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Model Two-Electron Chemical Bonds and the Concept of Electronegativity*

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Complete variationally correct calculations have been performed for model two-electron diatomic "molecules" using the Cottrell and Sutton Hamiltonian and Weinbaum, Wang and MO wave functions. Both homonuclear and heteronuclear systems have been studied. In homonuclear bonds between high Z atoms the MO function gives lower energies than the Wang function. The presence of ionic terms in the wave function is not necessary to show Pauling-type "ionic resonance energy stabilization" of heteronuclear molecules. The presence of ionic terms is important, however, to get the best energies, and is essential to achieve even approximately correct values of the dipole moments. The model systems predict that Pauling's correlation of dipole moments and electronegativity differences should show a dependence on $\chi_A + \chi_B$. This appears to be indicated by the experimental data.

Variationsrechnungen an zweiatomigen Zweielektronen-Modellmolekülen werden unter Verwendung des Hamilton-Operators von Cottrell und Sutton und einer MO-Funktion bwz. der Funktionen von Wang sowie Weinbaum durchgeführt. In homonuklearen Molekülen mit hoher Kernladungszahl gibt eine MO-Funktion eine tiefere Energie als die von Wang. Ionische Terme in der Wellenfunktion sind nicht nötig, um zu zeigen, daß eine Bindung in heteropolaren Molekülen gegenüber einer homöopolaren Bindung stabilisiert ist, wohl aber, um einen guten Wert für Energie und Dipolmoment zu erhalten. Die Paulingsche Korrelation von Dipolmoment und Elektronegativitätsdifferenz ist von der Summe der Elektronegativitäten abhängig.

Des calculs variationels complets ont été faits pour des „molécules" modèles diatomiques à deux électrons, en utilisant l'hamiltonien de Cottrell et Sutton et des fonctions d'onde O.M, de Weinbaum et de Wang. On a étudié des systèmes homonucléaires et hétéronucléaires. Pour les liaisons homonucléaires entre atomes à Z élevé la fonction O.M. donne des énergies plus faibles que la fonction de Wang. La présence des termes ioniques dans la fonction d'onde n'est pas nécessaire pour manifester une „énergie de stabilisation par résonance ionique" du type de Pauling pour les molécules hétéronucléaires. La présence de termes ioniques est importante cependant pour obtenir les meilleures énergies, et est essentielle pour avoir des valeurs même approximativement exactes des moments dipolaires. Les systèmes modèles prévoient que la corrélation de Pauling entre les moments dipolaires et les différences d'électronagativité devrait dépendre de $\chi_A + \chi_B$. C'est ce que semblent montrer les données expérimentales.

1. Introduction

Recently Ruedenberg [*1*] has developed an interpretive analysis which permits a detailed conceptual understanding of the anatomy of the chemical bond and, particularly, of the origin of the energy lowering accompanying bond formation. In addition to studies on the hydrogen molecule-ion [*2*, *3*], and the hydrogen

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[*1*] and water molecules [*4*], RUEDENBERG and co-workers have also analyzed the binding energies of several homonuclear first row diatomic molecules [*5*] and first row diatomic hydrides [*6*]. The particular interest in these last two investigations is that they offer an examination of the interpretive scheme with respect to trends in the various defined energetic fragments comprising the binding energy.

To extend the analysis to additional series of similar molecules requires the availability of equivalent and reasonable wave functions which must, as a minimum requirement, provide a proper partitioning of the total energy into its kinetic and potential components as governed by the virial theorem. In order to provide wave functions for such an analysis which do meet this criterion, we have carried out a series of calculations based on a model introduced by COTTRELL and SUTTON [*7*] some years ago.

The model treats the two center chemical bond as a two electron problem defined by the Hamiltonian operator

$$\mathscr{H} = -\tfrac{1}{2}\nabla_1^2 - \tfrac{1}{2}\nabla_2^2 - \frac{Z_A}{r_{A1}} - \frac{Z_B}{r_{B1}} - \frac{Z_A}{r_{A2}} - \frac{Z_B}{r_{B2}} + \frac{1}{r_{12}} + \frac{Z_A Z_B}{R}. \qquad (1)$$

The interactions of the remaining electrons are approximated by assigning non-integral values to the nuclear charges Z_A and Z_B. In essence, the model treats a many-electron diatomic molecule by collapsing into each of the nuclei their respective core electrons, and representing the effect of this approximation solely as the coulombic interactions of screened nuclei with each other and the two valence electrons forming the bond. Hence by assigning different values to $Z_A = Z_B$, it is possible to approximate the Hamiltonian operators of a series of homonuclear molecules, and likewise, by assuming different sets of $Z_A \neq Z_B$, various series of heteronuclear bonds.

COTTRELL and SUTTON used a simple Heitler-London wave function constructed from 1*s* STO's with the orbital exponents selected as $\zeta_A = Z_A$ and $\zeta_B = Z_B$. In addition, a few calculations were performed with a Weinbaum function where, in both the covalent and ionic parts, the ζ's were again chosen equal to their respective nuclear charges. Since no attempt was made to determine the orbital exponents by a variational procedure, the wave functions do not satisfy the virial theorem [*8*].

