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The Nature of the Two-electron Chemical Bond. I. The Homopolar Case[1]

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By using the artifice of dividing space into two parts by means of a plane perpendicular to the internuclear axis and passing through its midpoint, it is shown that there is possible a division of a two-configuration two-electron wave function into two orthogonal parts each of which has optimum properties associated with the plane intuitively corresponding to the names "ionic" and "atomic." The division of the density distributions for the Wang, Weinbaum and Rosen functions into ionic, atomic and ionic-atomic cross-term parts is considered, and it is shown that the first two parts are roughly non-bonding, whereas it is the last part which contributes most to the density between the nuclei in the binding region. Analysis of the energetic parameters also leads to this conclusion. Consequently, the term covalent seems best applied to the cross-term. The analysis seems to supply the need for a sound theoretical basis to the kind of empirical concept embodied in the phrases "ionic and covalent character" but suggests that the language needs to be modified to some extent. The method is capable of extension to the heteropolar bond.

I. Introduction

We consider in this paper the nature of the general idea of ionic and covalent character as applied to the homopolar two-electron chemical bond and in particular, to the specific case of the hydrogen molecule. The original identification[3] of the covalent bond type in this case with the Wang[4] trial variation function of the form $\Psi_W = N\{1s_a(1)\ 1s_b(2) + 1s_b(1)\ 1s_a(2)\}$ where $1s_a$ and $1s_b$ are hydrogen-like orbitals with variable exponents centered on atoms a and b, respectively, and the ionic bond type with terms of the form $\Psi_I = N\{1s_a(1)\ 1s_a(2) + 1s_b(1)\ 1s_b(2)\}$ added by Weinbaum[5] has many theoretical drawbacks. In the first place it is unsatisfactory to base a rather general concept upon a specific quite arbitrary functional form. Thus the Rosen function,[6] which has $\Psi_R = N_R\{(1s_a + \mu 2p\sigma_a)(1)(1s_b + \mu 2p\sigma_b)(2) + (1s_b + \mu 2p\sigma_b)(1)(1s_a + \mu 2p\sigma_a)(2)\}$ and which is usually discussed in terms of polarization rather than in terms of ionic character, is very similar indeed to the Weinbaum function,[7] and if the concepts of ionic and covalent character were to have any general validity, then it should be possible to substitute the Rosen function for the Weinbaum function in the description. The definition of the concepts as given originally by Pauling is not satisfactory therefore since the definition is not independent of the original choice of the basis of mathematical functions used in describing the wave function.

Beyond the limitation implied in this necessarily narrow choice of basis, there is an even more objectionable feature of the usual definition. Namely, the covalent function of Wang and the ionic terms added by Weinbaum are by no means orthogonal. This was most clearly demonstrated by Braunstein and Simpson[8,9] who pointed out that the two opposing concepts actually had an overlap of about 0.95! Braunstein and Simpson tried to overcome this deficiency in the definition by introducing an "atomic" function in addition to covalent and ionic terms functions which were now chosen orthogonal. With the particular atomic function they chose, no consistent scheme of ionic and covalent functions was found. The basic trouble, as they themselves pointed out, was that the nature of the definition became very dependent upon small changes in the particular atomic function chosen. In other words, they failed to satisfy the criterion that the definition must be independent of the choice of basis function.

The theoretical inadequacies, however, of the definitions of these concepts used hitherto must not be allowed to obscure the brilliantly successful utilization of the concepts, especially in the hands of Pauling. We therefore adopt the viewpoint for the purpose of the present paper that the concepts themselves are valid but only the theoretical foundation is at fault. It is our purpose to make an effort to establish a sound foundation.

In order to remove the difficulty concerning the arbitrary nature of the basis, we use a natural orbital expansion as our point of departure. In the development that follows, we show that the requirement of orthogonality follows in a natural way. The final picture differs in some fundamental respects from that originally offered by Pauling but nevertheless it seems clear that the essence of the empirically useful quantities still remains.

II. The Natural Expansion

If one has an arbitrary complete set of one-electron functions, or orbitals ϕ_i, any two-electron function may be expressed as an infinite sum of products over these orbitals in which both diagonal terms, $\phi_i(1)\phi_i(2)$, and non-diagonal terms, $\phi_i(1)\phi_j(2)$, $(i \neq j)$ appear. It is possible, however, to find a linear transformation of the ϕ_i to a new orthogonal set of orbitals, χ_i, such that no cross-terms appear in the expansion. This latter expansion is known as the natural expansion and χ_i referred to as natural orbitals for the two-electron system. The natural expansion becomes more complex for poly-electronic wave functions and in these cases one must refer directly to the

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(2) On leave from the Chemistry Department, Indiana University, February 1958–September 1959.

(3) L. Pauling, "Nature of the Chemical Bond," Cornell University Press, Ithaca, New York, 1939.

(4) S. C. Wang, *Phys. Rev.*, **31**, 579 (1928).

(5) S. Weinbaum, *J. Chem. Phys.*, **1**, 593 (1933).

(6) N. Rosen, *Phys. Rev.*, **38**, 2099 (1931).

(7) H. Shull, *J. Chem. Phys.*, **30**, 1405 (1959).

(8) J. Braunstein and W. T. Simpson, *ibid.*, **23**, 174 (1955).

(9) J. Braunstein and W. T. Simpson, *ibid.*, **23**, 176 (1955).

first order density matrix from which it is derived in general.

The natural orbital expansion[10] for two electron systems has been shown to have a number of advantages. In the first place, there is a marked reduction in the number of necessary configurations with any finite basis set. Secondly, the expansion truncated to some finite number of terms is a well-defined approximation to the complete function, namely, that function of the particular rank involved having maximum overlap with the complete function. Thirdly, the natural expansion based on a complete set of functions is independent of the particular complete basis set chosen. Furthermore this independence is remarkable even when the basis set is not complete. Thus in both the case of He[11] and for H_2[7] it has been shown that the "occupation numbers" or alternatively the coefficients in the natural expansion are very nearly given correctly for even very simple trial functions. It is in particular this relative independence to the choice of original basis and the well-defined nature of the truncated approximation that make the natural expansion a particularly suitable starting point for an analysis of ionic and covalent character.

