

# Valence Bond Treatment on the B State of the Hydrogen Molecule

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to obtain the coupling anisotropy function using accurate wave functions. But the present analysis suggests that quite crude functions may often be adequate. In the first place, the tightly bound inner electrons can be rigorously excluded in so far as the wave function can be written as an antisymmetrized product of two parts. Second,  $Q_{ca}(1, 2; 1', 2')$  is antisymmetric in each pair of variables (1, 2 and 1', 2') and  $Q_{ca}(1, 2; 1, 2)$  therefore vanishes at least as rapidly as  $r_{12}^2$  as two particles approach (cf. McConnell 1959<sup>6</sup>); it is therefore unnecessary that the wave function shall accurately describe electron correlation. And, finally, integrals such as (12) appear to be rather insensitive to the values of  $\gamma_{ik}^{||}$ ,  $\gamma_{ik}^{\perp}$ ,  $\gamma_{ik}^{\circ}$  and to be determined largely by molecular geometry. In conclusion therefore we report some calculations for naphthalene, in which all

the above approximations were made. The triplet state was described by promoting one electron from the top bonding orbital into the lowest antibonding, both being taken as Huckel orbitals. All pairs of atoms were considered in evaluating (12) and substitution in (6) led to

$$X/hc = 0.85 \times 10^{-2}, \quad Y/hc = 4.91 \times 10^{-2}, \\ Z/hc = -5.77 \times 10^{-2} \text{ cm}^{-1}$$

( $x$  and  $y$  axes being in the plane, with  $x$  along the central bond). The zero-field splittings are then

$$(Y-Z)/hc = 0.107 \text{ cm}^{-1}, \quad (X-Z)/hc = 0.066 \text{ cm}^{-1}$$

and are in reasonable agreement with the observed values of 0.1143 and 0.0863  $\text{cm}^{-1}$ , respectively.

## Valence Bond Treatment on the $B$ State of the Hydrogen Molecule

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The potential energy of the lowest  $^1\Sigma_u^+$  state of the hydrogen molecule is given as a function of the internuclear distance. Calculations were carried out by the valence bond method using Slater  $1s$  and  $2p$  atomic orbitals. Both ionic and covalent structures were considered. The  $1s$  orbitals of the ionic and covalent functions included a variational parameter but the orbital exponent of the  $2p$  orbital was kept constant. It is found that the introduction of the  $2p$  orbital into the wave function results in a considerable improvement of the dissociation energy and that further the state is essentially covalent in character rather than ionic, as previously reported.

### INTRODUCTION

FOR a long time it has been assumed that the state of lowest energy of symmetry  $^1\Sigma_u^+$  of the hydrogen molecule, often called  $B$  or  $V$  state, is ionic.<sup>1-3</sup> The large equilibrium internuclear distance, and also the unusually slow approach of potential energy curve to its asymptotic value with increasing internuclear distance were thought to be properties belonging to an ionic, rather than a covalent state. Another important fact supporting this idea was that the only possible wave function with the right symmetry made up from  $1s$  orbitals is the ionic function,  $s_a(1) s_a(2) - s_b(1) s_b(2)$ , where  $a$  and  $b$  are the nuclei, and 1 and 2 the electrons. In order to have a covalent wave function a higher energy orbital is needed, for example a  $2p$  orbital. It was assumed that such a covalent wave function would have very small weight on account of the high energy of the excited orbital used.

In spite of the above considerations, calculations

were not conclusive. Zener and Guillemin<sup>4</sup> were not able to decide whether the  $B$  state was ionic or not. Brackman's calculations, published by Altmann and Cohan,<sup>5</sup> using the above ionic function, give a very poor value for the dissociation energy at the equilibrium internuclear distance: 0.44 eV compared with the experimental value of 3.7 eV. Phillipson and Mulliken<sup>6</sup> calculated the energy of the  $B$  state applying the molecular orbital theory. The wave function they use is the antisymmetrized product of molecular orbitals  $\sigma_g$  and  $\sigma_u$ , which are made up from linear combinations of  $1s$  atomic orbitals; they take the exponential parameters of these orbitals,  $\zeta_g$  and  $\zeta_u$ , as variation parameters. Their results also suggest that the ionic structure alone must be a poor approximation. In fact, their wave function reduces to the ionic function mentioned above when both exponential parameters are equal, but when  $\zeta_g \neq \zeta_u$  a considerable improvement of the results is obtained. Huzinaga<sup>7</sup> performed a molecular orbital

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<sup>1</sup> R. S. Mulliken, Phys. Rev. **50**, 1017 (1936).