In 1954, HURLEY [*9*] used this model to make additional calculations within the context of a perturbation treatment [*10*]. The Hamiltonian was rewritten as the sum of a symmetric part and an antisymmetric part. Approximate wave functions and energies for the symmetric part were obtained by a variationally determined scaling of the Weinbaum function and internuclear distance for the H_2 molecule. The resulting wave functions for these homonuclear molecules were then taken as zeroth order wave functions to obtain results for heteropolar bonds using the antisymmetric part of the total Hamiltonian as the perturbation. The results of these calculations gave energies significantly lower than those of COTTRELL and SUTTON.

The idea of approximating inner shell interactions by screened nuclei to simplify the Hamiltonian of more complex problems has been subsequently used by other investigators [*11*]. These studies indicate the utility and mathematical tractability of such an approximation for obtaining wave functions and energies which reproduce essential features of the chemical bond in a series of similar molecules.

The present calculations make use of the COTTRELL and SUTTON Hamiltonian and the following three wave functions:

WANG: $\psi = N\,[a(1)\,b(2) + a(2)\,b(1)]$ (2a)

MO: $\psi = N[a(1) + \lambda b(1)]\,[a(2) + \lambda b(2)]$ (2b)

WEINBAUM: $\psi = C_1[a(1)\,b(2) + a(2)\,b(1)] + C_2 a(1)\,a(2) + C_3 b(1)\,b(2)\,.$ (2c)

The orbital exponents in the $1s$ orbitals, a and b, and the linear coefficients were all treated as variation parameters. The resulting wave functions thus satisfy the virial theorem. They will be used in a subsequent application of the interpretive analysis mentioned above.

Our purpose in the present paper is to report some of the results of these calculations and compare them with the earlier work. Systematic computations were carried out over a range of internuclear distances for three sets of nuclear charge values:

1. Homonuclear, with $Z_A = Z_B = 0.5$ to 2.0;
2. Heteronuclear, with $Z_A = 1 + \varepsilon$, $Z_B = 1 - \varepsilon$, $\varepsilon = 0.05$ to 0.8;
3. Heteronuclear "hydrides" with $Z_A = 1$ and $Z_B = 0.5$ to 2.0 .

The value of R_{eq} was determined by minimizing the molecular energy with R included as a variation parameter. In addition, the value of $2\langle T\rangle + \langle V\rangle$ was used as a check on the correctness of the minimization.

In the subsequent discussion it will be seen that some modifications of the conclusions drawn in the COTTRELL and SUTTON, and HURLEY papers are necessary. Since the above wave functions provide varying degrees of flexibility, within the variation procedure, to adjust to the asymmetry of the screened nuclear charges in heteronuclear bonds, the results for these molecules are used as a basis for discussing factors influencing properties peculiar to heteropolar situations.

II. Results of the Energy Calculation

(Z, Z) *molecules*

A summary of the binding energies of homonuclear molecules (Z,Z) for the three trial wave functions of Eq. (2) and the Hurley function is given in Tab. 1. All of the binding energies are calculated relative to the energies of the separated atoms at infinite distance.

The positive entries in Tab. 1 deserve some comment at this point. When $Z \neq 1$, the results for the Wang and Weinbaum energies show the following behavior as a function of the internuclear distance. As R increases from zero, $E(R)$ decreases to a minimum. A further increase in R is accompanied by an increase in $E(R)$ until it reaches a maximum value above the zero of energy. Finally, as R increases without bound, $E(R)$ decreases and approaches the proper limiting value of zero as expected from the nature of these two wave functions.

The left hand portion of Fig. 1 displays the Weinbaum energy values of these maxima and minima as a function of the ordinate Z. The right hand side of the diagram gives the values of R at which the maxima and minima occur. For example, if the ordinate $Z = 1.4$ is selected and a horizontal line drawn across the graph, the abscissae of the intersections of this line with the four curves give, respectively, the energy at the minimum, the energy at the maximum, R at the minimum and R at the maximum. For $Z > 1.65$ and $Z < 0.55$, the relative minima

Table 1. *Binding Energies*[a] *of Homonuclear Molecules (Z,Z)*

Z	Wave Function			
	Wang	MO	Weinbaum	Hurley
0.5	+0.0148	+0.0250	+0.0131	+0.024
0.6	-0.0185	-0.0056	-0.0189	-0.008
0.7	-0.0548	-0.0401	-0.0549	-0.047
0.8	-0.0895	-0.0744	-0.0907	-0.085
0.9	-0.1186	-0.1048	-0.1227	-0.120
1.0	-0.1391	-0.1282	-0.1479	-0.148
1.1	-0.1481	-0.1419	-0.1637	-0.162
1.2	-0.1434	-0.1437	-0.1677	-0.161
1.3	-0.1233	-0.1317	-0.1581	-0.140
1.4	-0.0865	-0.1045	-0.1334	-0.095
1.5	-0.0316	-0.0599	-0.0921	-0.025
1.6	+0.0412	+0.0021	-0.0337	+0.074
1.7	+0.1314	+0.0830	+0.0428	—
1.8	+0.2382	+0.1833	+0.1375	—
1.9	—	+0.3026	+0.2503	—
2.0	—	+0.4415	+0.3801	+0.810

[a] Energies in atomic units.

occur with energy values greater than zero. These molecules may be considered stable in the sense that energy of the amount $E_{\max} - E_{\min}$ is required to get the molecule over the hump to dissociate. The positive values in the Weinbaum column of Tab. 1 are the energies at these relative minima with respect to the separated atoms.