In the previous analysis[7] of hydrogen molecule trial wave functions in terms of approximate natural orbitals, it was shown that the first natural orbital, χ_1, was an approximation to the SCF orbital and was Σ_g in symmetry. The natural orbital with second highest occupation number, χ_2, was Σ_u in symmetry, whereas the third was Π, *i.e.*, not axially symmetric. Now clearly the intuitive concept of ionic terms and covalent character cannot be realized in terms of a single configuration (the MO approximation). Nor does the concept involve any axial correlation such as is introduced with the Π term. It seems logical, therefore, to limit the present discussion to a truncated natural orbital expansion containing just the first two configurations. Both the Wang and Weinbaum functions utilized by Pauling fit in this general category,[7] but of course our point of departure is in principle a considerably better function than either of these. Whereas the Wang function has an expectation value of -1.139 *H*,[12] and the Weinbaum function, -1.148 *H*, it seems likely that the best function to which our truncated expansion corresponds has an expectation value near -1.156 *H*. Most of the remaining discrepancy between this value and the experimental result of -1.174 *H* lies in the angular terms.[13]

We will therefore assume that we have available to us the natural expansion for the hydrogen molecule derived from some complete basis set. We truncate this to two terms, renormalize to unity and write for our approximation to the exact wave function[14]

$$\Psi = n_1{}^{1/2}\chi_1(1)\chi_1(2) - n_2{}^{1/2}\chi_2(1)\chi_2(2) \qquad (1)$$

Since χ_1 and χ_2 are orthogonal, we have the condition

$$n_1 + n_2 = 1 \qquad (2)$$

The coefficients, $n_1{}^{1/2}$ and $n_2{}^{1/2}$, are both chosen positive. The negative sign appearing in eq. 1 has been shown to be a necessity for the present case.[11]

III. Atomic and Ionic Forms

We define an atomic "form" of wave function by

$$\Psi_A = N_+\{u(1)v(2) + v(1)u(2)\} \qquad (3)$$

a plus ionic "form" by

$$\Psi_{1+} = N_+\{u(1)u(2) + v(1)v(2)\} \qquad (4)$$

and a minus ionic "form" by

$$\Psi_{1-} = N_-\{u(1)u(2) - v(1)v(2)\} \qquad (5)$$

where u and v are arbitrary normalized space orbitals, and the normalization constants are given by

$$N_\pm = \{2(1 \pm S^2_{uv})\}^{-1/2} \qquad (6)$$

S_{uv} is the overlap integral between u and v, $\int uv\,d\tau$. We justify the choice of names "atomic" and "ionic" later in the paper. It is obvious that the form of eq. 3 is indeed similar to that of the Heitler–London (or Wang) function,[15] whereas eq. 4 takes the form of the ionic terms added by Weinbaum. The form Ψ_{I-} does not appear in the usual treatments of the homopolar molecule when u and v are chosen symmetrically related but will appear with an unsymmetrical choice of u and v. We want to ascertain whether these forms have some significance in themselves irrespective of the nature of the functions u and v.

To investigate this we consider that u and v are linear combinations of the natural orbitals χ_1 and χ_2 introducing arbitrary parameters, α and β, such that

$$u = \chi_1 \cos\alpha + \chi_2 \sin\alpha \qquad (7a)$$

$$v = \chi_1 \sin\beta - \chi_2 \cos\beta \qquad (7b)$$

It follows that u and v are normalized and the overlap integral between them is given by

$$S_{uv} = \sin(\beta - \alpha) \qquad (8)$$

From equation 8, it follows that u and v are orthogonal if $(\beta - \alpha) = \eta\pi$. By proper choice of relative phases, we need deal only with the principal case, $\beta - \alpha = 0$. In that case, of course, Ψ_A, Ψ_{I+}, and Ψ_{I-} all become mutually orthogonal.

Provided $(\alpha - \beta) \neq \pi/2$ the transformation inverse to (7) exists and we may substitute this into eq. 1. Collecting terms, one obtains

$$\Psi = \lambda_A\Psi_A + \lambda_{1+}\Psi_{1+} + \lambda_{I-}\Psi_{1-} \qquad (9)$$

where

$$\lambda_A = N_+\{(n_1{}^{1/2} + n_2{}^{1/2}) \sin(\alpha + \beta) + (n_1{}^{1/2} - n_2{}^{1/2}) \sin(\alpha - \beta)\}/2\cos^2(\alpha - \beta) \qquad (10a)$$

$$\lambda_{1+} = N_+\{(n_1{}^{1/2} - n_2{}^{1/2}) \cos(\alpha - \beta)\}/2\cos^2(\alpha - \beta) \qquad (10b)$$

$$\lambda_{1-} = N_-\{(n_1{}^{1/2} + n_2{}^{1/2}) \cos(\alpha + \beta)\}/2\cos^2(\alpha - \beta) \qquad (10c)$$

For the moment let us consider the symmetrical case in which the coefficients of $u(1)u(2)$ and of $v(1)v(2)$ are identical. Then λ_{I-} must vanish.

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[10] P. O. Löwdin and H. Shull, *Phys. Rev.*, **101**, 1730 (1956).

[11] H. Shull and P. O. Löwdin, *J. Chem. Phys.*, **30**, 617 (1959).

[12] In this paper we use uniformly the Hartree atomic unit, denoted *H*, as a unit of energy. 1*H* = 27.21 e.v. = 627.7 kcal./mole

[13] H. Shull, *Ann. Acad. Reg. Sci. Upsaliensis*, **3**, 65 (1959).

[14] We deal here only with the singlet ground state. The spin variables are not pertinent to the development and are uniformly omitted.

[15] We have referred earlier (ref. 10) to this as the (*u*,*v*) form.

The condition for the symmetrical case is therefore (see eq. 10c) that $\cos(\alpha + \beta) = 0$ or $(\alpha + \beta) = n\pi + \pi/2$. Once again, by appropriate choice of phases we can always take the case $n = 0$. In this case one obtains $S_{uv} = \pm \cos 2\alpha$ and

$$\lambda_{I+}/\lambda_A = (p - S_{uv})/(1 - pS_{uv}) \qquad (11)$$

where

$$p = (n_1^{1/2} - n_2^{1/2})/(n_1^{1/2} + n_2^{1/2})$$

Since $0 < p < 1$ and $-1 < S_{uv} < +1$, it is established that the ratio λ_{I+}/λ_A runs over the limits

$$(p - 1)/(1 + p) < \lambda_{I+}/\lambda_A < (p + 1)/(1 - p)$$

Summarizing, we conclude that by a choice of $(\beta - \alpha)$ in the symmetric case, functions u and v can be formed with any arbitrary overlap such that Ψ of eq. 1 can be expressed in the form of eq. 9 (with $\lambda_{I-} = 0$). In the latter form, the ratio λ_{I+}/λ_A is a function of the arbitrarily chosen S_{uv} and covers an extensive range. In the case of the Wang function, for example, $-0.186 < \lambda_{I+}/\lambda_A < 5.387$. It is clear then that there is no special importance to be attached to the *forms* of Ψ_A or of Ψ_{I+} *per se*. In order to find a basis for discussion of ionic character, then, we must ascertain whether there is some particular choice of the transformation (7) which makes Ψ_A, Ψ_{I+}, and Ψ_{I-} take on optimum characteristics associated with the intuitive concepts we attribute to them.

We will consequently look for a quantitative property to associate with the intuitive idea suggested in Pauling's terminology. We will want an ionic function, for example, in which it is very probable that both electrons are simultaneously associated with one of the molecular centers as opposed to the situation in which each is associated with a different molecular center. By contrast, the opposing concept, which Pauling refers to as covalent, will have these two factors reversed in importance.

One might suggest as natural consequence of the Pauling definition that the choice in which u is centered upon one nucleus and v upon the other is of particular significance. This suggestion, however, is not very fruitful since an orbital function on one center may be expanded in terms of a complete set of functions based on another center and there is then no way of saying what amount "belongs" on either center. To solve the problem, we now turn to a study of the internal nature of Ψ_A, Ψ_{I+} and Ψ_{I-} as a function of α and β.

