality between any of the C_k and any of the D_m atomic orbitals.

4. Quadratic Character of the Energy Equation

ϱ_A can take any value in the range 0 to 1. If $\varrho_A = 0$ (i. e. $\varrho_B = 1$) or if $\varrho_A = 1$ (i. e. $\varrho_B = 0$), the bonding is completely ionic, and the molecule consists of ion pairs $X^+\,Y^-$ or $X^-\,Y^+$ respectively. If $\varrho_A = \varrho_B = 0.5$ then $a = \pm\, b$ and the two electrons are equally shared between the two atoms. Other values of ϱ_A and ϱ_B correspond to various degrees of ionic and covalent character of the bond.

However, we can evaluate the energy of the molecule, with the help of atomic spectral data, only for the three values of ϱ_A specified above, since it is only for these cases that we can identify the atomic orbitals with those of specific atoms or ions. The unique determination of minimum energy with respect to ϱ_A therefore requires that equation (4) must be of the form:

$$E = c_0 + c_1\,\varrho_A + c_2\,\varrho_A^2 \tag{8}$$

with

$$\begin{aligned} c_0 &= E_0 \\ c_1 &= 4\,E_{0.5} - 3\,E_0 - E_1 \\ c_2 &= 2\,(E_1 - 2\,E_{0.5} + E_0) \end{aligned} \tag{9}$$

where E_0, $E_{0.5}$ and E_1 are the energies of the molecule for $\varrho_A = 0, 0.5$ and 1 respectively.

In this case, the minimum energy, E^*, is given by:

$$E^* = c_0 + \tfrac{1}{2}\, c_1\, \varrho_A^* \tag{10}$$

with

$$\varrho_A^* = -\, c_1/2\, c_2\,. \tag{11}$$

Equation (4) is approximately quadratic in ϱ_A and equations (8) to (11) can be used to evaluate the minimum energy, and the corresponding value of ϱ_A (ϱ_A^*) if the following statements are true.

Using Koopman's Theorem

$$E\,(A) = -\, IP\,(A); \qquad E\,(B) = -\, IP\,(B) \tag{12}$$

where IP (A) and IP (B) are the ionisation potentials of the specified orbitals. Section (4b) of the energy equation is therefore linear with respect to ϱ_A. (However, see Birss and Laidlaw [2].)

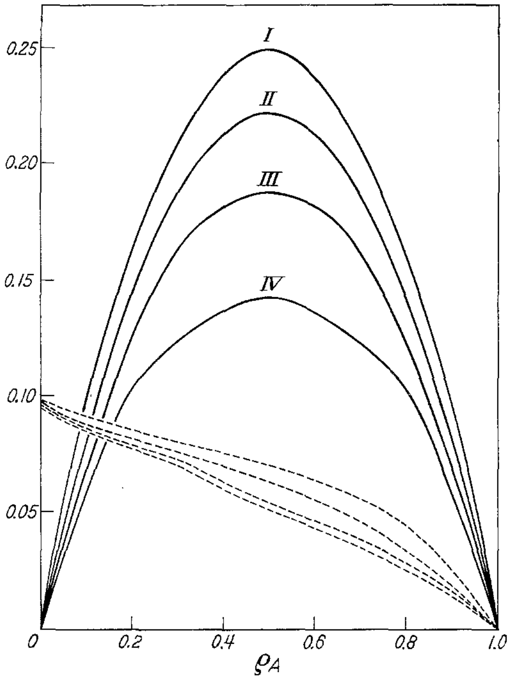


Fig. 2. Plots of abS/d and $a'b'S'/(a'^2 + b'^2 + 2a'b'S')$ vs. ϱ_A. —— abS/d, ----- orthogonality term with $S' = 0.3$, $[I] = 1$. I $S = 1.0$, II $S = 0.8$, III $S = 0.6$, IV $S = 0.4$
(The dotted lines are to be numbered from I to IV, beginning from the bottom)

It can also be assumed that section (4c) is linear, since the values of the two-centre integrals will not change significantly with ϱ_A.

Sections (4d) and (4e) will be quadratic in ϱ_A if we assume that [12]

$$\begin{aligned} |\, AA \,|\, AA \,| &= IP\,(A) - EA\,(A) \\ |\, BB \,|\, BB \,| &= IP\,(B) - EA\,(B) \end{aligned} \tag{13}$$

where EA (A) and EA (B) are the electron affinities of orbitals A and B respectively.

It is shown in Fig. 2 that, provided S is reasonably large, abS/d tends to be quadratic in ϱ_A, and the orthogonality correction terms tend to be linear in ϱ_A. We therefore use equations (8) to (11) to calculate the energy of the molecule and the electron distribution in the bond.

III. Diatomic Hydrides of Second Row Elements

1. Introduction

We have calculated from equations (4), (9), (10) and (11), the potential energy curves of some spectroscopic states of the diatomic hydrides XH of the second row elements Li to F inclusive. Experimental data on these molecules are fairly comprehensive, and numerous calculations have been made on them [*1*]. They therefore provide a good test of the validity of the assumptions made in the derivation of equation (4).

We have considered only those states of the hydrides which can be assumed to be derived mainly from appropriate combinations of $2s$ and $2p$ atomic orbitals of the second row element X and the $1s$ atomic orbital of hydrogen.

2. Atomic Orbitals

We use Slater type orbitals

$H\,(1s) = [\delta_H^3/\pi]^{\frac{1}{2}} \cdot \exp\,(-\,\delta_H\, r)$ labelled H

$X\,(1s) = [\delta_1^3/\pi]^{\frac{1}{2}} \cdot \exp\,(-\,\delta_1 r)$ labelled $1s$

$X\,(2s) = [\delta^5/\pi]^{\frac{1}{2}}\, r \exp\,(-\,\delta r)$ labelled s

$X\,(2\,p\sigma) = [\delta^5/\pi]^{\frac{1}{2}}\, r \exp\,(-\delta r) \cdot \cos\theta$ labelled $p\sigma$

$X\,(2\,p\pi) = [\delta^5/2\,\pi]^{\frac{1}{2}}\, r \exp\,(-\,\delta r) \cdot \sin\,\theta \cdot \exp\,(i\, m_l\, \Phi)$ labelled π for $m_l = +1$
labelled π' for $m_l = -1$.

The bonding atomic orbital A is assumed to be a hybrid of the form:

$$A = (s + \lambda p)/(1 + \lambda^2)^{\frac{1}{2}} . \qquad (14)$$

There are no non-bonding atomic orbitals D_m associated with the hydrogen atom, and the non-bonding atomic orbitals C_k are orthogonal to A. Neglecting lack of orthogonality between Slater type $1s$ and $2s$ orbitals, the possible C_k orbitals are the $1s$ orbital of X, the orbitals π and π' and the hybrid orbital σ given by:

$$\sigma = (\lambda s - p_\sigma)/(1 + \lambda^2)^{\frac{1}{2}} . \qquad (15)$$

The exponent δ_1 for the $1s$ orbital of X was chosen to be the Slater value, $Z - 0.3$, where Z is the nuclear charge. The value of δ was assumed to be the same for $2s$, $2p_\delta$ and $2p_\pi$ atomic orbitals, and was calculated from spectroscopic data (Appendix 6). The values of δ were found to be approximately equal to those derived from SLATER's rules [*18*]. The exponent of the hydrogen $1s$ orbital is calculated from data on the species H^+, H and H^-.

3. Electronic States

We have considered only those states which can be expressed generally as follows:

$$1s^2\,\sigma^x\,(\pi\pi')^{Z-3-x}\,(AH)^2 \tag{16}$$

where $(AH)^2$ signifies two electrons with opposed spin in the bonding molecular orbital of the form

$$(aA + bH)/(a^2 + b^2 + 2\,abS)^{\frac{1}{2}} \tag{17}$$

x can take the values 0, 1 and 2, specific states being derived from the possible arrangements of the non-bonding electrons in the σ, π and π' atomic orbitals as shown in Tab. 1. States bracketted together differ only in the arrangements of electron spin in the σ, π and π' atomic orbitals. $(Z - 3 - x)$ is the total number of electrons in both the π and π' orbitals.

For convenience in computation, we calculated initially the energies of molecules with randomised spin (denoted $\overset{\uparrow}{\top}$) for the non-bonding orbitals, e. g. for two electrons in π and π' orbitals we calculated the energy of the state involving $\pi\overset{\uparrow}{\top}\pi'\overset{\uparrow}{\top}$, and for an electron in a σ orbital and two electrons in π orbitals we considered only the state involving $\sigma\overset{\uparrow}{\top}\pi\overset{\uparrow}{\top}\pi\overset{\uparrow}{\top}$. These are not true spin states of the molecule, but these were readily obtained from the randomised spin states using the exchange integrals for the σ, π and π' orbitals, e. g. the $^3\Pi$ and $^1\Pi$ states of *BH* arise from one electron in a σ orbital and one in a π orbital. We calculated the energy of the state

$$1s^2\,\sigma\overset{\uparrow}{\top}\,\pi\overset{\uparrow}{\top}\,(AH)^2\,.$$

The $^3\Pi$ state can be written as:

$$1s^2\,\sigma\overset{\uparrow}{\top}\,\pi\uparrow\,(AH)^2$$

which is lower in energy than the randomised spin state by $\frac{1}{2}K_{\sigma\pi}$, where $K_{\sigma\pi}$ is the exchange integral for a σ and a π orbital, obtained from atomic spectral data as shown in Appendix 5.

The two states with opposed spin

$$1s^2\,\sigma\uparrow\,\pi\downarrow\,(AH)^2 \text{ and } 1s^2\,\sigma\downarrow\,\pi\uparrow\,(AH)^2$$

are $\frac{1}{2}K_{\sigma\pi}$ higher in energy than the spin randomised state. The configuration interaction $K_{\sigma\pi}$ between these two states gives one of the components of the $^3\Pi$ state and the $^1\Pi$ state as shown in Fig. 3.

The energy relationships between the $^3\Sigma^-$, $^1\Delta$, $^1\Sigma^+$ and randomised spin states of *BH* derived from two electrons in π orbitals are shown in Fig. 4.

Using randomised spin means that initially we needed to consider only one molecular state for given values of Z and x [in $1\,s^2\sigma^x\,(\pi\pi')^{Z-3-x}\,(AH)^2$] which simplified the program for the calculations considerably. The randomised states were then split into true spin components as exemplified by Figs. 3 and 4.

However, we found that it was impossible, using this simple theory, to calculate the effects of the very important configuration interactions between the two $^1\Sigma^+$ states of *BH*, and the two $^2\Pi$ states of *CH* and the two $^1\Sigma^+$ states of *NH*, since in these cases the form of the molecular orbital is not necessarily the same for the two states concerned i. e. the percentages of $2s$ and $2p$ character and the degrees of ionic character may be different in the two states. The interaction between the two states can no longer be represented simply by an atomic exchange integral.

We should also have included contributions to the specified states from structures having a single electron in the molecular orbital AH or even no electrons in AH, and considered the possibility of the two bonding electrons occupying different molecular orbitals.

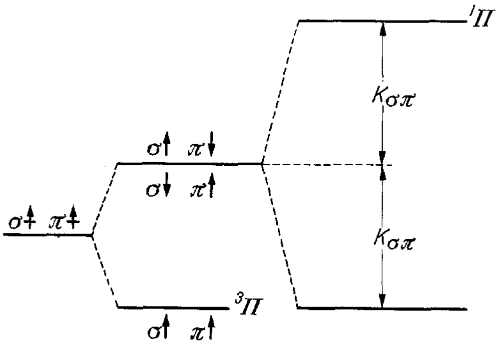


Fig. 3

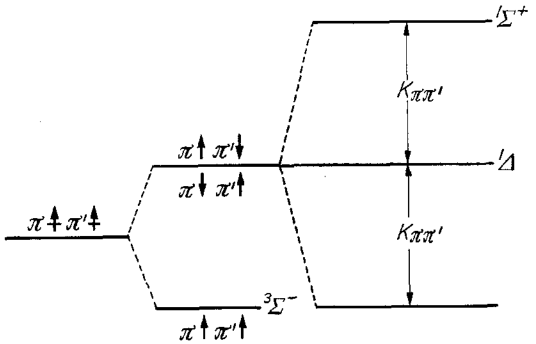


Fig. 4

Fig. 3. Configuration interaction for $^3\Pi$ and $^1\Pi$ states of BH

Fig. 4. Configuration interaction for $^3\Sigma^-$, $^1\Delta$ and $^1\Sigma^+$ states of BH

The consequences of omitting interactions of this type are discussed later.