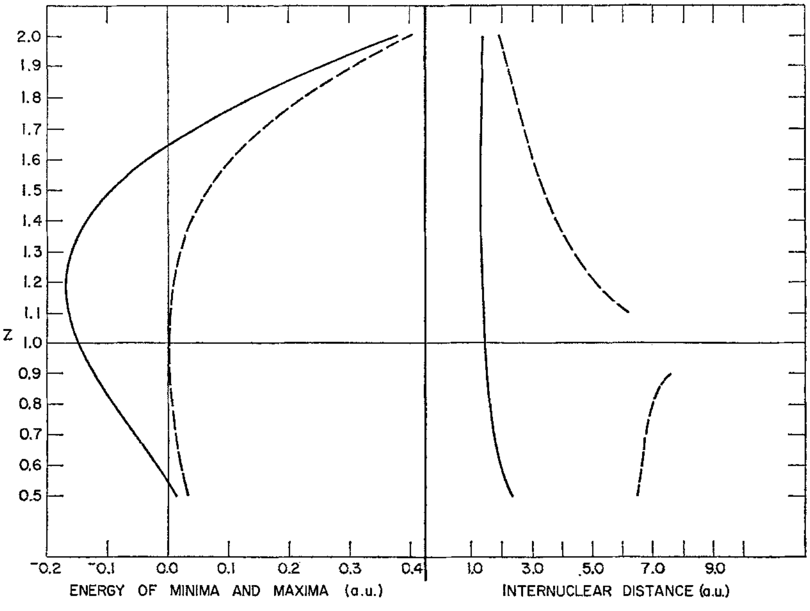

Fig. 1. Binding energy maxima and minima and associated internuclear distances for the Weinbaum (Z,Z) molecules. ——— refers to properties of the minima and - - - - to properties of the maxima. Curves for the internuclear distances at the maxima are approximate

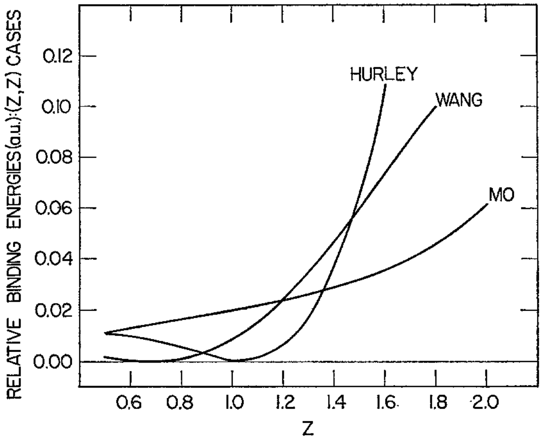

Fig. 2. Comparison of the MO, Wang and Hurley binding energies with the Weinbaum results for the (*Z*,*Z*) molecules

Fig. 1 also shows that the energies at the maxima and minima as well as their respective R values approach each other as Z goes above 2.0 or below 0.5. Thus *at some value* $Z > 2.0$ *and* $Z < 0.5$, *the molecules with these* Z *values will no longer bind and* $E(R)$ *will monotonically decrease* with increasing R. The analogous Wang results exhibit the same general behavior with the exception that the coalescence of the minimum and maximum occurs at a Z value slightly greater than 1.8.

The binding energies summarized in Tab. 1 show the same trend with Z but important differences appear in their relative values which are related to the manner in which ionic terms are incorporated into the four trial functions. The Wang function neglects these terms, the MO weights them equally with the covalent term, and the Weinbaum allows an optimal mixture of covalent and ionic parts. Finally, the Hurley function fixes the relative ionic contribution to that value determined from the Weinbaum function for the hydrogen molecule.

In Fig. 2 we have chosen the Weinbaum as our best function and have plotted as a function of Z the differences between the minimum energies obtained from this function and those of the MO, Wang and Hurley functions. From the way the wave functions are constructed, it is apparent why Hurley's results agree best with the Weinbaum energies for Z values near unity. However, both the Wang and MO functions give better relative values for other ranges of Z. At low Z values, $Z < 0.8$, the Wang energies approach those of the Weinbaum function. The reason for this behavior can be partially understood by examining Fig. 3 which displays the Z dependence of the optimal ionic and covalent coefficients as well as the ratio of their squares. As Z decreases from unity, the ionic coefficient, C_2, becomes progressively smaller in magnitude, passes through zero at $Z \sim 0.67$, and then becomes negative. At $Z \sim 0.67$, $C_2 = C_3 = 0$, and the Weinbaum and Wang functions become identical. For $Z < 0.67$, the variational adjustment of the linear coefficients of the Weinbaum function necessitates negative ionic coefficients to meet the energy minimization requirement. The origin of this interesting result and its relationship to electron correlation will be discussed more extensively in a future report. From the Z dependence of C_2^2/C_1^2 in Fig. 3, it can be said that, within the