IV. Optimal Choice of Ψ_A, Ψ_{I+} and Ψ_{I-}

Let us consider that space is divided in half by a plane passing through the molecular midpoint and perpendicular to the molecular axis. Denoting the two regions of space thus resulting by L (left) and R (right), we can divide the normalization integral into parts depending upon whether both electrons are in the same half of space or in different halves of space. In particular

$$\int \Psi_A^2 \, d\tau = 1 = A_A + I_A$$

where

$$A_A = \int \Psi_A^2 \, d\tau_{1R} d\tau_{2L} + \int \Psi_A^2 d\tau_{1L} d\tau_{2R} \qquad (12)$$

and

$$I_A = \int \Psi_A^2 d\tau_{1R} d\tau_{2R} + \int \Psi_A^2 d\tau_{1L} d\tau_{2L} \qquad (13)$$

In a similar manner,

$$A_{I\pm} = \int \Psi^2_{I\pm} \, d\tau_{1R} d\tau_{2L} + \int \Psi^2_{I\pm} \, d\tau_{1L} d\tau_{2R} \quad (14)$$

$$I_{I\pm} = \int \Psi^2_{I\pm} \, d\tau_{1R} d\tau_{2R} + \int \Psi^2_{I\pm} \, d\tau_{1L} d\tau_{2L} \quad (15)$$

It seems intuitively obvious that, for example, I_A and $I_{I\pm}$ are intimately associated with our *a priori* intuitive concepts of the ionic nature of the respective functions. Similarly A_A and $A_{I\pm}$ are associated with the alternant or left-right kind of correlation implicit in the Heitler–London wave function. If we now introduce the transformation (7) into (12–15), we can attempt to find that choice of α and β which maximizes A_A, I_{I+} and I_{I-}. We note in advance that it is not necessarily to be expected that the same values of α and β which maximize one of the three will also make either of the others a maximum as well.

In the expressions for these quantities there appear three integrals over the natural orbitals, $R_{11} = \int \chi_1^2 d\tau_R$, $R_{22} = \int \chi_2^2 d\tau_R$ and

$$R_{12} = \int \chi_1 \chi_2 d\tau_R$$

In the homopolar case as a result of the symmetry of χ_1 and χ_2, $R_{11} = R_{22} = 1/2$. The third integral is in general non-zero. Corresponding integrals occur over the left-hand side of space but are easily related to these three by the orthonormality of χ_1 and χ_2. Performing the integration and rearranging somewhat,[16] we arrive at the general expressions

$$A_A = \frac{1}{2} + 2R_{12}^2 - 4R_{12}^2 \cdot \frac{\cos^2(\alpha + \beta) + \sin^2(\alpha - \beta)}{1 + \sin^2(\alpha - \beta)} \quad (16a)$$

$$I_{I+} = \frac{1}{2} + 2R_{12}^2 - 4R_{12}^2 \cdot \frac{\sin^2(\alpha + \beta)\sin^2(\alpha - \beta)}{1 + \sin^2(\alpha - \beta)} \quad (16b)$$

$$I_{I-} = \frac{1}{2} + 2R_{12}^2 - 4R_{12}^2 \cdot \frac{\cos^2(\alpha + \beta)\cos^2(\alpha - \beta)}{1 - \sin^2(\alpha - \beta)} \quad (16c)$$

Maximization of eq. 16 in the above trigonometric form is particularly simple since in each case the coefficient of the term $-4R_{12}^2$ is positive definite. Hence the optimum case is always that one in which this coefficient vanishes. Beginning with A_A, we have that $\cos^2(\alpha+\beta) + \sin^2(\alpha - \beta) = 0$ and hence both $\cos^2(\alpha + \beta) = 0$ and $\sin^2(\alpha - \beta) = 0$. The former condition leads to $\alpha + \beta = \pi/2$ and the latter $\alpha - \beta = 0$ in the principal case. Hence the condition for maximum A_A is that $\alpha = \beta = \pi/4$.

For I_{I+}, from eq. 16b we have that either $\sin^2(\alpha + \beta) = 0$ or $\sin^2(\alpha - \beta) = 0$. From the former condition $\alpha + \beta = 0$ and from the latter $\alpha - \beta = 0$. The second condition is precisely the one for orthogonality. The first condition is a new one which we note is incompatible with the symmetry condition. It leads to the particular choice that $u \equiv \chi_1$ and $v \equiv \chi_2$ or *vice versa*.

Finally we have the case of I_{I-}. Here either $\cos(\alpha + \beta) = 0$ or $\cos(\alpha - \beta) = 0$. The latter condition is, however, not permitted since in that case the transformation inverse to (7) does not exist ($u \equiv v$). Hence the only remaining condi-

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[16] This is recommended as a splendid exercise in trigonometric identities.

tion is that $\alpha + \beta = \pi/2$ which is precisely the symmetry condition.

We have summarized the results in Table I. If we combine the two conditions $\alpha - \beta = 0$ and $\alpha + \beta = \pi/2$, we find $\alpha = \beta = \pi/4$ and this choice simultaneously satisfies every condition in the table. No other choice of α and β satisfies all the conditions, and hence this particular choice seems to be the most suitable one from every point of view.

TABLE I

CONDITIONS IMPOSED UPON α AND β BY VARIOUS POSSIBLE CRITERIA

Criterion	Resulting conditions
Orthogonality of u and v	$\alpha - \beta = 0$
Symmetry of u and v	$\alpha + \beta = \pi/2$
A_A a maximum	$\alpha + \beta = \pi/2$ and $\alpha - \beta = 0$
I_{I+} a maximum	$\alpha - \beta = 0$ or $\alpha + \beta = 0$
I_{I-} a maximum	$\alpha + \beta = \pi/2$

V. Characteristics of the Optimal Choice

We have now reached the desired conclusion. Namely, by introducing new parameters in a two-configuration natural orbital expansion, it has been possible to choose these so that the complete wave function can be expressed in the form of eq. 9 in which each of Ψ_A, Ψ_{I+} and Ψ_{I-} has a certain optimum characteristic that is intuitively associated with the nature of the Heitler–London or the ionic terms, respectively. In the homopolar case, the rather natural symmetric case then prevails such that $\lambda_{I-} = 0$. Finally, and very important, this parameter choice is just that one which makes u and v orthogonal, and hence the set Ψ_A, Ψ_{I+} and Ψ_{I-} is orthonormal. We can conclude in this case then that $\lambda_A^2 + \lambda_{I+}^2 = 1$, and it becomes proper to speak of λ_{I+}^2, for example, as the fractional ionic character.