4. Energy Equation for Diatomic Hydrides

The energy equation for the diatomic hydrides was obtained from equation (4) by substituting atomic orbital H for the general atomic orbital B, by replacing Z_Y by Z_H (equal to 1), by putting $m = 0$ (no D_m orbitals), and by treating the $1s$ orbital of X, the σ, π and π' orbitals as C_k orbitals. The $1s$ and σ orbitals required orthogonality corrections [equations (6) and (7)].

The energies (in eV) were computed for $\varrho_A = 0$, 0.5 and 1, for $\lambda^2/(1+\lambda^2)$ equal to 0.0 to 1.0 in steps of 0.2 and for the internuclear separation R equal to 1.0 to 5.0 a. u. in steps of 0.25 a. u. using the Atlas computer.

a) $\varrho_A = 0$

If $\varrho_A = 0$ we have the ion X^+ with electronic structure $1s^2\,\sigma^x\,(\pi\pi')^{Z-3-x}$ and the ion H^- $1s^2$. The energy of this state of X^+ relative to the ground state of atom X is equal to the ionisation potential of X plus the excitation (valence state) energy required to produce the above state of X^+ from the ground state of X^+. The energy of H^- relative to the hydrogen atom is equal to the *increase* in energy when H^- is formed from the hydrogen atom (i. e. $-$ 0.75 eV [*4*]).

The ionisation potential of atom X was taken from Moore's compilation [*10*], and the valence state energies of X^+ were expressed in terms of Slater-Condon parameters [*3*], then as a mixture of spectroscopic states using the procedure of Moffitt [*9*]. Atomic energy levels were taken from Moore, the energies of any unobserved terms being obtained by linear extrapolation of the energy levels of corresponding isoelectronic atoms or ions. (See Rohrlich [*15*].) Details are given in Appendix 5.

The energy of interaction between X^+ and H^- was calculated from the appropriate nuclear attraction, coulomb repulsion and exchange integrals and from the orthogonality correction terms for the 1s and σ orbitals of X. There is no 'bonding term' since for $\varrho_A = 0$, $abS/d = 0$.

The two-centre coulomb and exchange integrals for the $1s$ orbital of hydrogen and either the $1s$, the σ or the π orbital of X are rather difficult to evaluate. Fortunately, the exchange integrals are fairly small, and it was found that the coulomb repulsion integrals could be calculated sufficiently accurately by the following method.

We expressed the nuclear atttaction integral for a $2s$ orbital and a proton at a distance R as

$$s\,(2s)\cdot e^2/R\,. \tag{18}$$

Similarly, the attraction of an electron in a $1s$ atomic orbital to a proton at the same distance R was taken to be

$$s\,(1s)\cdot e^2/R\,. \tag{19}$$

$s\,(2s)$ and $s\,(1s)$ tend to unity for large values of R and lie in the range 0.8 to 1.0 for most of the cases treated here. They are readily calculated from equations given by ROOTHAAN [*16*] for two centre nuclear attraction integrals, and are relatively simple functions of the product of the exponent of the orbital and R, see Appendix 7. We assumed that

$$|\,1s\,1s\,|\,2s\,2s\,| = s\,(1s)\,s\,(2s)\,.\,e^2/R\,. \tag{20}$$

Equation (20) was tested using the tabulated integrals of KOTANI et al. [*7*], and it was found that errors no greater than 0.3 eV were introduced by neglecting the exchange integrals and using equation (20), for the diatomic hydrides.

Similar approximations were made for the integrals $|\,1s\,1s\,|\,2p_\sigma\,2p_\sigma\,|$, $|\,1s\,1s\,|\,2p_\pi\,2p_\pi\,|$ and $|\,1s\,1s\,|\,2s\,2p_\sigma\,|$, and hence the potential energy of attraction between the ions X^+ and H^- was calculated at the specified internuclear separations solely from the equations of Roothaan for the two-centre nuclear attraction integrals. The orthogonality terms for $\varrho_A = 0$ are dealt with in section (d).

b) $\varrho_A = 0.5$

In this case the 'atoms' in the molecule are

$$X\ [1s^2\,\sigma^x\,(\pi\pi')^{Z-3-x}\,A\,\overset{\uparrow}{+}]\ \text{and}\ H\ (1s\,\overset{\uparrow}{+})\,.$$

$\overset{\uparrow}{+}$ signifies randomised spin, and from the model this involves 'half an electron' having spin α and 'half an electron' having spin β, the repulsion between the two half electrons giving energy terms $|\,AA\,|\,AA\,|/4$ and $|\,HH\,|\,HH\,|/4$. The energies of the bonding states of the atoms relative to the ground state atoms is therefore given by the valence state energy of X plus the terms $|\,AA\,|\,AA\,|/4$ and $|\,HH\,|\,HH\,|/4$, calculated as shown in Appendix 5.

The two-centre nuclear attraction and coulomb integrals for interaction between the two atoms were calculated using the procedure described for $\varrho_A = 0$.

The leading term of the bonding energy [equation (*4* f)] becomes $S/2\ (1 + S)$ for $\varrho_A = 0.5 = \varrho_B$ (i.e. $a = b$ for a *bonding* molecular orbital). This term and the orthogonality correction terms are dealt with in section (d).

c) $\varrho_A = 1$

For $\varrho_A = 1$, we have the ion pair $X^-\ (1s^2\,\sigma^x\,(\pi\pi')^{Z-3-x}\,A^2)$ and H^+.

The energies of the two isolated ions will therefore be given by the ionisation potential of hydrogen, the electron affinity of X (taken from EDLÉN's paper [*4*]), and the valence state energy of X^-. Spectroscopic data for X^- were obtained by linear extrapolation of the data for corresponding isoelectronic atoms and positive ions.

The potential energy of attraction of a proton to the ion X^- was obtained directly from the appropriate nuclear attraction integrals for $1s$, σ and π orbitals.

The bonding and orthogonality terms are zero for $\varrho_A = 1$ (i.e. $b = 0$).

d) Bonding and Orthogonality Terms

For $\varrho_A = 0.5$

$$abS/d = S/2\,(1 + S)\,. \tag{21}$$

The one-centre integrals in the bonding term were calculated from the energies of atoms and ions using the Virial Theorem (Appendix 6) and were found to be equal to

$$-\,13.6\,[(Z - 2)\,(\delta_1 - \delta_3) + \delta_1 + \delta_3]\,\delta_2 - 16.67 \tag{22}$$

where δ_1, δ_2 and δ_3 are the exponents of the $2s$, $2p_\sigma$ and $2p_\pi$ orbitals of the species X^-, X and X^+ respectively, and 16.67 is the value for the one-centre integrals involving the hydrogen $1s$ orbital.

The two-centre integrals in the bonding term were evaluated in the usual way.

The form of $[I]$ in equation (6) is the same as the corresponding term in braces in the bonding term (4 f). We therefore used the value given by equation (22) for a pair of electrons in the σ orbital, and half this value for a single electron in the σ orbital.

$[I]$ for the orthogonality term of the $1s^2$ shell involves the potential energy of attraction of a $1s$ electron to the nucleus given by:

$$-\,27.2\,Z\delta_{1s}\,. \tag{23}$$

The above term is so much greater than all the other terms in $[I]$ that these were neglected. The whole orthogonality term is very small due to the small value of the overlap integral of the $1s$ orbital of X and the hydrogen $1s$ orbital at the internuclear separation of interest.

e) Minimisation of Energy

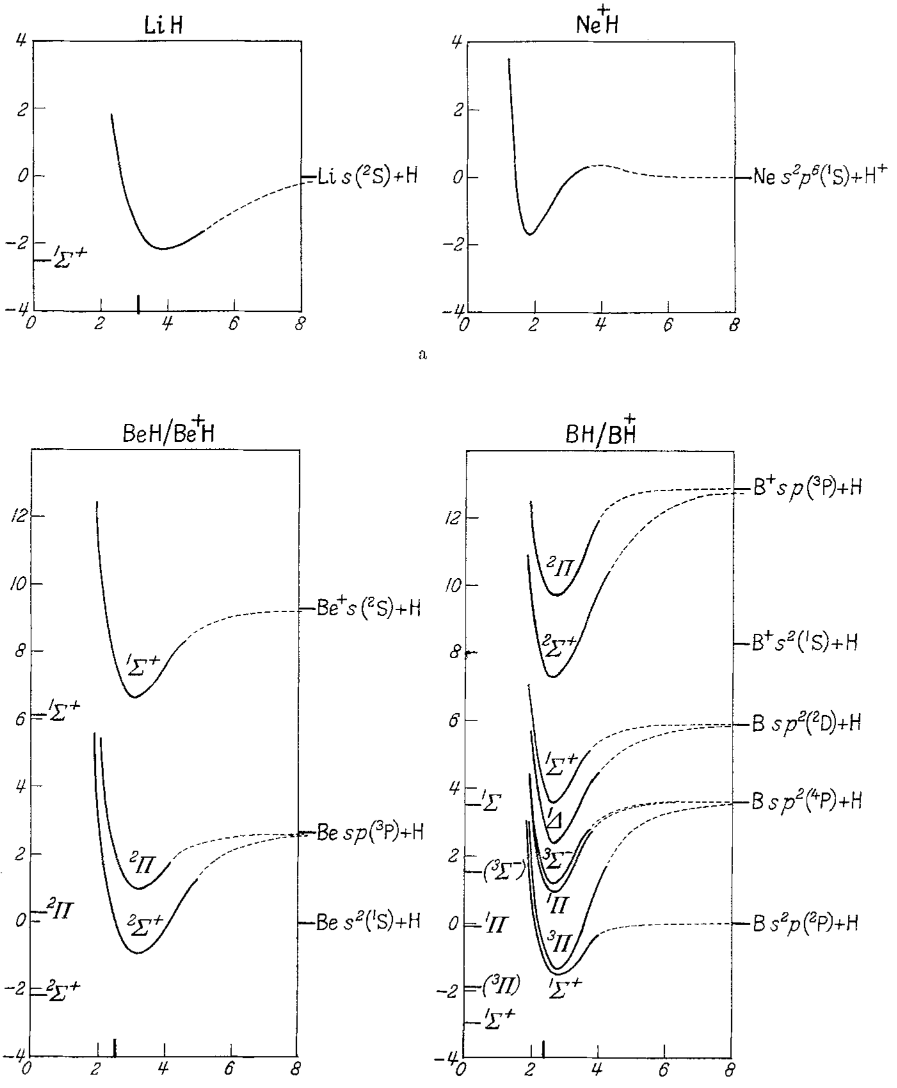
Minimum energy with respect to ϱ_A for given values of λ and R was obtained using equations (8), (9) and (10). The corresponding value of ϱ_A (ϱ_A^*) was given by equation (11). Minimum energy, for a given value of R, with respect to ϱ_A *and* λ was then calculated by plotting the minimum energies with respect to ϱ_A against $\lambda^2/(1 + \lambda^2)$, (the fraction of $2p_\sigma$ character in atomic orbital A).

This procedure gave the potential energy curves for the spin randomised states of the diatomic hydrides. The curves for the true spin states of these molecules were then derived by applying the appropriate atomic exchange integrals as shown in Section III 3. The results of the calculations are shown in Fig. 5.

5. Results for Diatomic Hydrides

In most cases we compare the results obtained with experimentally observed quantities such as dissociation energy, force constant, dipole moment etc. Where experimental data is not available we make comparisons with calculations based on conventional methods.

Fig. 5 gives the calculated potential energy curves for the electronic states considered, the curves being extrapolated by dotted lines to the dissociation products (Fig. 5 also includes the results of calculations on the corresponding positively charged molecular ions discussed in section IV). Experimental values of



a

b

Fig. 5 a—f. Potential energy curves for diatomic hydrides (energy scale in eV, internuclear separation in a. u.)

potential energy minima [5] are marked on the energy axes. Where experimental data are not available, the results of HURLEY's calculations [6] are inserted in brackets. The experimental value of r_e, which does not change significantly from state to state or from the neutral to the positively charged molecule, is shown by the line on the R axis.