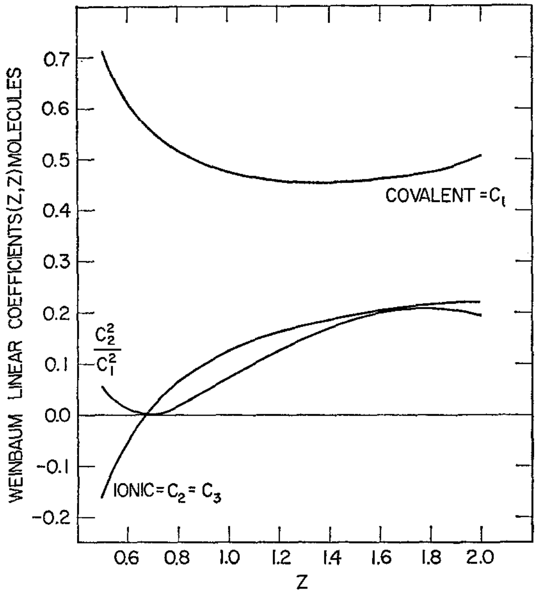

Fig. 3. Optimal values of the ionic and covalent coefficients and the ratio of their squares for the Weinbaum (Z,Z) molecules

framework of the present model, an attempt to associate the "ionic" character of a homonuclear bond with the relative magnitude of the ionic and covalent coefficients must be viewed with caution [*12*].

Whereas the Wang energies are a good approximation to the Weinbaum results for low Z values, at $Z > 1.2$, the MO function proves better. Again a partial explanation is provided in Fig. 3 where it is seen that as Z increases, C_2 shows a general increase in value with the result that the ionic contribution in the Weinbaum function increases in importance.

(1, Z) *and* (1 + ε, 1 − ε) *molecules*

The energy minima for the heteronuclear molecules (1,Z) and (1 + ε, 1 − ε) are presented in Tab. 2 and 3 respectively. Since Hurley's paper contains no explicit treatment of the (1,Z) cases, they are absent from Tab. 2. It should be noted that the binding minima are calculated with respect to the dissociation products determined by the particular ε or Z under consideration. Simple calculation shows that when $\varepsilon \gtrsim 0.38$ or $Z \gtrsim 1.70$, the "neutral atoms" with one electron at each nucleus are of lower energy than the "ions" $(1 + \varepsilon)^-$ and Z^-. For ε and Z greater than these critical values, the ions are more stable and entries in Tab. 2 and 3 take this into account where appropriate.

Fig. 4 shows how the MO, Wang and Hurley functions compare energetically to the Weinbaum function as the nuclear charge asymmetry, ε, increases. The trends for the (1,Z) cases are similar. These results can be understood in terms of the inherent flexibility of the trial functions to allow charge transfer to the more electronegative center and dissimilar orbital exponents in the $1s_A$ and $1s_B$ orbitals

Table 2. *Binding Energies*[a] *of Heteronuclear Molecules (1,Z)*

	Wave Function		
Z	Wang	MO	Weinbaum
0.5	−0.0917	−0.0827	−0.0983
0.7	−0.1134	−0.1025	−0.1192
0.9	−0.1312	−0.1193	−0.1380
1.1	−0.1464	−0.1386	−0.1591
1.3	−0.1590	−0.1660	−0.1875
1.5	−0.1688	−0.2074	−0.2286
1.7	−0.1758	−0.2690	−0.2884
2.0	+0.1669	−0.0684	−0.0816

[a] Energies in atomic units. Energy zero is taken as the energy of the separated atoms, except for $Z = 2.0$ for which the separated ion energy is the zero.

on their respective centers. The Hurley and Weinbaum results compare well for small ε. This is to be expected since the Hurley values originate from a perturbation treatment of the Weinbaum approximation to the H_2 molecule. As will be seen below, the former function permits charge transfer. However, it allows no asymmetry in the orbital exponents which are fixed at the value of ζ for the parent H_2 molecule.

By contrast, the Wang approximation does not allow charge transfer but is able to adjust to nuclear asymmetry by having unequal orbital exponents. The lack of charge transfer as it affects the energy is dramatic, as illustrated in Fig. 4. These results make apparent the need for including charge transfer flexibility in the form of ionic terms within this approximation.