We can finally insert the values $\alpha = \beta = \pi/4$ in the respective equations to find

$$u = (\chi_1 + \chi_2)/\sqrt{2};\ v = (\chi_1 - \chi_2)/\sqrt{2} \qquad (17)$$

and

$$\Psi_A = \{\chi_1(1)\chi_1(2) - \chi_2(1)\chi_2(2)\}/\sqrt{2} \qquad (18)$$

$$\Psi_{I+} = \{\chi_1(1)\chi_1(2) + \chi_2(1)\chi_2(2)\}/\sqrt{2} \qquad (19)$$

At this point it is interesting to see how the present function Ψ_A, for example, derived from the Wang trial function compares with the Wang function itself with respect to A character. For the complete Wang function, we can use eq. 1 to calculate A_{Wang} defined in a manner similar to (12) and (14). Then

$$A_{\text{Wang}} = \frac{1}{2} + 2(n_1n_2)^{1/2}R_{12}^2 \qquad (20)$$

where now n_1 and n_2 refer to occupation numbers derived from the Wang function. By contrast

$$A_A = I_I = \frac{1}{2} + 2R_{12}^2 \qquad (21)$$

The computation of R_{12} is straightforward, using conventional integration techniques. In Table II we compare A_{Wang} with A_A for the Wang function as a function of the internuclear distance. For the occupation numbers we have used the data of Eliason and Hirschfelder.[17] The small errors in their results[7] will certainly not affect those listed in Table II significantly.

TABLE II

A_{Wang} AND A_A FOR THE WANG FUNCTION AS A FUNCTION OF THE INTERNUCLEAR DISTANCE R

$q = ZR$[a]	R[a]	R_{12}^2[b]	A_{Wang}[c]	A_A
0.0	0.0000	0.18750	0.50000	0.87500
1.0	0.7339	.19081	.55782	.88162
1.5	1.2099	.19590	.62174	.89179
1.637[d]	1.404[d]	.19761[d]	.64186[d]	.89522[d]
1.75	1.4731	.19913	.65899	.89826
2.0	1.7976	.20269	.69789	.90538
2.5	2.4169	.21037	.77468	.92074
3.0	2.9916	.21813	.84176	.93627
3.5	3.5204	.22534	.89393	.95068
4.0	4.0274	.23158	.93112	.96315
4.5	4.525	.23666	.95610	.97331
5.0	5.050	.24059	.97229	.98118
6.0	6.026	.24561	.98905	.99122
7.0	7.014	24807	99565	99615
8.0	8.038	.24919	.99828	.99838
10 0	10.02	24986	.99972	.99973
12.0		.24998	.99995	.99996

[a] R is the internuclear distance expressed in atomic units, or Bohrs, b. $1b = 0.592$ Å. Z is the scale factor yielding optimum energy for the reported R value. [b] $R_{12} = \int \chi_1\chi_2 d\tau_R$. [c] See eq. 20. We use the occupation number data of ref. 17 except for entry labeled [d]. [d] The calculated equilibrium case for the Wang function; occupation number data are from ref. 7.

From Table II it is readily apparent how much more suitable Ψ_A is than Ψ_{Wang} for describing the essential feature that the electrons are in different parts of space. At the equilibrium distance, for example, the Wang function normalization integral has a contribution of almost 36% from that part of six-dimensional space in which both electrons are on the same side of our imaginary dividing partition. In our optimum function Ψ_A, this is reduced to just over 10%. It now also becomes obvious that we do not wish to identify Ψ_A as a "covalent" function since this becomes a travesty on words, especially as R becomes large. It seems far preferable for this and for other reasons developed below to refer to it as "atomic," and we will adhere to that name henceforth.

It is not our purpose, however, to attach any deep significance to the quantities A_A and I_I, for such quantities derived by use of an artifice of dividing space in half by an imaginary plane can have little fundamental meaning. Rather it is suggested that the self-consistency and ideal nature of the results would lead one to believe that there probably exists some more sophisticated approach which will lead to precisely the functions Ψ_A and Ψ_I derived here by the use of an unsophisticated method. Consequently we wish to deëmphasize quantities which are primarily dependent upon the plane, and emphasize quantities based only on the functions themselves and on the natural expansion. Thus we turn first to look at λ_A^2 and λ_I^2 for the Wang function as a function of R and then study

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(17) M. A. Eliason and J. O. Hirschfelder, *J. Chem. Phys.*, **30**, 1397 (1959).

the explicit nature of Ψ_A, Ψ_I in the case of three well-known trial functions for hydrogen.

In Table III we have gathered the coefficients in the square of the natural expansion of the Wang function as determined largely from the data of Eliason and Hirschfelder.[17] The gradual decrease of ionic character to 0 as R increases and the accompanying gradual increase of atomic character to unity when the exact wave function of the separated atoms is reached are trends to be expected from this approximation. The variation of the coefficients with R emphasizes a characteristic which is largely ignored in the Pauling analysis. For, there too, the coefficient of the ionic terms must drop gradually to zero as R increases leaving the function 100% "covalent." But the latter name is hardly suitable for two separated hydrogen atoms and it is again suggested that "atomic" might well be a better choice. At first sight the magnitude of λ_I^2 is very surprising. Rather than the 5% ionic contribution suggested by Pauling,[3] at the equilibrium distance the present division leads to 32% ionic character for the Wang function. This would indeed be extraordinary if our function Ψ_I were an ionic function having a high energy expectation value. We show below, however, that Ψ_A and Ψ_I are each almost non-bonding and the high coefficient then becomes more understandable.

TABLE III

ATOMIC AND IONIC CHARACTER OF WANG FUNCTION AS A FUNCTION OF R

$q = ZR$[a]	R[a]	λ_A^2	λ_I^2	$2\lambda_A\lambda_I$
0.0	0.0000	0.5361	0.4639	0.9974
1.0	0.7339	.5758	.4242	.9885
1.5	1.2099	.6554	.3446	.9505
1.637[b]	1.404[b]	.6795[b]	.3205[b]	.9334[b]
1.75	1.4731	.6996	.3004	.9169
2	1.7976	.7441	.2559	.8727
2.5	2.4169	.8264	.1736	.7575
3	2.9916	.8917	.1083	.6215
3.5	3.5204	.9370	.0630	.4858
4	4.0274	.9654	.0346	.3654
4.5	4.525	.9818	.0182	.2672
5	5.050	.99076	.00924	.1914
6	6.026	.99779	.00221	.0940
7	7.014	.99951	.00049	.0444
8	8.038	.999896	.000104	.0204
10	10.02	.999996	.000004	.004
12		1.000000	.000000	.000

[a] See footnote a of Table II. [b] These data pertain to the equilibrium case calculated for the Wang function.

The last column of Table II emphasizes the fact that in the computation of the probability density distribution from a wave function of the form of eq. 9 there are, of course, cross-terms to be considered, only one, however, in the symmetric case we have here. This is also important, of course, in computing the energy. Now the magnitude of the coefficient of this cross-term is larger at small R values than either the atomic or ionic coefficients and it gradually goes to zero with increasing R, although much more slowly than that of the ionic coefficient. We should like to suggest that it is precisely this cross-term which is most closely connected with the concept embodied in the term "covalent." We believe that the diagrams and energy computations below support this contention.

VI. Graphic Representation

In order to acquire a better intuitive understanding of the nature of the three quantities Ψ_A^2, Ψ_I^2 and $\Psi_A\Psi_I$, we have plotted these quantities in contour maps similar to those of Braunstein and Simpson.[9] As abscissa we use the position of electron one along the internuclear axis and as ordinate the position of electron two along the same axis. A high density set of contours to the lower left and upper right then is what one expects for a very ionic function. Similarly, high contours to the upper left and lower right are associated with an atomic distribution. There are many inadequacies of such a diagram; for example, they concern the density only along the axis which is characteristic of but a small part of the total density; they reflect the discontinuities at the nuclear positions and hence have strange "corners" and straight lines. Nevertheless it is felt that they give a reasonably valid intuitive picture of what is going on.