Tab. 1 gives the force constants obtained from the parabola of best fit to the potential energy curves ([experimental values in brackets are taken from Herzberg), the fraction of $2p_\sigma$ character in orbital A (i. e. $\lambda^2/(1 + \lambda^2)$] and the charge density $2\varrho_A$ in orbital A. Dipole moments were calculated by assuming charges $2\varrho_A$ and $2\varrho_B$ in orbitals A and H respectively. This assumption involves Mulliken type approximations for the atomic dipole terms arising from the conventional molecular orbital approach to dipole moments. The centroids of the $1s$, π and π' orbitals of X on the bond axis are at the nucleus of X, so that for the dipole moment calculations we can take an effective positive charge of $(x + 1)$ at the nucleus, a negative charge x at the centroid of the σ' orbital and a negative charge $2\varrho_A$ at the centroid of orbital A as shown in Fig. 6. Negative charges are denoted by forces pointing downwards and nett positive charges by forces pointing upwards.

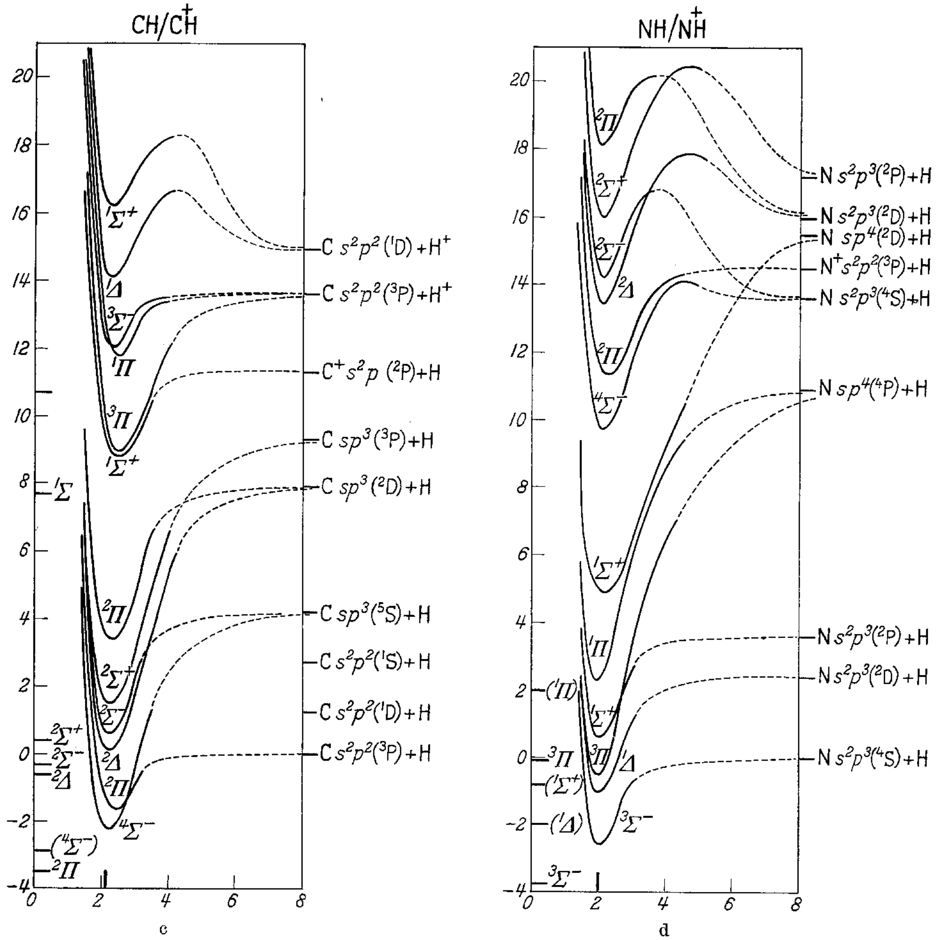


Fig. 5

The distance of the centroid of orbital A from the nucleus is given by the formula:

$$\bar{z} = \int (s + \lambda p_\sigma)^2 \, r \cos\theta \, d\tau/(1 + \lambda^2) \,. \tag{24}$$

Substituting Slater type orbitals in equation (24) gives

$$\bar{z} = 2.887\,\lambda/(1+\lambda^2)\,\delta \tag{25}$$

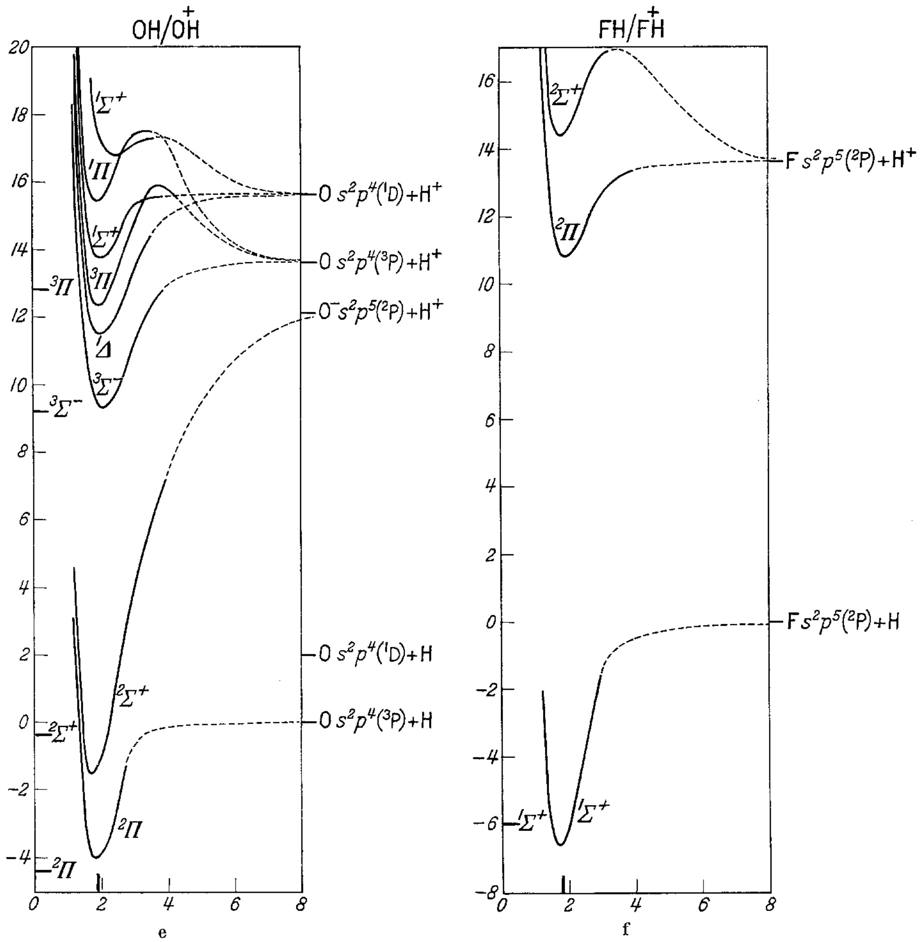


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Fig. 5

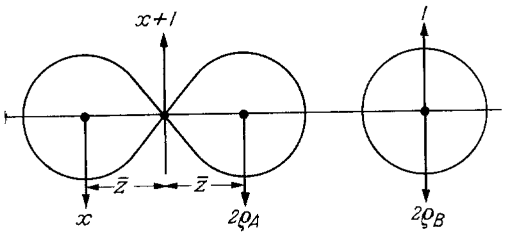

Fig. 6. Effective charges in hydrides

$\bar{z}$ for the σ orbital is equal in magnitude but opposite in sign to that for orbital A. The calculated dipole moments are compared with those calculated by Ransil [14] except for the value for FH which is experimental.

The values of the force constants could only be determined to an accuracy of *ca* 0.3×10^{-5} dynes/cm, but the results are of the correct order of magnitude. The dipole moments are in the same direction as Ransil's values (or the experimental value) and, considering their sensitivity to variation in ϱ_A the agreement is quite good.

Note that states bracketted together in Tab. 1 differ only in the arrangements of electron spin in the σ, π and π' orbitals. The method of calculation outlined in section III 3 relates the differences in the energies of these states solely to the exchange integrals for the various pairs of atomic orbitals. This procedure automatically means that these states have minimum energies for the same values of ϱ_A, $\lambda^2/(1+\lambda^2)$ and R. The experimental value of k_e is the average over the states concerned.

6. Dissociation Products and Configuration Interaction

The dissociation products are taken to be the ground state of the hydrogen atom, and the spectral state of lowest energy which occurs in the valence state expression for the atom X in the molecule. There are 3 types of valence state which are considered, namely, $1s^2\,\sigma^x\,(\pi\pi')^{Z-3-x}\,A \frac{\uparrow}{|}$ with $x = 0$, 1 and 2.

$x = 0$

If A is a pure $2s$ orbital, the valence state is represented by a mixture of terms derived from the configuration $1s^2\,2s\,2p^{Z-3}$, and, if A is a pure $2p$ orbital the valence state is represented by a mixture of terms derived from the configuration $1s^2\,2p^{Z-2}$. If A is a hybrid, we have a mixture of the two sets of terms. As the internuclear separation increases, the fraction of $2s$ character of orbital A will tend to one, to give a dissociation product which is the lowest $1s^2\,2s\,2p^{Z-3}$ term present in the valence state equation. The dissociation products are in agreement with those predicted by the Wigner-Witmer rules (see HERZBERG p. 315 [5]) provided account is taken of the exchange integrals $K_{\sigma\pi}$ or $K_{\pi\pi'}$ which may be required to obtain the valence state equations for the true spin states.

$x = 2$

In this case, the fraction of $2s$ character in orbital A will *decrease* as R increases to give a dissociation product of the form $1s^2\,2s^2\,2p^{Z-4}$.

$x = 1$

The only spectral states present in the valence state have the form $1s^2\,2s\,2p^{Z-3}$, and this would be expected to be the form of the dissociation product, whereas, in fact, the dissociation product is of the form $1s^2\,2s^2\,2p^{Z-4}$.

For example, Fig. 5 shows the BeH $^2\Sigma^+$ state dissociating to Be $1s^2\,2s\,2p$ (^3P), whereas the true product is Be $1s^2\,2s^2$ (^1S). However, we have not taken into account, in this simple treatment of the effects of configuration interaction with, in this case, the $^2\Sigma^+$ state of the form $1s^2\,\sigma^2\,(AH)'$ (i. e. having a one electron bond). The latter state is capable of dissociating to the product Be $1s^2\,2s^2$ (^1S). As the internuclear separation increases, the percentage of the latter form in the ground state wave function would increase and simultaneously the percentage $2s$ character in the σ orbital would increase to give Be $1s^2\,2s^2$ (^1S) and H $1s$ (^2S). The same considerations would apply to all the molecular states having a single electron in the σ orbital.

The possibility of configuration interaction between the σ^2 and $\pi\pi'$ $^1\Sigma^+$ functions of BH is particularly important since it would decrease the calculated energy of the $^1\Sigma^+$ ground state. The same applies to the $\sigma^2\,\pi$ and $\pi^2\,\pi'$ $^2\Pi$ functions of CH, and to the $\sigma^2\,\pi\pi'$ and $\pi^2\,\pi'^2$ $^1\Sigma'^+$ functions of NH. The above three pairs of states also involve some of the larger differences between calculation and experiment, but unfortunately the consideration of this type of interaction was beyond the scope of the present programme.

There is also the difficulty presented by the terms $\frac{1}{4}\mid AA \mid AA \mid$ and $\frac{1}{4}\mid HH \mid HH \mid$ which according to this simple theory would be retained in the energy of the atoms even for $R = \infty$. This could be resolved by allowing interaction with the function, involving two *different* molecular orbitals for the two bonding electrons, which would become more predominant as R increased, and would eventually achieve the situation where one molecular orbital has $\varrho_A = 1$ i. e. is involved solely with the atomic orbital A, and the other has $\varrho_A = 0$ i. e. is associated solely with atomic orbital H $1s$. This situation would not involve the repulsion between 'half electrons' present in the unrefined theory.

We also did not allow for the possibility of orbital contraction during bonding which RUEDENBERG [*17*] claims to be one of the important factors in bonding. We have introduced the Virial Theorem to calculate the energies of the isolated atoms (Appendix 6), and could have extended the approach further by allowing the kinetic energies of the electrons to increase as the potential energy decreases during bonding. This would automatically involve orbital contraction (i. e. an increase in the exponent of the Slater type orbitals) and the Virial Theorem could have been imposed on the molecular calculations, just as it was imposed on the atomic calculations. However, the computational effort involved in this procedure would have been very considerable and orbital contraction was neglected.