Finally, the MO function allows both charge transfer and different ζ values. However, the charge transfer flexibility of the MO is more limited than that of the Weinbaum because of the different ways in which the ionic terms are introduced into the two functions. We note that the MO function provides the best approxima-

Table 3. *Binding Energies*[a] *of Heteronuclear Molecules* $(1+\varepsilon, 1-\varepsilon)$

	Wave Function			
ε	Wang	MO	Weinbaum	Hurley
0.1	−0.1436	−0.1357	−0.1551	−0.155
0.2	−0.1566	−0.1582	−0.1764	−0.174
0.3	−0.1773	−0.1956	−0.2120	−0.206
0.4	−0.1826	−0.2251	−0.2393	−0.230
0.5	−0.0806	−0.1544	−0.1659	−0.151
0.6	+0.0120	−0.0979	−0.1068	−0.085
0.7	+0.0913	−0.0552	−0.0616	−0.032
0.8	+0.1491	−0.0259	−0.0301	+0.009

[a] Energies in atomic units. The energy zero is taken as the energy of the separated atoms for $\varepsilon < 0.4$, and for separated ions $(1+\varepsilon)^-$ and $(1-\varepsilon)^+$ for $\varepsilon \geq 0.4$.

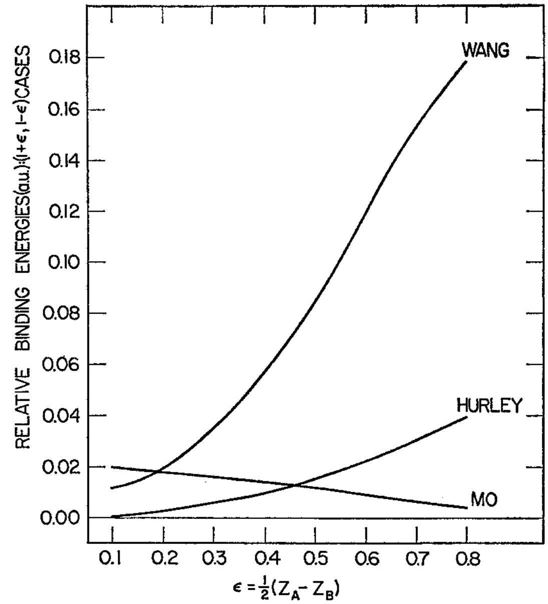

Fig. 4. Comparison of the MO, Wang and Hurley binding energies with the Weinbaum results for the $(1 + \varepsilon, 1 - \varepsilon)$ molecules

tion to the Weinbaum function for large values of ε. As ε gets small, both the Wang and Hurley functions prove better because of their greater merit as trial functions for the homonuclear H_2 molecule.

III. Charge Asymmetries and Dipole Moments

Since the asymmetric electronic charge distribution characteristic of heteronuclear diatomic molecules is reflected in many of the chemical and physical properties of these bonds, we wish to consider briefly how the wave functions in our calculations describe the electronic distributions of the model molecules. If we wish to understand the total electronic asymmetry in terms of its atomic constituents, there are at least three factors which must be considered:

1. electronic charge transfer to the valence active atomic orbitals on the more electronegative atom;
2. differences in the spatial extensions of the electronic densities associated with the two atoms;
3. distortion polarization and hydridization of the atomic orbitals.

Orbital populations

As mentioned previously, asymmetry is introduced into the wave functions used here by only the first two factors mentioned above. In order to isolate these, it is convenient to write the molecular density associated with the wave functions of Eq. (2) as

$$\varrho(1) = q(A)\, a^2(1) + q(B)\, b^2(1) + 2p(A,B)\, \left\{a(1)\, b(1) - \frac{S}{2}\, [a^2(1) + b^2(1)]\right\} \qquad (3)$$

with

$$q(A) = 2[C_1^2 + C_2^2 + 3C_1C_2S + C_1C_3S + (C_1^2 + C_2C_3)\,S^2]$$

$$q(B) = 2[C_1^2 + C_3^2 + 3C_1C_3S + C_1C_2S + (C_1^2 + C_2C_3)\,S^2]$$

$$p(A,B) = 2[C_1C_2 + C_1C_3 + (C_1^2 + C_2C_3)\,S]$$

and

$$S = \int a(1)\,b(1)\,d\tau_1\,.$$

The detailed physical significance of this density partitioning has been discussed elsewhere [*1*]. For our purposes it is sufficient to note that the terms $q(A)\,a^2(1)$ and $q(B)\,b^2(1)$ can be regarded as the contributions to the total molecular density arising from the modified atoms A and B *as they appear in the molecule.* The quantities $q(A)$ and $q(B)$ are defined as the populations of orbitals a and b, respectively, and are found to obey the relationships

$$\int q(A)\,a^2(1)\,d\tau_1 = q(A)\,,\ \int q(B)\,b^2(1)\,d\tau_1 = q(B)$$

with

$$\int \varrho(1)\,d\tau_1 = q(A) + q(B) = 2\,.$$

Thus, we may define the contribution to the total charge asymmetry which results from charge transfer as the difference in the orbital populations