In the accompanying figures we have given contour diagrams of $\lambda_A^2\Psi_A^2$, $\lambda_I^2\Psi_I^2$ and $2\lambda_A\lambda_I\Psi_A\Psi_I$ as well as of Ψ^2 itself (the sum of the other three) for the Wang,[4] Weinbaum[5] and Rosen[6] functions for the hydrogen molecule. The figures speak rather well for themselves once one has become accustomed to what they present. There are certain outstanding features, however, which deserve emphasis.

First of all, comparison of corresponding diagrams for the three cases shows that they are remarkably similar despite the apparent differences in the trial functions themselves. This is a reflection of the contention made earlier that the natural orbital expansion is already nearly independent of basis for even very simple trial functions. Since the three trial functions compared here are all at the two configuration level,[7] it can be expected that they will be similar in appearance. In particular, the Rosen and Weinbaum functions in this representation are so similar as to belie a description of the one in terms of "polarization" and of the other in terms of "ionic character."

Next, examination of Ψ_A^2 and Ψ_I^2 shows that they indeed have the characteristics associated with the names atomic and ionic. In the present case there is a close relationship between Ψ_A^2 and Ψ_I^2 since the respective diagrams are precisely the same but rotated by $\pi/2$. The nodal lines in these diagrams pass roughly 0.3 of the way from one nucleus to the other and consequently each represents only a relatively small build-up of charge between the nuclei. One can expect that the respective functions are relatively non-bonding. This again suggests the appropriateness of the term "atomic" for Ψ_A.

Finally, examination of the cross-term is especially revealing. This term is, of course, negative in some regions of space and positive in others (and zero when integrated over all of space). In particular, the diagrams show that the cross-term depletes the density contributions of both Ψ_A^2 and Ψ_I^2 near the nuclei, in fact almost completely cancelling

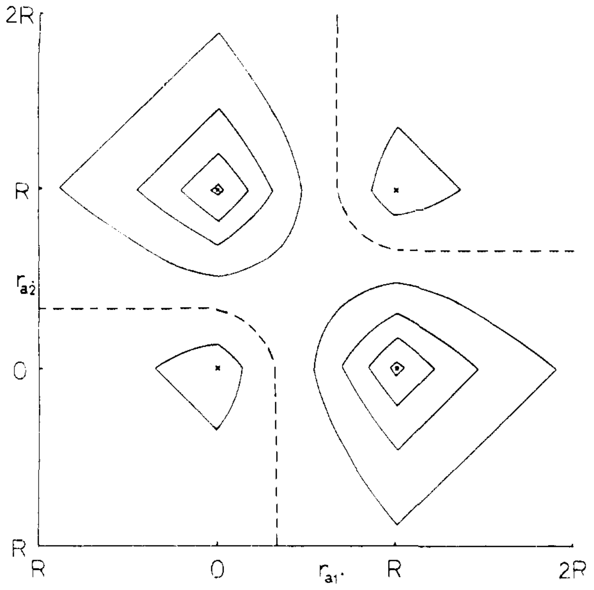

Fig. 1a.—$\lambda_A^2\Psi_A^2$ for the Wang trial function; $\lambda_A^2 = 0.6795$.

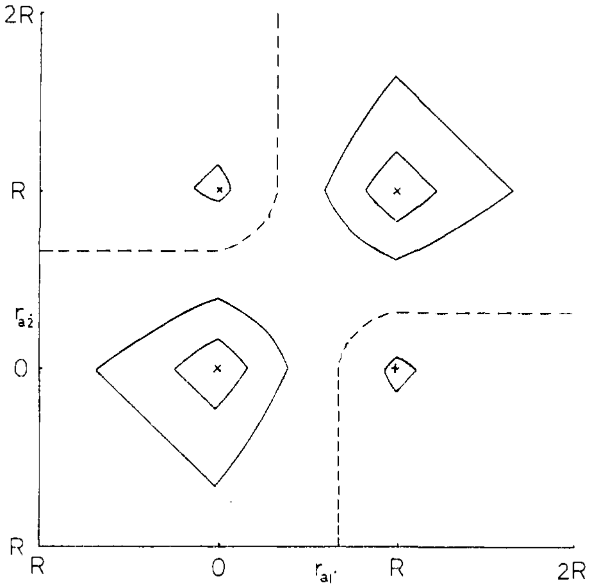

Fig. 1b. —$\lambda_I^2\Psi_I^2$ for the Wang trial function; $\lambda_I^2 = 0.3205$.

The figures give density contours along the internuclear axis of the hydrogen molecule for the respective approximation. Abscissa: distance of electron 1 from nucleus a (at 0) in units of the calculated equilibrium distance for that trial function. Ordinate: distance of electron 2 from nucleus a (at 0) in units of the calculated equilibrium distance for that trial function. Density contours are given at 0, ±0.01, ±0.04, ±0.09, ±0.16. ——— Positive density contributions; -------- zero density contribution (node); —·—· negative density contribution.

out the latter, while building up the density precisely in the middle of the bond. Because of electron repulsion the maximum of the positive contribution does not occur when both electrons are at the midpoint, but rather at those points where one electron is at a nucleus and the other is at the

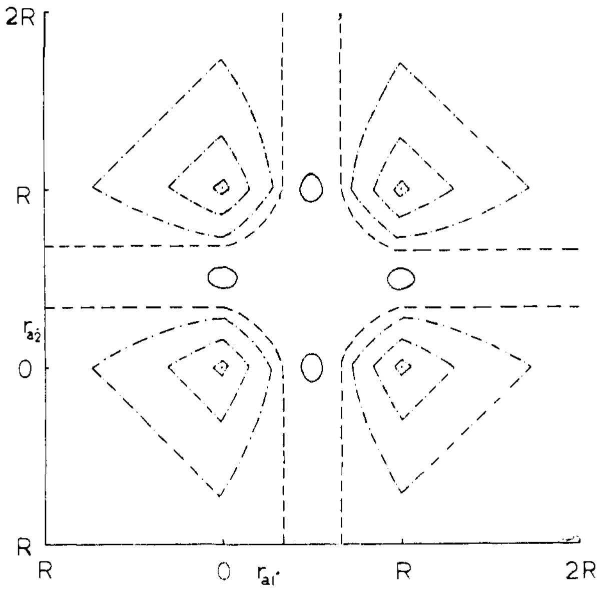

Fig. 1c.—$2\lambda_A\lambda_I\Psi_A\Psi_I$ for the Wang trial function; $2\lambda_A\lambda_I = 0.9334$.