IV. Singly Charged Molecular Ions

We have also calculated the potential energy curves of the singly charged molecular ions $\overset{+}{\mathrm{Be}}\mathrm{H}$ to $\overset{+}{\mathrm{Ne}}\mathrm{H}$, the procedure used being exactly the same as that for the neutral molecules.

The three values of ϱ_A in this case correspond to the ion (atom) pairs $X^{2+}$and H^- ($\varrho_A = 0$) X^+ and H ($\varrho_A = 0.5$) X and H^+ ($\varrho_A = 1.0$). The molecular ion XH can be represented by the formula

$$1s^2\,\sigma^x\,(\pi\pi')^{Z-4-x}\,(AH)^2$$

and is isoelectronic with the neutral diatomic hydride derived from the element preceding it in the Periodic table.

The energy of the ion X^{2+} in the molecule was calculated from the second ionisation potential of X and from the atomic spectral data of X^{2+} taken from MOORE [*10*]. The valence state energies and the derivation of the exponents of the orbitals of the species X^{2+}, X^+ and X are given in Appendices 5 and 6. The two centre coulombic and bonding terms were calculated as previously described, the energies of the molecular ions were minimised with respect to ϱ_A and $\lambda^2/(1 + \lambda^2)$ and the resulting potential energy curves are shown in Fig. 5. The few experimental data are marked on the energy scale, the r_e values for the molecular ions being approximately the same as those for the corresponding parent molecules.

On the whole, the agreement with experiment is about the same as that for the parent molecules, and the same remarks concerning the effects of configuration interaction apply.

The dissociation products are in a few cases the ion X^+ and the hydrogen atom, but in most cases they are atom X and the ion H^+. In the latter case the atom X has a valence state of the form

$$1s^2\,\sigma^x\,(\pi\pi')^{Z-4-x}\,A^2$$

and *all* the molecular states are capable of dissociating to an atom having electronic structure

$$1s^2\,2s^2\,2p^{Z-4}\,.$$

The introduction of configuration interaction with the function corresponding to a single electron in the bonding orbital is therefore not necessary to explain the dissociation products of those states having a single σ electron.

Similarly, the energy terms $\frac{1}{4} \mid AA \mid AA \mid$ and $\frac{1}{4} \mid HH \mid HH \mid$ will not be present when the dissociation products are X and H^+, but configuration interaction of the type considered for the neutral molecules should have been included to produce more suitable functions.

An interesting point about the potential energy curves of the positive molecular ions is that many of them show pronounced humps, whereas this did not occur in the curves for the neutral molecules. Presumably this arises because at fairly large values of R (say 3 to 4 a. u.) the energy required to transfer electrons from the atom X to the proton to form a bond is greater than the stabilisation due to bonding. Alternatively, if no charge transfer takes place there will be a coulombic repulsion between the neutral atom and the proton. For the formation of a neutral molecule from atoms no *nett* charge transfer from one atom to the other is required to produce bonding.

The values of ϱ_A and $\lambda^2/(1+\lambda^2)$ corresponding to minimum energy are given in Tab. 1.

V. Comparison with Mulliken and Pauling Electronegativity Scales

The deviation of the bond from pure covalent character can be represented by the variable Δ where:

$$\Delta = 2\,\varrho_A - 1. \tag{26}$$

Δ is equal to the *excess negative charge* in the atomic orbital A (i. e. in excess of one which corresponds to pure covalent character) and equal to the deficiency of negative charge in atomic orbital B. Δ can take any value in the range -1 to $+1$, the extremes corresponding to the ion pairs $X^+\,Y^-$ and $X^-\,Y^+$ respectively. The product of Δ and r_e will be approximately equal to the dipole moment for a neutral diatomic molecule.

From equations (11) and (9)

$$\Delta = -(c_1 + c_2)/c_2 = (E_0 - E_1)/2\,(E_1 - 2\,E_{0.5} + E_0)\,. \tag{27}$$

1. Neutral molecule XY

E_0, $E_{0.5}$ and E_1 correspond to the energies of the pairs $X^+\,Y^-$, XY and $X^-\,Y^+$ respectively. Taking energies relative to the valence states of the atoms X and Y and neglecting orthogonality correction terms

$$E_0 \simeq IP\,(A) - EA\,(B) - e^2/R \tag{28}$$

$$E_{0.5} \simeq \tfrac{1}{4} \mid AA \mid AA \mid + \tfrac{1}{4} \mid BB \mid BB \mid - \tfrac{1}{2}\,e^2/R + [I]\,S/2\,(1+S) \tag{29}$$

$$E_1 \simeq IP\,(B) - EA\,(A) - e^2/R\,. \tag{30}$$

The approximation signs of equations (28), (29) and (30) arise from the assumption that the two centre coulombic terms are equal to e^2/R. The form of equation (29) is derived from equation (4) by substituting $\varrho_A = \varrho_B = 0.5$ by equating the two centre integrals to e^2/R and by equating sections (4a) and (4b) to the energy of the valence states of X and Y. $[I]$ represents all the integrals in the braces in section (4f), and IP and EA are the *valence state* ionisation potential and electron affinity respectively.

Using the Pariser approximation [equation (*13*)] and equation (27)

$$\Delta = \left\{[IP\,(A) + EA\,(A)] - [IP\,(B) + EA\,(B)]\right\} / \left\{|\,AA\,|\,AA\,| + |\,BB\,|\,BB\,| - 2\,e^2/R - 4\,[I]\,S/2\,(1+S)\right\} \tag{31}$$

$$\Delta = (\chi_A - \chi_B)/\tfrac{1}{2}\left\{|\,AA\,|\,AA\,| + |\,BB\,|\,BB\,| - 2\,e^2/R - 4\,[I]\,S/2\,(1+S)\right\} \tag{32}$$

where χ_A and χ_B are the Mulliken electronegativities of the two orbitals involved in bonding. We found that for the diatomic hydrides the last two terms in the denominator of equation (32) tend to be approximately equal to each other but opposite in sign whence Δ is approximately independent of R and given by:

$$\Delta \simeq (\chi_A - \chi_B)/\tfrac{1}{2}\,(|\,AA\,|\,AA\,| + |\,BB\,|\,BB\,|)\,. \tag{33}$$

If the repulsion between two electrons in a given orbital is approximately independent of the type of orbital concerned then the deviation from pure covalent character in a bond will be approximately proportional to the difference in the electronegativities of the two orbitals concerned in bonding. Certainly the values of $|\,AA\,|\,AA\,|$ and $|\,BB\,|\,BB\,|$ do not change as rapidly from atom to atom as the electronegativity, but we can not in general relate the deviation from pure covalent character solely to the difference in Mulliken electronegativities of the orbitals concerned.

We compared the values of Δ derived from equation (33) with those calculated from the values of ϱ_A given in Tab. 1, and, in general, the agreement between the two values was rather poor, presumably because the assumptions used to derive equation (33) are too drastic. Namely, that the two-centre integrals are not all equal to e^2/R, and probably the most drastic approximation is the neglect of the orthogonality correction terms.

The ionic-covalent resonance energy of the molecule XY is $E^* - E_{0.5}$ which from equations (9) to (15) and (33), is given by:

$$E^* - E_{0.5} = -\,(\chi_A - \chi_B)^2/(|\,AA\,|\,AA\,| + |\,BB\,|\,BB\,|)\,. \tag{34}$$

Equation (34) corresponds to the Pauling concept of electronegativity apart from the presence of the variables $|\,AA\,|\,AA\,|$ and $|\,BB\,|\,BB\,|$. The reliability of equation (34) is subject to the same reservations as equation (33).

2. Positive Molecular Ion XY$^+$

If XY^+ is derived from the species X^+ and Y then, when $\varrho_A = 0, 0.5$ and 1, we have the pairs X^{2+} and Y^-, X^+ and Y and X and Y^+ respectively whence from equation (4)

$$E_0 \simeq IP\,(X^+) - EA\,(B) - 2\,e^2/R \tag{35}$$

$$E_{0.5} \simeq \tfrac{1}{4}\,|\,AA\,|\,AA\,| + \tfrac{1}{4}\,|\,HH\,|\,HH\,| - \tfrac{1}{2}\,e^2/R + [I]\,S/2\,(1+S) \tag{36}$$

$$E_1 \simeq IP\,(B) - EA\,(X^+) \tag{37}$$

Table 1

Symmetry	C_k orbitals	Molecule	$\frac{\lambda^2}{1+\lambda^2}$	ϱ_A	k_e (dynes /cm × 10^5)	μ_e (Debye)	Mole-cule	$\frac{\lambda^2}{1+\lambda^2}$	ϱ_A
$^1\Sigma^+$		LiH	0.19	0.25	1.0 (1.0)	$\overrightarrow{7.1}$ $(\overrightarrow{5.92})$	$\overset{+}{\text{BeH}}$	0.12	0.52
$^2\Sigma^+$	σ	BeH	0.51	0.44	2.0 (2.3)	$\overrightarrow{0.5}$	$\overset{+}{\text{BH}}$	0.35	0.65
$^2\Pi$	π	BeH	0.17	0.50	2.0 (2.3)	$\overrightarrow{3.0}$		0.11	0.66
$^1\Sigma^+$	σ^2	BH	0.70	0.55	2.5 (3.0)	$\overleftarrow{2.9}$ $(\overleftarrow{1.58})$	$\overset{+}{\text{CH}}$	0.62	0.69
$^3\Pi$, $^1\Pi$	$\sigma\pi$	BH	0.36	0.63	3.0 (3.0)	$\overleftarrow{1.0}$		0.26	0.74
$^3\Sigma^-$ $^1\Delta$ $^1\Sigma^+$	$(\pi\pi')^2$	BH	0.12	0.64	3.0 (2.9)	$\overrightarrow{0.6}$		0.08	0.74
$^2\Pi$	$\sigma^2\pi$	CH	0.65	0.64	3.5 (4.5)	$\overleftarrow{3.1}$	$\overset{+}{\text{NH}}$	0.53	0.75
$^4\Sigma^-$ $^2\Delta$ $^2\Sigma^+$ $^2\Sigma^-$	$\sigma\,(\pi\pi')^2$	CH	0.27	0.74	4.5 (4.2)	$\overleftarrow{1.6}$		0.17	0.81
$^2\Pi$	$(\pi\pi')^3$	CH	0.12	0.74	4.0	$\overleftarrow{0.5}$		0.00	0.82
$^3\Sigma^-$ $^1\Delta$ $^1\Sigma^+$	$\sigma^2\,(\pi\pi')^2$	NH	0.47	0.78	5.5 (6.0)	$\overleftarrow{3.5}$ $(\overleftarrow{2.01})$	$\overset{+}{\text{OH}}$	0.48	0.78
$^3\Pi$, $^1\Pi$	$\sigma\,(\pi\pi')^3$	NH	0.20	0.82	5.5	$\overleftarrow{2.1}$		0.14	0.84
$^1\Sigma^+$	$(\pi\pi')^4$	NH	0.07	0.77	4.0	$\overleftarrow{1.4}$		0.00	0.85
$^2\Pi$	$\sigma^2\,(\pi\pi')^3$	OH	0.40	0.83	6.5 (7.8)	$\overleftarrow{3.3}$	$\overset{+}{\text{FH}}$	0.49	0.83
$^2\Sigma^+$	$\sigma\,(\pi\pi')^4$	OH	0.16	0.86	7.5	$\overleftarrow{2.2}$		0.15	0.87
$^1\Sigma^+$	$\sigma^2\,(\pi\pi')^4$	FH	0.38	0.83	8.0 (9.7)	$\overleftarrow{3.1}$ $(\overleftarrow{1.73})$	$\overset{+}{\text{NeH}}$	0.39	0.86

where IP (X^+) and EA (X^+) are the valence state ionisation potential and electron affinity of orbital A *in the ion* X^+.