$$\delta = q(A) - q(B) = 2[C_2^2 - C_3^2 + 2C_1(C_2 - C_3)\,S]\,.$$

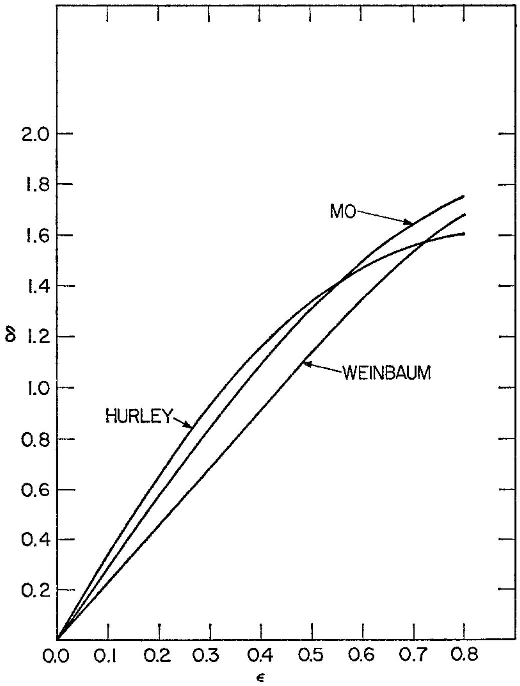

Fig. 5. Orbital population differences as a function of the nuclear charge asymmetry for three approximate wave functions

The consequences of this definition are immediate. Since $C_2 = C_3$ for homopolar bonds, $\delta = 0$ as expected. Secondly, for any bond described by a Heitler-London or Wang wave function, $C_2 = C_3 = 0$, and again $\delta = 0$. In the present calculation only the Weinbaum and MO functions allow charge transfer. In addition, the Hurley function may be written in the form of Eq. (2c) with the result that $\delta \neq 0$ since $C_2 \neq C_3$.

The parameter δ has been calculated for these three wave functions at the energy minima for the heteropolar series $(1 + \varepsilon, 1 - \varepsilon)$. The results are shown in Fig. 5 as a function of ε. In general all three wave functions show the same trend with increasing nuclear asymmetry. In order to achieve the best energy, however, the MO function must allow a greater charge difference than the corresponding Weinbaum results. The Hurley function shows the largest δ values for $\varepsilon < 0.55$, but as ε increases beyond this point, δ increases less rapidly and eventually at $\varepsilon = 0.8$, lies below both the MO and Weinbaum results. This behavior may be traced to the form of the approximate wave function used by Hurley in his perturbation treatment.

Dipole moment

A property closely related to the charge difference δ but characteristic of the total asymmetric electronic distribution is the electronic contribution to the dipole moment. Application of the dipole moment operator to the density of Eq. (3) and subsequent integration gives as the electronic moment or negative

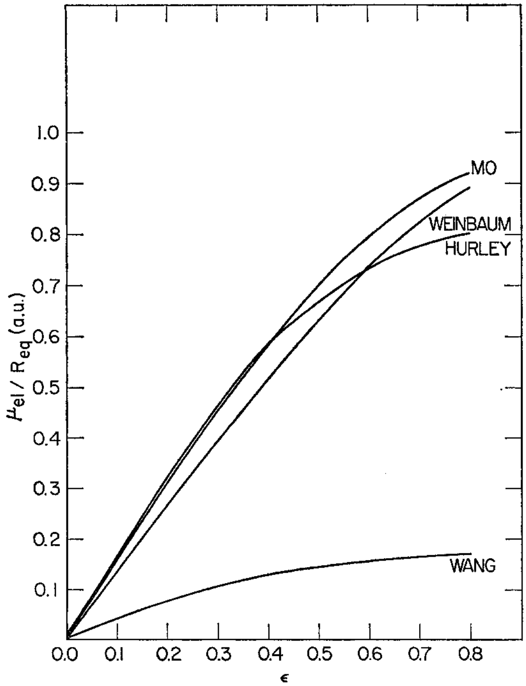

Fig. 6. Reduced electronic dipole moments as a function of the nuclear charge asymmetry for the four trial wave functions

center of electronic charge, the expression

$$\mu_{el} = \tfrac{1}{2} R_{eq}\, q(A) - \tfrac{1}{2} R_{eq}\, q(B) - 2p(A,B) \langle a \mid z \mid b\rangle = \tfrac{1}{2}\delta R_{eq} - 2p(A,B) \langle a \mid z \mid b\rangle$$

with the origin of coordinates taken at the midpoint of the bond distance. The electronic moment is seen to consist of two terms. The first, $\frac{1}{2}\,\delta R_{eq}$, originates from the atomic contributions to the total density and is directly related to the difference in orbital populations. The second term, $2p(A,B) \langle a \mid z \mid b\rangle$, is nonzero only if the spatial extensions of the a and b orbitals are different and, hence, reflects that portion of the total charge asymmetry due to this factor.

The electronic moments divided by R_{eq} have been calculated for the $(1+\varepsilon, 1-\varepsilon)$ molecules with all four wave functions. The results are displayed in Fig. 6 as a function of ε. Not surprisingly, the Wang function is quite unsuitable for reproducing the total charge asymmetry in a heteropolar bond between atoms of different electronegativities since it allows only contributions of the second kind. Charge transfer is essential as shown by the similar behavior of the electronic moments for the other three functions. In fact, the Hurley function achieves its moment solely through charge transfer effects. The similarity of the Hurley moments with those calculated from the MO and Weinbaum functions clearly indicates that the charge transfer asymmetry is the dominant contribution in these calculations.