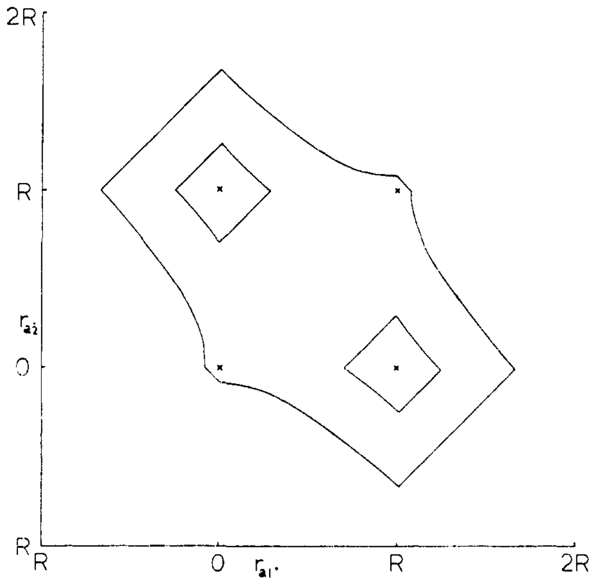

Fig. 1d.—Ψ^2 for the Wang function (sum of Figs. 1a–c).

bond midpoint.[18] It seems clear that this term is the one instrumental in the chemical binding.

The comparison of Wang, Weinbaum and Rosen functions is especially interesting for the binding cross-term. The positive maxima are definitely higher for the functions with lower energy. This is at least in part due to the higher fractional ionic character, λ_I^2, for the Weinbaum and Rosen functions as compared to the Wang function. The 0.32 fractional ionic contribution in the latter at the calculated equilibrium parameters is increased to 0.38 for the Weinbaum and Rosen functions. There is thus just 6% more ionic character in the Weinbaum function than in the Wang function, strangely enough precisely the increase

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[18] As Professor W. T. Simpson has pointed out, this indicates that the two-electron chemical bond can be regarded as a superposition of one-electron bonds, at least to a considerable extent.

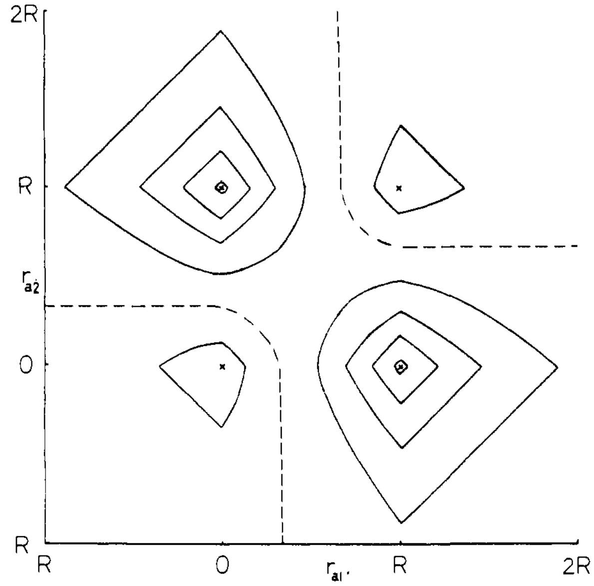

Fig. 2a.—$\lambda_A^2\Psi_A^2$ for the Weinbaum trial function; $\lambda_A^2 = 0.6146$.

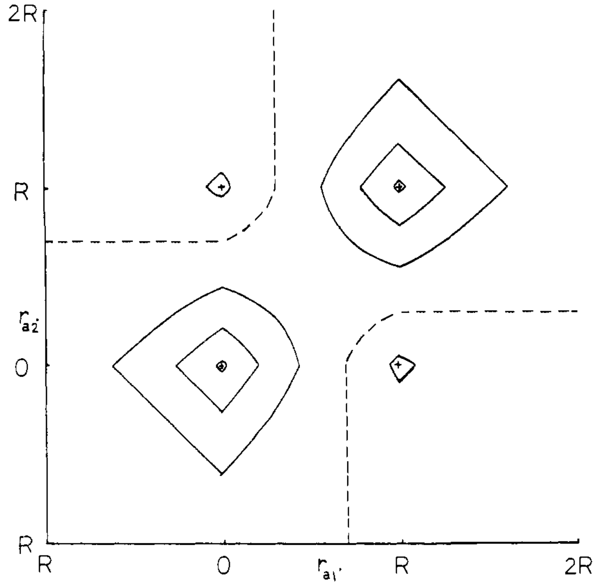

Fig. 2b.—$\lambda_I^2\Psi_I^2$ for the Weinbaum trial function; $\lambda_I^2 = 0.3854$.

suggested by Pauling on the basis of the Weinbaum calculation.

VII. Energetic Considerations

To complete the analysis of the homopolar case we include here an analysis of the contributions to the energy made by the various terms in the present division of the Wang and Weinbaum functions. For the present purpose we write the molecular Hamiltonian as

$$\mathcal{H} = \mathcal{H}_1 + \mathcal{H}_2 + \mathcal{H}_{12} \qquad (22)$$

with

$$\mathcal{H}_1 = -\frac{1}{2}\Delta_1 - \frac{1}{r_{a1}} - \frac{1}{r_{b1}} + \frac{1}{R} \qquad (23)$$

$$\mathcal{H}_2 = -\frac{1}{2}\Delta_2 - \frac{1}{r_{a2}} - \frac{1}{r_{b2}} + \frac{1}{R} \qquad (24)$$

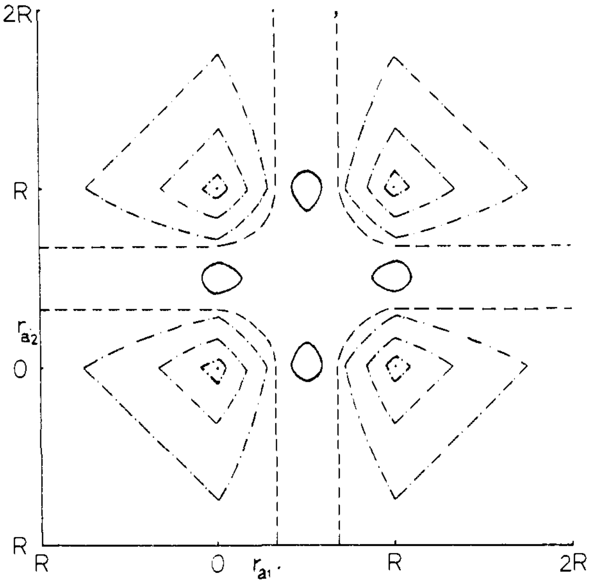

Fig. 2c.—$2\lambda_A\lambda_I\Psi_A\Psi_I$ for the Weinbaum trial function; $2\lambda_A\lambda_I = 0.9734$.