Using the approximations given in section IV 1

$$\Delta \simeq (\chi_{X^+} - \chi_B - e^2/R)/(| AA | AA | + | BB | BB |) . \qquad (38)$$

The electronegativity of orbital A in the *ion* X^+ will be appreciably greater than the electronegativity in the *atom* X but the effect of this is moderated in equation (38) by the presence of the term e^2/R. For this reason it is not surprising that the values of ϱ_A for the neutral molecules XH and for the molecular ions XH in Tab. 1 are of a similar size. In other words, for values of R approximately equal to r_e the greater desire of X^+ for electrons compared with atom X is compensated by the very strong coulombic stabilisation when electrons drift towards Y to produce, in the limit, the ion pair X^{2+} Y^-.

The authors wish to express their graditude to friends and colleagues at the Universities of Leeds, Manchester and Sussex for many helpful discussions. H. D. B. J. expresses appreciation to D. S. I. R. for their financial support.

VI. Appendices

Appendix 1. Integrals from M. O. Theory

The wave function for the diatomic molecule XY is given by a determinental function of the form:

$$\Psi = det\,[(aA + bB)(1)s_1 \quad (aA + bB)(2)s_2 \quad C_1(3)s_3 \,..\, C_k\,(i)\,s_i \,..\, D_m\,(N)\,s_N]/d\,.\,\sqrt{N!}\,. \qquad (39)$$

In some cases a combination of determinantal functions must be used e.g. if we have two non-bonding electrons with opposed spin in two different orbitals say p and q, then we must take the two possible combinations of determinantal functions involving electrons in $p\alpha$ and $q\beta$ or $p\beta$ and $q\alpha$ where α and β signify spins $+\frac{1}{2}$ and $-\frac{1}{2}$. This only has the effect of introducing an extra exchange integral between orbitals p and q. We therefore consider the eigenvalue derived from equation (39), and, if necessary, modify it for configuration interaction of the above type.

The energy corresponding to equation (39) can be expressed as four sets of integrals as shown in equation (40).

$$\begin{aligned} E &= \int (a^4\,\Phi_1 + a^2\,b^2\,\Phi_2 + a^3\,b\,\Phi_3 + a^3\,b\,\Phi_4)\,H\Phi_1\,d\tau/d^2 && (40a)\\ &+ \int (b^4\,\Phi_2 + a^2\,b^2\,\Phi_1 + ab^3\,\Phi_3 + ab^3\,\Phi_4)\,H\Phi_2\,d\tau/d^2 && (40b)\\ &+ \int (a^2\,b^2\,\Phi_3 + a^2\,b^2\,\Phi_4 + a^3\,b\,\Phi_1 + ab^3\,\Phi_2)\,H\Phi_3\,d\tau/d^2 && (40c)\\ &+ \int (a^2\,b^2\,\Phi_4 + a^2\,b^2\,\Phi_3 + a^3\,b\Phi_1 + ab^3\,\Phi_2)\,H\Phi_4\,d\tau/d^2 && (40d) \end{aligned}$$

where $d = a^2 + b^2 + 2\,abS$
and

$$\begin{aligned} \Phi_1 &= det\,[A(1)s_1\,A(2)s_2\,C_1(3)s_3 \,..\, C_k(i)s_i \,..\, D_m(N)s_N]/\sqrt{N!} && (41a)\\ \Phi_2 &= det\,[B(1)s_1\,B(2)s_2\,C_1(3)s_3 \,..\, C_k(i)s_i \,..\, D_m(N)s_N]/\sqrt{N!} && (41b)\\ \Phi_3 &= det\,[A(1)s_1\,B(2)s_2\,C_1(3)s_3 \,..\, C_k(i)s_i \,..\, D_m(N)s_N]/\sqrt{N!} && (41c)\\ \Phi_4 &= det\,[B(1)s_1\,A(2)s_2\,C_1(3)s_3 \,..\, C_k(i)s_i \,..\, D_m(N)s_N]/\sqrt{N!} && (41d) \end{aligned}$$

Appendix 2. Atomic Orbital Approximation

The Hamiltonian H in equation (40) can be written as follows:

$$H = H_X + H_Y + H' + H'' \qquad (42)$$

where H_X is the operator for electrons in orbitals A and C_k only, and H_Y the operator for electrons in B and D_m only, i.e. for the isolated atoms or ions of X and Y respectively.

H' is the operator which gives the interaction between two positive ions X^+ and Y^+ formed by removal of electrons from the molecular orbital, and H'' is the operator for all other interactions arising from the bonding between the two atoms X and Y.

Φ_1 and Φ_2 are the wave functions for the ion pairs $X^- Y^+$ and $X^+ Y^-$ respectively. Φ_3 is the function for the atoms X and Y in which the electron spin is α in atomic orbital A and β in atomic orbital B; and Φ_4 is the same function with spin β in atomic orbital A and spin α in atomic orbital B. A linear combination of Φ_3 and Φ_4 can be said to correspond to *randomised* electron spin in orbitals A and B.

Since H_X and H_Y are the proper Hamiltonians for electrons in orbitals associated with X and Y respectively, then the energy terms arising from H_X and H_Y in equation (40) are:

$$\varrho_A^2\, E\,(X^-) + \varrho_A^2\, E\,(Y^+) \tag{43a}$$

$$+\, \varrho_B^2\, E\,(X^+) + \varrho_B^2\, E\,(Y^-) \tag{43b}$$

$$+\, \varrho_A\, \varrho_B\, E\,(X) + \varrho_A\, \varrho_B\, E\,(\overline{Y}) \tag{43c}$$

$$+\, \varrho_A\, \varrho_B\, E\,(\overline{X}) + \varrho_A\, \varrho_B\, E\,(Y) \tag{43d}$$

where the first two terms are derived from the first integral, the next two terms from the second integral etc., and

$$\begin{aligned} \varrho_A &= (a^2 + abS)/(a^2 + b^2 + 2\,abS) \\ \varrho_B &= (b^2 + abS)/(a^2 + b^2 + 2\,abS) = 1 - \varrho_A\,. \end{aligned} \tag{44}$$

$E\,(X^-)$, $E\,(Y^+)$, $E\,(X^+)$ and $E\,(Y^-)$ are the energies of the separated ions which would be produced by the two bonding electrons being restricted either to orbital A or to orbital B. $E\,(X)$ and $E\,(Y)$ are the energies of the isolated atoms X and Y in appropriate valence states with electron spin α in atomic orbitals A and B. $E\,(\overline{X})$ and $E\,(\overline{Y})$ are the energies for the same situation except with spin β.

Combination of equations (43c) and (43d) gives the energies of the isolated atoms when the electrons in orbitals A and B have randomised spin.

PARISER has suggested the following approximation for the coulomb integral $|\,AA\,|\,AA\,|$ [*12*]

$$|\,AA\,|\,AA\,| = IP\,(A) - EA\,(A) \tag{45}$$

where $IP\,(A)$ and $EA\,(A)$ are the valence state ionisation potential and electron affinity of the atomic orbital A. Using this approximation we can put

$$E\,(X^-) = E\,(X^+) + 2\,E\,(A) + |\,AA\,|\,AA\,| \tag{46}$$

$$[E\,(X) + E\,(\overline{X})]/2 = E\,(X^+) + E\,(A) \tag{47}$$

$E\,(A)$, which is approximately equal to $-\,IP\,(A)$, is the 'energy' of an electron having *randomised spin* in orbital A, and $|\,AA\,|\,AA\,|$ is the potential energy of repulsion between two electrons in orbital A.

Substituting equations (46) and (47), and similar equations for $E\,(Y^-)$, $E\,(Y)$ and $E\,(\overline{Y})$ into the expression 43 gives the following result for the energy terms arising solely from the operators H_X and H_Y

$$\begin{aligned} &E\,(X^+) + 2\,\varrho_A\, E\,(A) + \varrho_A^2\, |\,AA\,|\,AA\,| \\ &+ E\,(Y^+) + 2\,\varrho_B\, E\,(B) + \varrho_B^2\, |\,BB\,|\,BB\,|\,. \end{aligned} \tag{48}$$

Appendix 3. Approximations to Two-Centre Integrals

The energy terms derived from H' correspond to the energy of repulsion between the ions X^+ and Y^+ formed by loss of electrons from the molecular orbital. We denote these terms

$$E_{rep}\,(X^+\,Y^+)\,. \tag{49}$$

The integrals derived from H'' are given in equation (50), where section (50a) is derived from section (40a), (50b) is derived from (40b) and (50c) from (40c) and (40d).

$$\begin{aligned} &(a^4 + a^3\,bS)\,[\,-\,2\,|\,Z_Y\,|\,AA\,| + 2\sum_m (|\,AA\,|\,D_m\,D_m\,| - \tfrac{1}{2}\,|\,AD_m\,|\,AD_m\,|)]/d^2 \\ &+ (a^2\,b^2\,S + a^3\,b)\,[\,-\,2\,|\,Z_Y\,|\,BA\,| + 2\sum_m (|\,BA\,|\,D_m\,D_m\,| - \tfrac{1}{2}\,|\,BD_m\,|\,AD_m\,|)]/d^2 \qquad (50a) \\ &+ (b^4 + ab^3\,S)\,[\,-\,2\,|\,Z_X\,|\,BB\,| + 2\sum_k (|\,BB\,|\,C_k\,C_k\,| - \tfrac{1}{2}\,|\,BC_k\,|\,BC_k\,|)]/d^2 \end{aligned}$$

$$
\begin{aligned}
&+ (a^2 b^2 S + ab^3) \left[- 2 \mid Z_X \mid AB \mid + 2 \sum_k (\mid AB \mid C_k C_k \mid - \tfrac{1}{2} \mid AC_k \mid BC_k \mid)\right]/d^2 && \text{(50b)}\\
&+ 2 (a^2 b^2 + a^3 bS) \left[- \mid Z_Y \mid AA \mid + \sum_m (\mid AA \mid D_m D_m \mid - \tfrac{1}{2} \mid AD_m \mid AD_m \mid)\right]/d^2 &&\\
&+ 2 (a^2 b^2 S + ab^3) \left[- \mid Z_Y \mid BA \mid + \sum_m (\mid BA \mid D_m D_m \mid - \tfrac{1}{2} \mid BD_m \mid AD_m \mid)\right]/d^2 &&\\
&+ 2 (a^2 b^2 + ab^3 S) \left[- \mid Z_X \mid BB \mid + \sum_k (\mid BB \mid C_k C_k \mid - \tfrac{1}{2} \mid BC_k \mid BC_k \mid)\right]/d^2 &&\\
&+ 2 (a^2 b^2 S + a^3 b) \left[- \mid Z_X \mid AB \mid + \sum_k (\mid AB \mid C_k C_k \mid - \tfrac{1}{2} \mid AC_k \mid BC_k \mid)\right]/d^2 &&\\
&+ 2\, a^2 b^2 \mid AA \mid BB \mid/d^2 + 2\, a^2 b^2 \mid AB \mid AB \mid/d^2 &&\\
&+ 2\, a^3 b \mid AA \mid AB \mid/d^2 + 2\, ab^3 \mid BB \mid AB \mid/d^2 && \text{(50c)}
\end{aligned}
$$

The above integrals are of the following types (see ROOTHAAN [*16*]). Nuclear attraction integrals e.g. $\mid Z_X \mid BB \mid$ and $\mid Z_X \mid AB \mid$. Coulomb, exchange and hybrid integrals e.g. $\mid AA \mid BB \mid$, $\mid AB \mid AB \mid$, $\mid AA \mid AB \mid$.

Collecting like terms in equation (50) gives equation (51).

$$
\begin{aligned}
&2\, a^2 \left[- \mid Z_Y \mid AA \mid + \sum_m (\mid AA \mid D_m D_m \mid - \tfrac{1}{2} \mid AD_m \mid AD_m \mid)\right]/d \\
&+ 2\, b^2 \left[- \mid Z_X \mid BB \mid + \sum_k (\mid BB \mid C_k C_k \mid - \tfrac{1}{2} \mid BC_k \mid BC_k \mid)\right]/d \\
&+ 2\, ab \left[- \mid Z_Y \mid BA \mid + \sum_m (\mid BA \mid D_m D_m \mid - \tfrac{1}{2} \mid BD_m \mid AD_m \mid)\right]/d \\
&+ 2\, ab \left[- \mid Z_X \mid AB \mid + \sum_k (\mid AB \mid C_k C_k \mid - \tfrac{1}{2} \mid AC_k \mid BC_k \mid)\right]/d \\
&+ 2\, a^2 b^2 \mid AA \mid BB \mid/d^2 + 2\, a^2 b^2 \mid AB \mid AB \mid/d^2 + 2\, a^3 b \mid AA \mid AB \mid/d^2 + 2\, ab^3 \mid BB \mid AB \mid/d^2
\end{aligned}
\tag{51}
$$

Some of the integrals in equation (51) (particularly the hybrid exchange integrals) are difficult to evaluate and MULLIKEN [*11*] suggested the following type of approximation to simplify their calculation

$$\mid XX \mid YZ \mid = S_{YZ} (\mid XX \mid YY \mid + \mid XX \mid ZZ \mid)/2 \tag{52}$$

where S_{YZ} is the overlap integral for two orbitals Y and Z.