IV. Electronegativity

As is well known, Pauling empirically established for many heteronuclear diatomic molecules that the quantity

$$\Delta = E^B_{\mathrm{AB}} - \tfrac{1}{2}\{E^B_{\mathrm{AA}} + E^B_{\mathrm{BB}}\} > 0$$

where E^B_{AB}, E^B_{AA} and E^B_{BB} are the absolute values of the binding energies for the diatomic molecules indicated in the subscripts. His explanation included a discussion of the relative contributions of the ionic terms in the approximate wave functions for these molecules. One of the most interesting results of the Cottrell and Sutton paper was the observation that Δ is positive even though the calculations were performed with a simple valence bond function which makes no explicit reference to ionic terms.

On the basis of their results Cottrell and Sutton formulated two rules for the model systems:

1. The electronic energy, E^{el}_{AB}, is constant for molecules with $Z_A + Z_B =$ constant, if $Z_A - Z_B$ is not too large.
2. $E^{el}_{AB} = \frac{1}{2}\{E^{el}_{AA} + E^{el}_{BB}\}$.

These authors concluded that the additional stability of the heteropolar bond could be attributed primarily to a decrease in the nuclear repulsion energy of the screened A and B nuclei relative to that of the hydrogen molecule. Hurley confirmed these conclusions with his improved calculations, and since his wave function contains ionic terms, the stabilization of the AB bond appears qualitatively independent of their inclusion.

The more precise calculations reported here bear out the principal qualitative conclusions of the previous investigations, but establish narrower limits on the

Table 4. *Electronic Energies*[a] *for* A_2 *and* AB *Molecules (Weinbaum-type Wave Function)*

Z_A	Z_B	$\frac{1}{2}\{E^{el}_{AA} + E^{el}_{BB}\}$	E^{el}_{AB}	ΔE^{el}
1.00	1.00	—	1.8472	—
1.10	0.90	1.8624	1.8569	-0.0055
1.20	0.80	1.9062	1.8858	-0.0204
1.30	0.70	1.9807	1.9339	-0.0468
1.40	0.60	2.0857	2.0013	-0.0844
1.50	0.50	2.2195	2.0880	-0.1315

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[a] The absolute values of the electronic energies have been taken and are given in atomic units. ΔE^{el} is the difference between the fourth and third columns.

validity of the two rules stated above. Examination of the fourth column of Tab. 4 shows the first rule to be accurate to 0.01 a.u. when $Z_A - Z_B < 0.2$. The fifth column of this table offers a test of the second rule, where we note that as the nuclear charge asymmetry increases for $Z_A + Z_B = 2.0$, ΔE^{el} becomes increasingly negative and results in a *destabilization* of the heteronuclear bond relative to the parent homonuclear molecules. Since Δ itself is positive, the stabilization of the AB bond results from the decrease in nuclear repulsion in spite of the opposite trend in the electronic energy. This result is clearly indicated in Fig. 7 where ΔE^{NR} is the negative of the difference between the nuclear repulsion of AB and the average of that for AA and BB. The various energy differences appear as linear functions of ε^2 and have been calculated for values of ε such that AB dissociates to atoms. An additional feature of Fig. 7 is the fact that trends for both the Heitler-London-Wang and Weinbaum calculations are qualitatively quite similar, making it unnecessary to appeal to relative ionic term contributions as the source of the stabilization.

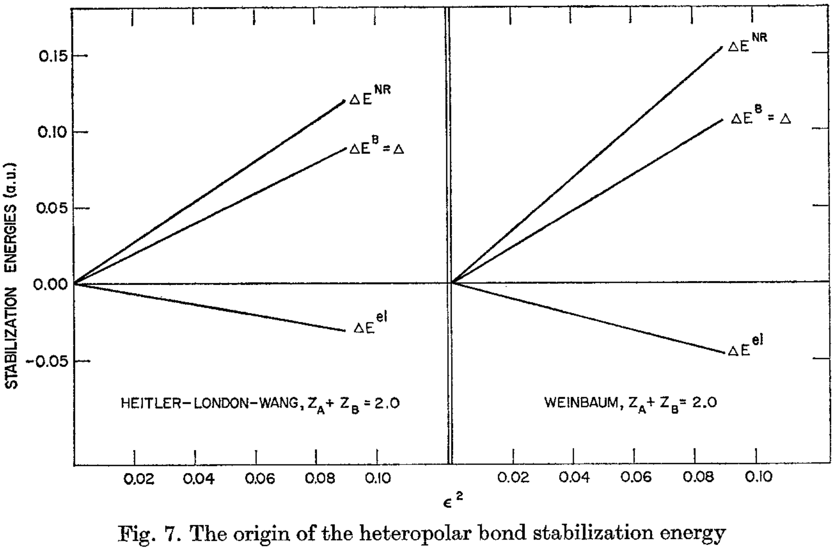

Fig. 7. The origin of the heteropolar bond stabilization energy

Table 5. *Electronic Moments and Electronegativity Differences for Various Nuclear Charge Sums*