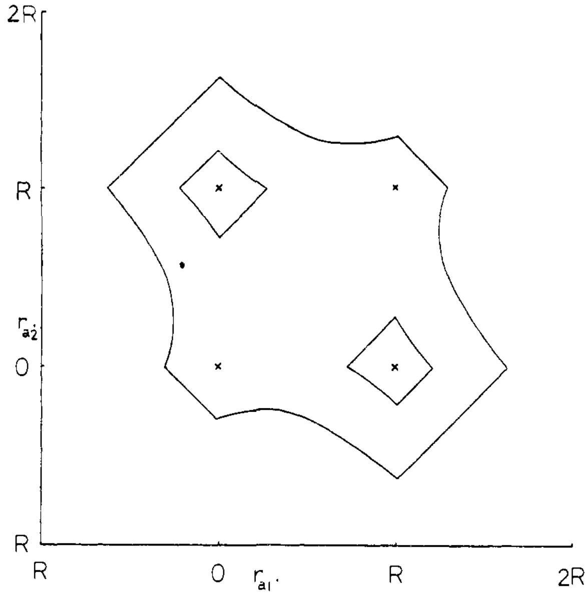

Fig. 2d.—Ψ^2 for the Weinbaum function (sum of Figs. 2a–c).

and

$$\mathcal{H}_{12} = \frac{1}{r_{12}} - \frac{1}{R} \qquad (25)$$

$\mathcal{H}_1$ and $\mathcal{H}_2$ may then be thought of as operators associated with a one-electon diatomic molecule problem, and $\mathcal{H}_{12}$ is an interaction operator in which the electron repulsion term is counteracted by a nuclear repulsion term taken negatively to compensate for its having been included both in (23) and in (24). Furthermore we define

$$H_{AA} = \int \Psi_A\mathcal{H}\Psi_A \, d\tau \qquad (26)$$

$$H_{AI} = H_{IA} = \int \Psi_A\mathcal{H}\Psi_I \, d\tau \qquad (27)$$

$$H_{II} = \int \Psi_I\mathcal{H}\Psi_I \, d\tau \qquad (28)$$

$$\epsilon_1 = \int \chi_1\mathcal{H}_1\chi_1 d\tau_1;\ \epsilon_2 = \int \chi_2\mathcal{H}_1\chi_2 d\tau_1 \qquad (29)$$

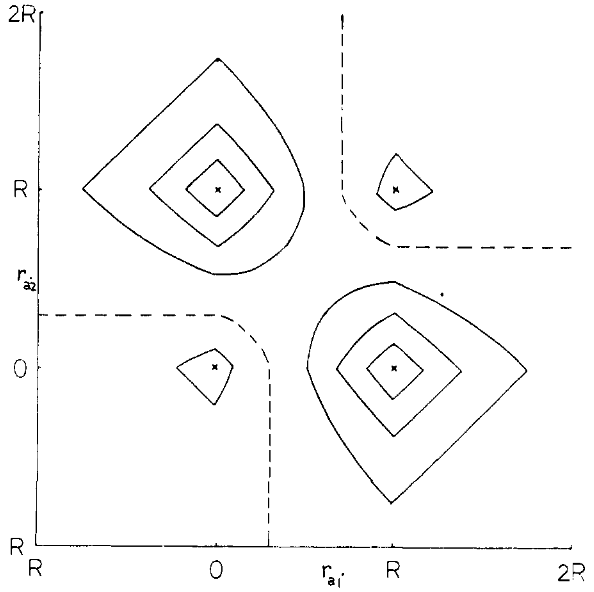

Fig. 3a.—$\lambda_A^2\Psi_A^2$ for the Rosen trial function; λ_A^2 = 0.6235.

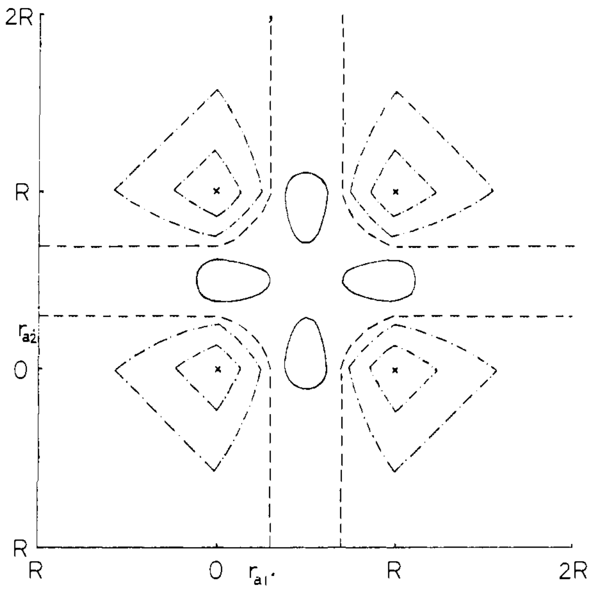

Fig. 3c.—$2\lambda_A\lambda_1\Psi_A\Psi_1$ for the Rosen trial function; $2\lambda_A\lambda_1$ = 0.9690.

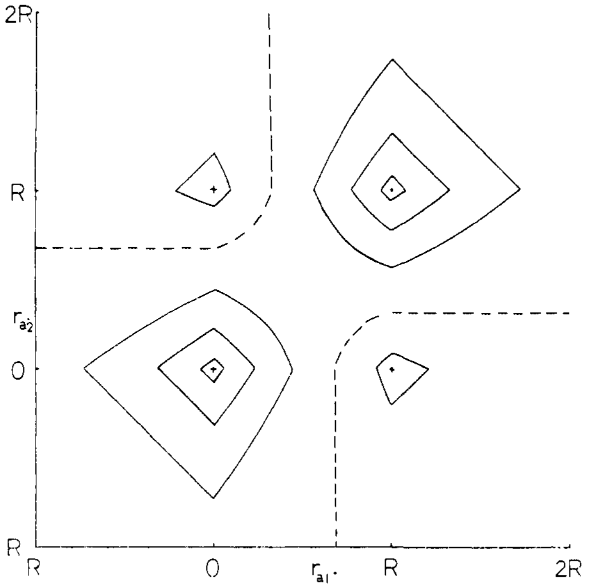

Fig. 3b.—$\lambda_1^2\Psi_1^2$ for the Rosen function; λ_1^2 = 0.3765.

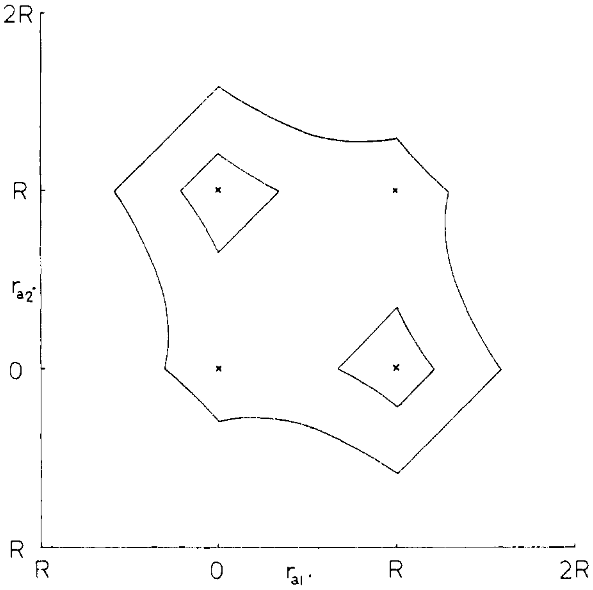

Fig. 3d.—Ψ^2 for the Rosen function (sum of Figs. 3a–c).