We make the following similar approximations

$$
\begin{aligned}
&\mid Z_Y \mid BA \mid \simeq S (\mid Z_Y \mid AA \mid + \mid Z_Y \mid BB \mid)/2 \\
&\mid Z_X \mid AB \mid \simeq S (\mid Z_X \mid BB \mid + \mid Z_X \mid AA \mid)/2 \\
&\mid BA \mid D_m D_m \mid \simeq S (\mid AA \mid D_m D_m \mid + \mid BB \mid D_m D_m \mid)/2 \\
&\mid AB \mid C_k C_k \mid \simeq S (\mid BB \mid C_k C_k \mid + \mid AA \mid C_k C_k \mid)/2 \\
&\mid BD_m \mid AD_m \mid \simeq S (\mid AD_m \mid AD_m \mid + \mid BD_m \mid BD_m \mid)/2 \\
&\mid AC_k \mid BC_k \mid \simeq S (BC_k \mid BC_k \mid + \mid AC_k \mid AC_k \mid)/2 \\
&\mid AB \mid AB \mid \simeq S^2 (\mid AA \mid AA \mid + \mid BB \mid BB \mid)/2 \\
&\mid AA \mid AB \mid \simeq S (\mid AA \mid AA \mid + \mid AA \mid BB \mid)/2 \\
&\mid BB \mid BA \mid \simeq S (\mid BB \mid BB \mid + \mid BB \mid AA \mid)/2\,.
\end{aligned}
\tag{53}
$$

The above approximations were tested for integrals involving Slater type $1s$ atomic orbitals and Slater type $2s$, $2p_\sigma$ and $2p_\pi$ atomic orbitals using the tables of KOTANI et al. [7]. Errors of less than 2% were found for the integrals involving $1s$ orbitals with $2s$ and $2p_\pi$ orbitals. Larger errors (up to 10%) were found for integrals involving the $2p_\sigma$ orbital. However, for interatomic distances of 2 to 4 a.u., the above approximations usually give errors of less than 0.5 eV.

We substituted equations (53) into the expression (51) and obtained the expression (54), for the integrals derived from that part of the Hamiltonian labelled H''

$$\begin{aligned}
&2\,\varrho_A\,[\,-\,|\,Z_Y\,|\,AA\,|\,+\sum_m(|\,AA\,|\,D_m\,D_m\,|\,-\tfrac{1}{2}\,|\,AD_m\,|\,AD_m\,|)]\\
&+2\,\varrho_B\,[\,-\,|\,Z_X\,|\,BB\,|\,+\sum_k(|\,BB\,|\,C_k\,C_k\,|\,-\tfrac{1}{2}\,|\,BC_k\,|\,BC_k\,|)]\\
&+2\,\varrho_A\,\varrho_B\,|\,AA\,|\,BB\,|\\
&+\frac{abS}{d}\,[\,-\,|\,Z_X\,|\,AA\,|\,+\sum_k(|\,AA\,|\,C_k\,C_k\,|\,-\tfrac{1}{2}\,|\,AC_k\,|\,AC_k\,|)\\
&\qquad-\,|\,Z_Y\,|\,BB\,|\,+\sum_m(|\,BB\,|\,D_m\,D_m\,|\,-\tfrac{1}{2}\,|\,BD_m\,|\,BD_m\,|)\\
&\qquad+\,\varrho_A\,|\,AA\,|\,AA\,|\,+\,\varrho_B\,|\,BB\,|\,BB\,|\\
&\qquad+\,|\,Z_Y\,|\,AA\,|\,-\sum_m(|\,AA\,|\,D_m\,D_m\,|\,-\tfrac{1}{2}\,|\,AD_m\,|\,AD_m\,|)\\
&\qquad+\,|\,Z_X\,|\,BB\,|\,-\sum_k(|\,BB\,|\,C_k\,C_k\,|\,-\tfrac{1}{2}\,|\,BC_k\,|\,BC_k\,|)\\
&\qquad-\,|\,AA\,|\,BB\,|]\,.
\end{aligned}\tag{54}$$

Equations (48), (49) and (54) give the total energy of the molecule [equation (4) of the main text].

Appendix 4. Orthogonality Correction

To make any atomic orbital C_k orthogonal to the bonding molecular orbital it is necessary to convert C_k into a molecular orbital of the form $(a'\,C_k + b'\,B)$ such that:

$$\int (a'\,C_k + b'\,B)\,(aA + bB)\,d\tau = 0 \tag{55}$$

or

$$a'\,bS' + ab'\,S + bb' = 0$$

or

$$b'/a' = -\,bS'/(b + aS) \tag{56}$$

where S' is the overlap integral for the orbitals B and C_k. If S' is zero no correction is required since, in this case, C_k is orthogonal to the molecular orbital.

The proposed 'model for bonding' of the general text indicates that if we have two electrons in the given C_k orbital then the molecular orbital $(a'\,C_k + b'\,B)$ is equivalent to charge densities $2\,(a'^2 + a'\,b'\,S')/d'$ and $2\,(b'^2 + a'\,b'\,S')/d'$ in orbitals C_k and B, respectively, where $d' = a'^2 + b'^2 + 2\,a'\,b'\,S'$.

There will be a corresponding bonding term of the form

$$a'\,b'\,S'\,[\Pi]/d'\,. \tag{57}$$

However, if S' is reasonably small (i.e. less than 0.3) then the 'density' in C_k tends to two, and that in B resulting from the correction tends to zero, to within 2% for all values of a, b and S. We can therefore regard the molecule as having 2 electrons in C_k, the only significant contribution to the energy of the molecule arising from lack of orthogonality being that given by the expression (57).

Appendix 5. Valence State Energies

We required the energies of the following atoms or ions, in the molecule XH, relative to ground state atoms.

$X^+\ 1s^2\sigma^x\,(\pi\pi')^{Z-3-x}$	$H^-\ 1s^2$
$X\ 1s^2\sigma^x\,(\pi\pi')^{Z-3-x}A\ \overset{\uparrow}{+}$	$H\ 1s\ \overset{\uparrow}{+}$
$X^-\ 1s^2\sigma^x\,(\pi\pi')^{Z-3-x}A^2$	H^+

where $\overset{\uparrow}{+}$ signifies 'randomised spin', which introduces the energy terms $|\,AA\,|\,AA\,|/4$ and $|\,HH\,|\,HH\,|/4$ associated with the repulsion between two 'half electrons' in orbitals A and H respectively.

For the molecule $\overset{+}{XH}$ we required the energies of the following species

$X^{2+}\ 1s^2\sigma^x\,(\pi\pi')^{Z-4-x}$	$H^-\ 1s^2$
$X^+\ 1s^2\sigma^x\,(\pi\pi')^{Z-4-x}A\ \overset{\uparrow}{+}$	$H\ 1s\ \overset{\uparrow}{+}$
$X\ 1s^2\sigma^x\,(\pi\pi')^{Z-4-x}A^2$	H^+ .

The energies of the species derived from atom X were calculated initially relative to the ground state of the ion X^+.

Ionisation potentials were taken from MOORE [10] and electron affinities from EDLÉN [4].

The valence state energies of the spin randomised states (section III 3) were calculated in terms of Slater-Condon parameters [3] as shown in Tab. 2.

Table 2. *Valence State Energies in Terms of Slater-Condon Parameters*

$x = 0$

X^+ (or X^{2+}) $1s^2\pi^y$ $p^y - y\,(y-1)\,F_2{}^{pp}$

X (or X^+) $1s^2\pi^y A \overset{\uparrow}{\top}$ $c\,[sp^y - y\,G_1{}^{sp}/2 - y\,(y-1)\,F_2{}^{pp} + (1-c)\,p^{y+1} - (2\,y^2 + 5\,y)\,F_2{}^{pp}/2] +$
$+ \mid AA \mid AA \mid /4$

X^- (or X) $1s^2\pi^y A^2$ $c\,[s^2p^y - yG_1{}^{sp} - y\,(y-1)\,F_2{}^{pp}] + (1-c)\,[p^{y+2} - (y^2 + 6\,y - 4)\,F_2{}^{pp}] +$
$+\, e\,[4\,(G_1{}^{sp} - F_2{}^{pp}) - \Delta_0{}^{sp}]$

$x = 1$

X^+ (or X^{2+}) $1s^2\sigma\pi^{y-1}$ $c\,[p^y - (2\,y^2 + y - 3)\,F_2{}^{pp}/2] + (1-c)\,[sp^{y-1} - (y-1)\,G_1{}^{sp}/2 -$
$- (y^2 - 3\,y + 2)\,F_2{}^{pp}]$

X (or X^+) $1s^2\sigma\pi^{y-1}A \overset{\uparrow}{\top}$ $sp^y - yG_1{}^{sp}/2 - (2\,y^2 + y - 3)\,F_2{}^{pp}/2 - e\,[\,2(G_1{}^{sp} - F_2{}^{pp}) - \Delta_0{}^{sp}/2] +$
$+ \mid AA \mid AA \mid /4$

X^- (or X) $1s^2\sigma\pi^{y-1}A^2$ $c\,[s^2p^y - yG_1{}^{sp} - (2\,y^2 + y - 3)\,F_2{}^{pp}/2] + (1-c)\,[sp^{y+1} -$
$-(y+1)G_1{}^{sp}/2 - (y^2 + 4\,y - 9)\,F_2{}^{pp}]$

$x = 2$

X^+ (or X^{2+}) $1s^2\sigma^2\pi^{y-2}$ $c\,[p^y - (y^2 + 2\,y - 12)\,F_2{}^{pp}] + (1-c)\,[s^2\,p^{y-2} - (y-2)\,G_1{}^{sp} - (y^2 -$
$- 5\,y + 6)\,F_2{}^{pp}] + e\,[4\,(G_1{}^{sp} - F_2{}^{pp}) - \Delta_0{}^{sp}$

X (or X^+) $1s^2\sigma^2\pi^{y-2}A \overset{\uparrow}{\top}$ $c\,[sp^y - yG_1{}^{sp}/2 - (y^2 + 2\,y - 12)\,F_2{}^{pp}] + (1-c)\,[s^2p^{y-1} - (y-1)\,G_1{}^{sp}$
$- (2\,y^2 - 3\,y - 2)\,F_2{}^{pp}/2] + \mid AA \mid AA \mid /4$

X^- (or X) $1s^2\sigma^2\pi^{y-2}A^2$ $s^2p^y - yG_1{}^{sp} - (y^2 + 2\,y - 12)\,F_2{}^{pp}$

$y = Z - 3 - x$ for the molecules $XH\ _{+}$
$y = Z - 4 - x$ for the molecular ions XH.

π^y etc. signifies the total number of electrons in both the π and π' orbitals.

$$c = 1/(1 + \lambda^2) \quad e = \lambda^2/(1 + \lambda^2)^2$$
$$s^2p^y = 2\,I_s + yI_p + F_0{}^{ss} + 2\,yF_0{}^{sp} + y\,(y-1)\,F_0{}^{pp}/2$$
$$sp^y = I_s + yI_p + yF_0{}^{sp} + y\,(y-1)\,F_0{}^{pp}/2$$
$$p^y = yI_p + y\,(y-1)\,F_0{}^{pp}/2$$
$$\Delta_0{}^{sp} = F_0{}^{ss} - 2\,F_0{}^{sp} + F_0{}^{pp}$$

s and p denote $2s$ and $2p$ atomic orbitals.

The Slater-Condon parameters can be calculated from the atomic energy levels of the atoms and ions involved, but this procedure does not always give consistent values for $G_1{}^{sp}$ and $F_2{}^{pp}$ i.e. the value of $F_2{}^{pp}$, say, calculated from one pair of states differs from the value obtained from another pair. For this reason we transformed the valence state expressions of Tab. 2 into mixtures of spectroscopic terms, and evaluated the valence state energies by inserting the values of the appropriate atomic energy levels. This is the procedure developed by MOFFITT [9], and may be illustrated for the case of the BH molecule.