$Z_A + Z_B$	$Z_A - Z_B$	$\frac{\mu_{el}}{R_{eq}}$	$\Delta^{1/2}$
1.5	0.1	0.0527	0.0361
	0.3	0.1672	0.1072
	0.5	0.2907	0.1758
1.7	0.1	0.0640	0.0447
	0.3	0.1870	0.1334
	0.5	0.3145	0.2211
2.0	0.2	0.1315	0.1091
	0.4	0.2622	0.2173
	0.6	0.3910	0.3248
2.3	0.1	0.0665	0.0616
	0.3	0.1981	0.1857
	0.5	0.3280	0.3088
2.5	0.1	0.0659	0.0663
	0.3	0.1982	0.1979
	0.5	0.3294	0.3295

In addition to the Δ's and electronic moments calculated for $Z_A + Z_B = 2.0$, we have collected together in Tab. 5 some additional data from the Weinbaum approximation for other nuclear charge totals. We note that in each case both the

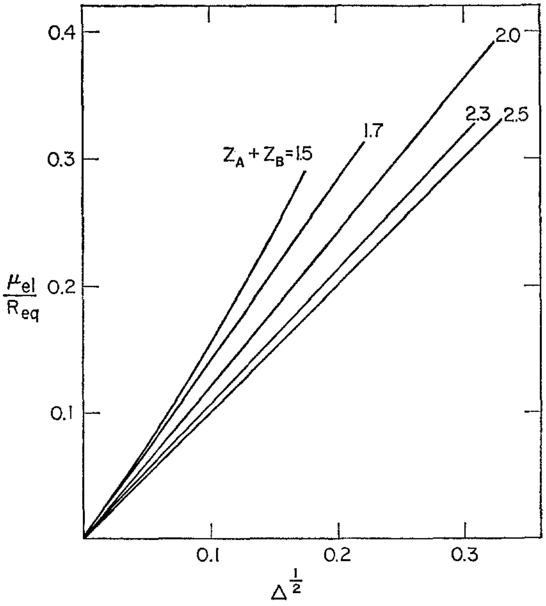

Fig. 8. The "partial ionic character" vs. the electronegativity difference as a function of the total screened nuclear charge

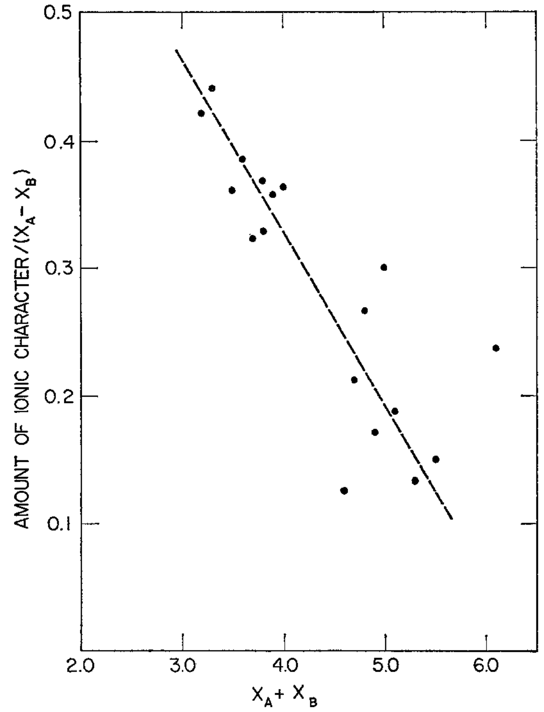

Fig. 9. Correlation of the "amount of ionic character" per unit electronegativity difference with the electronegativity sum. The dashed line is not a prediction from the model, but is included only to illustrate the trend

electronic moment and $\Delta^{1/2}$ show, to a very good approximation, a linear dependence on the nuclear charge difference, $Z_A - Z_B$. The result, then, that the electronic moment is linear in $\Delta^{1/2}$ is shown as the family of lines in Fig. 8. If we regard μ_{el}/R_{eq} as directly related to Pauling's "amount of ionic character" and $\Delta^{1/2}$ as proportional to the electronegativity difference, $\chi_A - \chi_B$, then Fig. 8 may be compared with the analogous graph given by PAULING [*13*].

Recognizing the inherent shortcomings and approximate nature of the model, there are several features of Fig. 8 which deserve some comment. PAULING [*14*] related ionic character to electronegativity difference with the curve

$$\text{"amount of ionic character"} = 1 - e^{-0.25\,(\chi_A - \chi_B)}\,.$$

However, if we regard $Z_A + Z_B$ as directly related to the electronegativity sum $\chi_A + \chi_B$, the results for the model predict a family of linear relationships which have the property that the slope of the lines increase as $\chi_A + \chi_B$ decreases. This result indicates a possible reason why Pauling's curve only roughly agrees with the experimental points on his graph. In order to test this prediction, we have determined the amount of ionic character from Pauling's graph for the molecules he lists there, divided this quantity by $\chi_A + \chi_B$ as determined from his electronegativity table [*15*], and plotted this quotient as a function of $\chi_A + \chi_B$. The result, shown in Fig. 9, appears to indicate a correlation between the slope and electronegativity sum in qualitative agreement with the behavior of the model.

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