Finally the electron repulsion integrals over the natural orbitals are defined in the usual manner. For example

$$(12|12) = \int \chi_1(1)\chi_1(2)\frac{1}{r_{12}}\chi_2(1)\chi_2(2)\,d\tau_1 d\tau_2 \qquad (30)$$

It is straightforward to establish that

$$H_{AA} = \epsilon_1 + \epsilon_2 + [(11|11) + (22|22)]/2 - (12|12) - 1/R \qquad (31)$$

$$H_{11} = \epsilon_1 + \epsilon_2 + [(11|11) + (22|22)]/2 + (12|12) - 1/R \qquad (32)$$

$$H_{A1} = \epsilon_1 - \epsilon_2 + [(11|11) - (22|22)]/2 \qquad (33)$$

with

$$E = \lambda_A^2 H_{AA} + 2\lambda_A\lambda_1 H_{A1} + \lambda_1^2 H_{11} \qquad (34)$$

The form of (31)–(33) suggests again the viewpoint proposed above. The natural orbital χ_1 should be a bonding orbital and χ_2 an antibonding orbital. In (31) and (32), therefore, ($\epsilon_1 + \epsilon_2$) should lead to an essentially non-bonding situation whereas in (33), a negative ϵ_1, and a positive ϵ_2 should lead to a strong binding contribution. The electron repulsion integrals in (31) and (32) should in part cancel the negative $1/R$ term and in (33) they should roughly cancel out altogether.

In Table IV are gathered the parameters used and values of the basic integrals in terms of the 1s functions on nucleus a and on nucleus b, denoted by a and b, respectively, and in Table V are listed the appropriate derived parameters. The parameters used for the Wang function are those reported by Wang,[19] whereas those given for the

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[19] Improved unpublished calculations by Shull and Löwdin indicate that better parameter values for the minimum energy of the Wang function are $q = \rho = 1.64888$, $Z = -1.16614$, $R = 1.41397$ with a corresponding energy of $-1.13910H$.

TABLE IV

PARAMETERS AND BASIC INTEGRALS FOR MINIMUM ENERGY OF THE WANG AND WEINBAUM FUNCTIONS[a]

Parameter or integral	Wang function	Weinbaum function
R^b	1.403945	1.43032
Z^c	1.166	1.193824
$q \equiv \rho = ZR$	1.637	1.70755
$(a\vert b)$	0.686857	0.667119
$(a\vert -{}^1/_2\Delta\vert a)$	.679778	.712608
$(a\vert -{}^1/_2\Delta\vert b)$	.230627	.224249
$(a\vert -1/r_a\vert a)$	−1.166000	−1.193824
$(a\vert -1/r_a\vert b)$	− .598231	−0.586052
$(b\vert -1/r_a\vert b)$	− .641177	− .636917
$(aa\vert aa)$	.728750	.746140
$(aa\vert ab)$	.440329	.434082
$(aa\vert bb)$	.550720	.552869
$(ab\vert ab)$	.306118	.293480

[a] Hartree atomic units are used throughout. [b] Equilibrium internuclear distance. [c] Effective nuclear charge or scale parameter.

TABLE V

ENERGY PARAMETERS FOR WANG AND WEINBAUM FUNCTIONS AT THE EQUILIBRIUM POSITION[a]

Energy quantity[b]	Wang function	Weinbaum function
ϵ_1	−0.52863	−0.54012
ϵ_2	+ .19634	+ .18762
$(11\vert 11)$	.64190	.65166
$(22\vert 22)$	.66486	.67522
$(12\vert 12)$	.16852	.17413
$1\vert R$	.71228	.69914
H_{AA}	− .55971	− .56234
H_{II}	− .22268	− .21407
H_{AI}	− .73644	− .73951
$\lambda_A{}^2H_{AA}$	− .38030	− .34561
$2\lambda_A\lambda_I H_{AI}$	− .68738	− .71982
$\lambda_I{}^2H_{II}$	− .07138	− .08250
E	−1.13905	−1.14794

[a] Hartree atomic units are used throughout. [b] See eq. 26–34 in text for definition of symbols.

Weinbaum function are improved values based on unpublished calculations by Shull and Löwdin. The integral values were recalculated explicitly by the author for the present work by standard procedures except for the hybrid and exchange integrals which were interpolated from the tables of Hirschfelder and Linnett[20] using Mulliken's approximation as an interpolation aid. The resulting integrals probably are accurate to at least five figures.

The quantitative results clearly support the qualitative picture. The first natural orbital is bonding and the second antibonding as suggested. The absolute magnitude of the energies should be considered in the light that the limiting energy of the one-electron functions at $R = \infty$ is -0.5. The electron repulsion integrals $(11|11)$ and $(22|22)$ do indeed largely cancel the $1/R$ term. Finally H_{AA} and H_{II} have slightly negative energies but still far from -1.0, the energy of the separated atoms. Ψ_A and Ψ_I are thus neither strongly bonding nor strongly antibonding. For comparison the energy of the bonding function $\chi_1(1)\chi_1(2)$ is $-1.12771H$ and that of the antibonding function $\chi_2(1)\chi_2(2)$ is $+0.35130H$ in the Weinbaum case. It is seen that over 60% of the total energy comes from the binding cross term, $2\chi_A\chi_I H_{AI}$.

VIII. Conclusion

We feel we have demonstrated that starting from a well-defined approximation to the hydrogen molecule wave function it is possible to separate it into independent orthogonal parts which have optimum characteristics associated with the names "atomic" and "ionic." Further analysis shows that physical observables which depend upon the square of the wave function then involve three well-defined parts, the third one being the atomic-ionic cross-term which can be associated with covalent binding. Even for rather simple trial functions, the division is almost invariant to the choice of basis, and in the limit of using the two-term truncated natural orbital expansion, it becomes completely independent of the original basis.

The final picture that results is a satisfying one in that it is directly capable of extension to the heteropolar case. In a subsequent publication we shall show that a quantity which bears resemblance to electronegativity difference is a direct consequence of the treatment. Consequently we feel rather justified in thinking that the present description is of fundamental significance. The fact that we were led to it by a rather unsophisticated method should not be allowed to detract from the picture and it is our hope that it may be possible to find a more satisfying method of reaching the same result.

The present description is closely related to several other semantic descriptions of binding in particular situations. We might, for example, have emphasized that our picture is that binding is a result of ionic–atomic resonance, although we prefer to avoid that term. From another point of view we have two hypothetical roughly non-bonding configurations, one of which is atomic and one ionic. The formation of the hydrogen molecule bond could then be described as an extreme example of a charge-transfer complex between two hydrogen atoms. Finally the designation of Ψ_A as "atomic" suggests that it may be worth considering as an appropriate basis function for the embodiment of the popular "atoms-in-molecules" concept.

Acknowledgments.—The author is particularly indebted to the stimulation provided by the papers and viewpoints of Professor W. T. Simpson who earlier tackled the present problem from a closely related approach and provided by Professor Linus Pauling's demonstration of the practical utility of the concepts at the Vålådalen summer institute in quantum chemistry. It is a real pleasure to thank Dr. Per-Olov Löwdin for helpful criticism concerning the structure of the paper and particularly for his generous hospitality in providing the stimulating environment in which the work was done.

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