For $x = 0$; the randomised spin state of BH is

$$1s^2\,\pi \overset{\uparrow}{\top}\, \pi' \overset{\uparrow}{\top}\, (AH)^2\,.$$

For $\varrho_A = 0, 0.5$ and 1 the valence state energies of the B^+, B and B^- species are respectively:

$$B^+ \quad [\tfrac{3}{4}\, 2p^2\, ({}^3P) + \frac{1}{12}\, 2p^2\, ({}^1D) + \tfrac{1}{6}\, 2p^2\, ({}^1S)]$$

$$B \quad c\,[\tfrac{1}{2}\, 2s2p^2\, ({}^4P) + \frac{1}{12}\, 2s2p^2\, ({}^2D) + \tfrac{1}{6}\, 2s2p^2\, ({}^2S) + \tfrac{1}{4}\, 2s2p^2\, ({}^2P)]$$
$$+ (1 - c)\,[\tfrac{1}{2}\, 2p^3\, ({}^4S) + \tfrac{1}{4}\, 2p^3\, ({}^2D) + \tfrac{1}{4}\, 2p^3\, ({}^2P)] + |\, AA \,|\, AA \,|/4$$

$$B^- \quad c\,[\tfrac{3}{4}\, 2s^2 2p^2\, ({}^3P) + \frac{1}{12}\, 2s^2 2p^2\, ({}^1D) + \tfrac{1}{6}\, 2s^2 2p^2\, ({}^1S)] +$$
$$+ (1 - c)\,[\tfrac{3}{4}\, 2p^4\, ({}^3P) + \frac{1}{12}\, 2p^4\, ({}^1D) + \tfrac{1}{6}\, 2p^4\, ({}^1S)] + e\,[4\,(G_1^{sp} - F_2^{pp}) - \Delta_0^{sp}]\,.$$

The terms in square brackets are the same as those given by MOFFITT for valence states derived for pure atomic orbitals. Combination of the two sets of states corresponds to the use of a hybrid orbital in the bonding molecular orbital. The extra term $e\,[4\,(G_1^{sp} - F_2^{pp}) - \Delta_0^{sp}]$ arises from the repulsion of two electrons in a hybrid orbital in the B^- ion.

If Slater-Condon parameters for the spectral states are introduced into the above equation, the first three expressions of Tab. 2 are obtained with $y = 2$.

The randomised spin state can be converted into true spin states of the molecule BH as shown in Fig. 4 of section III 3. These are the ${}^3\Sigma^-$ the ${}^1\Delta$ and the ${}^1\Sigma^+$ states, produced by introducing the exchange integral $K_{\pi\pi'}$ which changes the 'weights' of the spectral terms in the valence state e.g. the spectral state of B^+ required for the ${}^3\Sigma^-$ is only the ${}^3P$ term, that required for the ${}^1\Delta$ is only the ${}^1D$ term, and for the ${}^1\Sigma^+$ state the valence state of B^+ is $[\tfrac{2}{3}\,({}^1S) + \tfrac{1}{3}\,({}^1D)]$. Similar considerations apply to the application of $K_{\pi\pi'}$ to the B atom and the B^- ion.

The spin randomised case for $x = 1$ is

$$1s^2\sigma \underset{|}{\overset{\uparrow}{-}} \pi \underset{|}{\overset{\uparrow}{-}} (AH)^2$$

and this gives rise to the ${}^3\Pi$ and ${}^1\Pi$ states for BH by the use of the exchange integral $K_{\sigma\pi}$ (or $K_{\sigma\pi'}$). The appropriate valence state energies are given by:

$$B^+ \quad c\,[\tfrac{3}{4}\, 2p^2\, ({}^3P) + \tfrac{1}{4}\,{}'2p^2\, ({}^1D)] + (1 - c)\,[\tfrac{3}{4}\, 2s2p\, ({}^3P) + \tfrac{1}{4}\, 2s2p\, ({}^1P)]$$

$$B \quad [\tfrac{1}{2}\, 2s2p^2\, ({}^4P) + \tfrac{1}{4}\, 2s2p^2\, ({}^2D) + \tfrac{1}{4}\, 2s2p^2\, ({}^2P)] - e\,[2\,(G_1^{sp} - F_2^{pp}) - \Delta_0^{2p}/2] + |\, AA \,|\, AA \,|/4$$

$$B^- \quad c\,[\tfrac{3}{4}\, 2s^2 2\mathrm{p}^2\, ({}^3P) + \tfrac{1}{4}\, 2s^2 2p^2 ({}^1D)] + (1 - c)\,[\tfrac{3}{8}\, 2s2p^3\, ({}^3D) + \tfrac{3}{8}\, 2s2p^3\, ({}^3P) +$$
$$+ \tfrac{1}{8}\, 2s2p^3\, ({}^1D) + \tfrac{1}{8}\, 2s2p^3\, ({}^1P)]\,.$$

Application of $K_{\sigma\pi}$ results in only the ${}^3P$ term of B^+ being associated with the ${}^3\Pi$ state and only the ${}^1D$ and ${}^1P$ terms of B^+ being associated with the ${}^1\Pi$ state. Similar effects occur for the B atom and the B^- ion.

The extra terms involving $(G_1^{sp} - F_2^{pp})$, Δ_0^{sp} and $|\, AA \,|\, AA \,|/4$ were calculated from the monocentric integrals of ROOTHAAN [*16*].

$$G_1^{sp} = 2.1842\,\delta\ \mathrm{eV} \tag{57}$$
$$F_2^{pp} = 0.1912\,\delta\ \mathrm{eV} \tag{58}$$
$$\Delta_0^{sp} = 0$$

where δ is the Slater orbital exponent of the $2s$ and $2p$ orbitals.

$$|\, HH \,|\, HH \,| = 17.00\,\delta_H\ \mathrm{eV} \tag{59}$$

where δ_H is the orbital exponent for the hydrogen $1s$ orbital.

$$|\, AA \,|\, AA \,| = (F_0^{ss} + 2\,\lambda^2\, F_0^{sp} + \lambda^4\, F_0^{pp} + 4\,\lambda^2\, G_1^{sp} + 4\,\lambda^4\, F_2^{pp})/(1 + \lambda^2)^2 \tag{60}$$

where

$$F_0^{ss} = F_0^{sp} = F_0^{pp} = 9.8818\,\delta\ \mathrm{eV}\,. \tag{61}$$

Exchange integrals

$$K_{\sigma\pi} = G_1^{sp}\,.\,\lambda^2/(1 + \lambda^2) + 3\,F_2^{pp}/(1 + \lambda^2) \tag{62}$$
$$K_{\pi\pi'} = 6\,F_2^{pp} \tag{63}$$

and they were calculated from differences in the atomic energy levels used in the valence state expressions.

Atomic energy levels for atoms and positive ions were taken from MOORE [*10*], and for the negative ions they were obtained by linear extrapolation of the energy levels of the corresponding isoelectronic atoms or ions (see ROHRLICH [*15*]).

Appendix 6. Application of the Virial Theorem

The orbital exponent δ of the atom X was found from the energy of the atom, in its appropriate valence state, relative to the positive ion $X^{(Z-2)+}\,1s^2$.

Let I be the sum of the ionisation potentials required to produce $X^{(Z-2)+}\,1s^2$ from the *ground state* of atom X, and V the valence state of energy of X expressed as a mixture of spectroscopic terms, ignoring for the moment the terms involving $(G_1{}^{sp}-F_2{}^{pp})$ and $|\,AA|AA\,|/4$. If δ' is the exponent of the $2s$ and $2p$ orbitals then the kinetic energy of the electrons in these orbitals will be $13.6\,(Z-2)\,\delta'^2$ and by the Virial Theorem

$$13.6\,(Z-2)\,\delta'^2 = I - V\,. \tag{64}$$

The potential energy required to remove these electrons will be $27.2\,(Z-2)\,\delta'^2$.

The extra potential energy terms involving $(G_1{}^{sp}-F_2{}^{pp})$ and $|\,AA|AA\,|/4$ will cause δ' to change to δ, the exponent of the Slater type orbitals of the atom in the molecule.

If we regard the energy of the $1s^2$ as dependent only on the nuclear charge i.e. independent of the number of $2s$ and $2p$ electrons, the potential energy terms involving $2s$ and $2p$ orbitals can be shown to be proportional to δ [see equations (57) to (61) for example], so that the change from δ' to δ will cause the first potential energy term to change to $27.2\,(Z-2)\,\delta'\,\delta$. If we express the extra potential energy terms as $K\,\delta$, then the new total potential energy will, by the Virial Theorem, be given by:

$$27.2\,(Z-2)\,\delta^2 = 27.2\,(Z-2)\,\delta'\,\delta - K\,\delta\,. \tag{65}$$

From equation (64)

$$\delta = [(I-V)/13.6\,(Z-2)]^{\frac{1}{2}} - K/27.2\,(Z-2) \tag{66}$$

and the energy of the atom in the molecule relative to the ground state atom is

$$I - 13.6\,(Z-2)\,\delta^2\,. \tag{67}$$

The values of δ calculated from equation (66) are in fairly good agreement with those calculated from Slater screening constants except for some of the valence states of Li and Be. However, in contrast with Slater's values, we allow δ to vary with the percentage $2s$ and $2p$ character in the atom.

The values of δ and the energies for the ions X^- and X^+ and for the species X^{2+}, X^+ and X, appropriate for the molecule $X\overset{+}{H}$, were calculated in a similar way (see Tab. 3).

We also allow the exponent of the hydrogen $1s$ atomic orbital δ_H, to vary with ϱ_A. No value of δ_H is of course required for H^+. For the hydrogen atom in the molecule, the potential energy of attraction to the nucleus is $27.2\,\delta_H$, and the term $|\,HH\,|\,HH\,|/4$ is $4.25\,\delta_H$ [equation (59)]. From the Virial Theorem, the potential energy must be $27.2\,\delta_H{}^2$ whence

$$27.2\,\delta_H{}^2 = 27.2\,\delta_H - 4.25\,\delta_H$$

i.e.

$$\delta_H = 0.8437 \tag{68}$$

and the energy of the hydrogen atom in the molecule relative to the ground state atom is

$$13.6 - 13.6\,\delta_H{}^2 = 3.92\ \text{eV}\,. \tag{69}$$

If $\varrho_A = 0$, then we have the ion H^- in the molecule. The energy of the two electrons is:

$$2 \times 13.6\,\delta_H{}^2 = 13.60 + 0.75$$

i.e.

$$\delta_H = 0.7263\,. \tag{70}$$

The monocentric integrals of equation (4f) were expressed in terms of atomic energies via the Virial Theorem. The C_k atomic orbitals consist of the $1s$ orbital of X and the σ, π and π' orbitals. The potential energy of attraction of one electron in A to the nucleus of X $(|\,Z_X\,|\,AA\,|)$

Table 3. *Orbital exponents of some first row elements and their ions as a function of hybrid character* $(\lambda^2/1 + \lambda^2)$

Species	$\frac{\lambda^2}{1+\lambda^2}$						Species	$\frac{\lambda^2}{1+\lambda^2}$						Electronic Configuration
	0.0	0.2	0.4	0.6	0.8	1.0		0.0	0.2	0.4	0.6	0.8	1.0	
Li^-	0.478	0.440	0.414	0.398	0.392	0.398	Be	1.006	0.955	0.914	0.884	0.865	0.856	A^2
Be^-	0.819	0.786	0.761	0.743	0.732	0.728	B	1.323	1.283	1.252	1.227	1.210	1.200	$A^2\,(\pi\pi')^1$
Be^-	0.819	0.810	0.800	0.791	0.782	0.772	B	1.323	1.310	1.298	1.285	1.273	1.260	$A^2\,\sigma$
B^-	1.146	1.115	1.090	1.071	1.057	1.048	C	1.646	1.613	1.584	1.562	1.545	1.533	$A^2\,(\pi\pi')^2$
B^-	1.147	1.138	1.129	1.120	1.110	1.101	C	1.648	1.637	1.626	1.615	1.604	1.593	$A^2\,\sigma\,(\pi\pi')^1$
B^-	1.140	1.140	1.140	1.140	1.140	1.140	C	1.640	1.640	1.640	1.640	1.640	1.640	$A^2\,\sigma^2$
C^-	1.471	1.445	1.423	1.406	1.394	1.385	N	1.970	1.941	1.917	1.897	1.881	1.870	$A^2\,(\pi\pi')^3$
C^-	1.476	1.467	1.458	1.450	1.441	1.432	N	1.976	1.966	1.956	1.946	1.936	1.926	$A^2\,\sigma\,(\pi\pi')^2$
C^-	1.471	1.471	1.471	1.471	1.471	1.471	N	1.970	1.970	1.970	1.970	1.970	1.970	$A^2\,\sigma^2\,(\pi\pi')^4$
N^-	1.802	1.778	1.757	1.740	1.727	1.717	O	2.296	2.270	2.247	2.228	2.213	2.201	$A^2\,(\pi\pi')^4$
N^-	1.808	1.799	1.791	1.783	1.775	1.767	O	2.302	2.293	2.284	2.275	2.266	2.256	$A^2\,\sigma\,(\pi\pi')^3$
N^-	1.807	1.807	1.807	1.807	1.807	1.807	O	2.301	2.301	2.301	2.301	2.301	2.301	$A^2\,\sigma^2\,(\pi\pi')^2$
O^-	2.136	2.129	2.121	2.114	2.106	2.099	F	2.631	2.622	2.614	2.605	2.597	2.588	$A^2\,\sigma\,(\pi\pi')^4$
O^-	2.136	2.136	2.136	2.136	2.136	2.136	F	2.631	2.631	2.631	2.631	2.631	2.631	$A^2\,\sigma^2\,(\pi\pi')^3$
F^-	2.467	2.467	2.467	2.467	2.467	2.467	Ne	2.961	2.961	2.961	2.961	2.961	2.961	$A^2\,\sigma^2\,(\pi\pi')^4$
Li	0.545	0.512	0.484	0.460	0.439	0.422	Be^+	1.070	1.033	1.000	0.972	0.949	0.932	A
Be	0.898	0.877	0.857	0.841	0.827	0.815	B^+	1.407	1.384	1.363	1.345	1.330	1.317	$A\,(\pi\pi')^1$
Be	0.898	0.903	0.905	0.905	0.901	0.895	B^+	1.407	1.412	1.414	1.414	1.410	1.317	$A\,\sigma^2$
B	1.237	1.221	1.205	1.192	1.180	1.171	C^+	1.740	1.722	1.706	1.692	1.679	1.669	$A\,(\pi\pi')^2$
B	1.241	1.244	1.245	1.245	1.243	1.238	C^+	1.743	1.747	1.748	1.748	1.745	1.741	$A\,\sigma\,(\pi\pi')^1$
B	1.230	1.239	1.249	1.261	1.275	1.290	C^+	1.731	1.741	1.753	1.766	1.781	1.798	$A\,\sigma^2$
C	1.571	1.556	1.543	1.531	1.521	1.512	N^+	2.070	2.055	2.041	2.028	2.017	2.007	$A\,(\pi\pi')^3$
C	1.578	1.580	1.581	1.581	1.579	1.576	N^+	2.077	2.080	2.081	2.080	2.079	2.075	$A\,\sigma\,(\pi\pi')^2$
C	1.571	1.579	1.588	1.598	1.610	1.623	N^+	2.070	2.079	2.089	2.100	2.113	2.127	$A\,\sigma^2\,(\pi\pi')^1$
N	1.907	1.894	1.882	1.870	1.860	1.851	O^+	2.406	2.392	2.378	2.366	2.355	2.345	$A\,(\pi\pi')^4$
N	1.909	1.911	1.912	1.912	1.910	1.908	O^+	2.408	2.410	2.411	2.411	2.409	2.407	$A\,\sigma\,(\pi\pi')^3$
N	1.908	1.915	1.924	1.933	1.944	1.956	O^+	2.406	2.414	2.423	2.434	2.445	2.458	$A\,\sigma^2\,(\pi\pi')^2$
O	2.241	2.243	2.244	2.243	2.242	2.240	F^+	2.738	2.740	2.741	2.740	2.739	2.737	$A\,\sigma\,(\pi\pi')^4$
O	2.241	2.248	2.256	2.265	2.275	2.286	F^+	2.738	2.746	2.754	2.764	2.774	2.786	$A\,\sigma^2\,(\pi\pi')^3$
F	2.576	2.582	2.590	2.598	2.607	2.617	Ne^+	3.071	3.078	3.086	3.095	3.105	3.115	$A\,\sigma^2\,(\pi\pi')^4$

Table 3 (continuation)

Li^+	0.000	0.000	0.000	0.000	0.000	0.000	Be	0.000	0.000	0.000	0.000	0.000	0.000	
Be^+	1.024	1.024	1.024	1.024	1.024	1.024	B	1.532	1.532	1.532	1.532	1.532	1.532	$(\pi\pi')^1$
Be^+	1.024	1.052	1.079	1.106	1.132	1.157	B	1.532	1.561	1.589	1.616	1.643	1.670	σ
B^+	1.358	1.358	1.358	1.358	1.358	1.358	C	1.862	1.862	1.862	1.862	1.862	1.862	$(\pi\pi')^2$
B^+	1.365	1.383	1.401	1.418	1.435	1.452	C	1.869	1.887	1.905	1.923	1.941	1.958	$\sigma\,(\pi\pi')^1$
B^+	1.347	1.361	1.385	1.420	1.466	1.523	C	1.847	1.862	1.888	1.925	1.973	2.032	σ^2
C^+	1.693	1.693	1.693	1.693	1.693	1.693	N	2.191	2.191	2.191	2.191	2.191	2.191	$(\pi\pi')^3$
C^+	1.701	1.715	1.729	1.743	1.757	1.770	N	2.201	2.216	2.231	2.245	2.259	2.274	$\sigma\,(\pi\pi')^2$
C^+	1.693	1.706	1.726	1.754	1.788	1.831	N	2.191	2.205	2.227	2.256	2.293	2.337	$\sigma^2\,(\pi\pi')^1$
N^+	2.021	2.021	2.021	2.021	2.021	2.021	O	2.520	2.520	2.520	2.520	2.520	2.520	$(\pi\pi')^4$
N^+	2.032	2.044	2.056	2.068	2.080	2.092	O	2.532	2.544	2.557	2.569	2.581	2.594	$\sigma\,(\pi\pi')^3$
N^+	2.028	2.042	2.060	2.085	2.115	2.150	O	2.528	2.542	2.562	2.587	2.618	2.654	$\sigma^2\,(\pi\pi')^2$
O^+	2.364	2.375	2.386	2.397	2.407	2.418	F	2.861	2.874	2.892	2.915	2.942	2.973	$\sigma\,(\pi\pi')^4$
O^+	2.364	2.377	2.394	2.415	2.441	2.471	F	2.861	2.874	2.892	2.915	2.942	2.973	$\sigma^2\,(\pi\pi')^3$
F^+	2.696	2.708	2.725	2.745	2.768	2.796	Ne	3.194	3.207	3.223	3.244	3.268	3.296	$\sigma^2\,(\pi\pi')^4$

is a linear function of δ and so are the coulomb and exchange integrals between A and the σ or π or π' orbitals. If we regard the $1s^2$ shell as just screening the nucleus then the coulomb and exchange integral involving A and the $1s$ orbitals will also be directly proportional to the exponent of orbital A.

We therefore put

$$K_1\,\delta = -\,|\,Z_X\,|\,AA\,|\,+\sum_k(|\,AA\,|\,C_k\,C_k\,|\,-\,\tfrac{1}{2}\,|\,AC_k\,|\,AC_k\,|)\,. \qquad (71)$$

Similarly from equations (60) and (61)

$$K_2\,\delta = |\,AA\,|\,AA\,|\,. \qquad (72)$$

All other coulomb and exchange integrals involving σ, π and π' orbitals will also be proportional to δ, and we set these potential energy terms equal to $K_3\,\delta$.

The differences in the potential energies of the ions X^- and $X^{(z-2)+}$ and the ions X^+ and $X^{(z-2)+}$ are respectively:

$$-\,27.2\,(Z-1)\,\delta_1^2 = 2\,K_1\,\delta_1 + K_2\,\delta_1 + K_3\,\delta_1\;; \qquad (73)$$

$$-\,27.2\,(Z-3)\,\delta_3^2 = K_3\,\delta_3 \qquad (74)$$

where δ_1 and δ_3 are the exponents of the $2s$ and $2p$ orbitals in the ions X^- and X^+ respectively.

The potential energy term required is:

$$K_1\,\delta_2 + \tfrac{1}{2}\,K_2\,\delta_2 \qquad (75)$$

where δ_2 is the exponent of the orbitals in the neutral atom X and from equations (73) and (74).

$$K_1\,\delta_2 + \tfrac{1}{2}\,K_2\,\delta_2 = -\,13.60\,[(Z-2)\,(\delta_1-\delta_3) + \delta_1 + \delta_3]\,\delta_2\,. \qquad (76)$$

The monocentric integrals involving B and D_m reduce to:

$$-\,|\,Z_H\,|\,HH\,|\,+\,\tfrac{1}{2}\,|\,HH\,|\,HH\,| = -\,19.76\,\delta_H\,\mathrm{eV} \qquad (77)$$

for the diatomic hydrides, where δ_H is the exponent of the hydrogen $1s$ orbital in the molecule (for $\varrho_A = 0.5\,\delta_H = 0.8437$).

The bonding term in the molecular ion XH^+ was calculated in a similar way.

Appendix 7. Two-Centre Integrals [16]

a) Nuclear Attraction Integrals

The nuclear attraction integral for an electron in a given orbital to a proton at a distance R from the centroid of the orbital was given by:

$$s.e^2/R \qquad (78)$$

where

$$s\,(1s) = 1 - [1 + \delta\, R]\exp(-2\,\delta R) \tag{79}$$

$$s\,(2s) = 1 - [1 + 3\,\delta R/2 + (\delta R)^2 + (\delta R)^3/3]\exp(-2\,\delta R) \tag{80}$$

$$\begin{aligned} s\,(2p_\sigma) = 1 + 3/(\delta R)^2 - [7 &+ 11\,\delta R/2 + 3\,(\delta R)^2 + (\delta R)^3 \\ &+ 3/(\delta R)^2 + 6/(\delta R)]\exp(-2\,\delta R) \end{aligned} \tag{81}$$

$$s\,(2p_\pi) = 1 - 3/2(\delta R)^2 + [2 + 3/2(\delta R)^2 + 3/\delta R + \delta R/2]\exp(-2\,\delta R) \tag{82}$$

$$s\,(2s\,2p_\sigma) = 5/(3.4642\,\delta R)\,[1 - (1 + 2\,\delta R + 2\,(\delta R)^2 + 1.2\,(\delta R)^3 + 0.4\,(\delta R)^4\,]\exp(-2\,\delta R) \tag{83}$$

δ is the orbital exponent, R the internuclear separation. For the hybrid atomic orbitals A and σ

$$s\,(A) = \frac{1}{1+\lambda^2}\,s\,(2s) + \frac{\lambda^2}{1+\lambda^2}\,s\,(2p_\sigma) + \frac{2\,\lambda}{1+\lambda^2}\,s\,(2s\,2p_\sigma) \tag{84}$$

$$s\,(\sigma) = \frac{1}{1+\lambda^2}\,s\,(2p_\sigma) + \frac{\lambda^2}{1+\lambda^2}\,s\,(2s) - \frac{2\,\lambda}{1+\lambda^2}\,s\,(2s\,2p_\sigma) \tag{85}$$

b) Overlap Integrals

These integrals were taken direct from ROOTHAAN's paper [*16*].

The overlap integral between the orbitals A and H is given by:

$$S = \frac{1}{\sqrt{1+\lambda^2}}\,S_{1s2s} + \frac{\lambda}{\sqrt{1+\lambda^2}}\,S_{1s2p_\sigma} \tag{86}$$

and that between σ and H is given by

$$S' = \frac{1}{\sqrt{1+\lambda^2}}\,S_{1s2p_\sigma} - \frac{\lambda}{\sqrt{1+\lambda^2}}\,S_{1s2s}$$

where S_{1s2s} and S_{1s2p_σ} are the overlap integrals for the hydrogen $1s$ orbital and the $2s$ and $2p_\sigma$ orbitals respectively of X.

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