<sup>2</sup> R. S. Mulliken, Phys. Rev. **50**, 1028 (1936).

<sup>3</sup> R. S. Mulliken, J. Chem. Phys. **7**, 20 (1939).

<sup>4</sup> C. Zener and V. Guillemin, Phys. Rev. **34**, 999 (1929).

<sup>5</sup> S. L. Altmann and N. V. Cohan, Trans. Faraday Soc. **50**, 1151 (1954).

<sup>6</sup> P. E. Phillipson and R. S. Mulliken, J. Chem. Phys. **28**, 1248 (1958).

<sup>7</sup> S. Huzinaga, Progr. Theoret. Phys. (Kyoto) **20**, 15 (1958).

treatment, similar to the treatment of Phillipson and Mulliken, of the  ${}^1\Sigma_u^+$  state for internuclear distances up to and including 2.0 a.u. His results also indicate that different exponential parameters give better results than a single parameter. Huzinaga<sup>8</sup> also performed a calculation of this state based on the one center expansion method using wave functions which exhibit  $2p$  character. The energy values so obtained are higher than the values of Phillipson and Mulliken<sup>6</sup> for comparable distances.

It seems therefore worthwhile to study the  ${}^1\Sigma_u^+$  state of the hydrogen molecule by the valence bond method, using both the ionic function and a covalent function made up from  $1s$  and  $2p$  orbitals. Different screening constants for the  $1s$  orbitals in the ionic and covalent functions are used as parameters in a variational treatment. It is also useful to observe the values of the screening constants which minimize the energy, in order to compare the results with those obtained by similar treatments for the ground state of the hydrogen molecule, by Weinbaum<sup>9</sup> first and later by Altmann and Cohan.<sup>5</sup> They concluded that a better result for the dissociation energy is obtained when both screening constants, the one associated with the  $1s$  orbital of the covalent function and the other with the ionic function, are the same. Scherr<sup>10</sup> suggested that an improvement is obtained when the Slater's rules of atoms are extrapolated to the molecular case, instead of using both screening constants equal to unity. Altmann and Cohan<sup>5</sup> showed that the improvement found by Scherr was only due to a local maximum error. The effective nuclear charge for the  $2p$  orbital in our work is kept constant, and equal to one. We believe that this approximation does not introduce a serious error, for the extreme values of the effective nuclear charge for the  $2p$  orbital in the united atom (He in configuration  $1s2p$ ) and in the separated atoms [ $H(1s)+H(2s)$ ] are 1.15 and 1.0, respectively, while for the  $1s$  orbital in the covalent function they vary from 2.0 to 1.0, according to Slater rules. In order to study the variation of the parameters with the internuclear distance, this is taken as a further variational parameter.

#### METHODS AND RESULTS

The wave function used is  $\Psi = c_c\phi_c + c_i\phi_i$  where

$$\phi_c = N_c [s_a^c(1)p_b(2) + p_b(1)s_a^c(2) + s_b^c(1)p_a(2) + p_a(1)s_b^c(2)],$$

$$\phi_i = N_i [s_a^i(1)s_a^i(2) - s_b^i(1)s_b^i(2)],$$

$$s_m^k(j) = Z_k^{3/2} \pi^{-1/2} \exp(-Z_k r_{mj})$$

$$p_m(j) = \frac{1}{4} Z^{5/2} (2\pi)^{-1/2} r_{mj} \cos\theta_{mj} \exp[-(Z/2)r_{mj}],$$

$$\text{(with } Z=1.0\text{)}$$

and  $N_c$  and  $N_i$  are normalization factors. The index  $m$  indicates the nucleus  $a$  or  $b$ ,  $j$  the electron 1 or 2 and  $k$  the canonical structure covalent ( $c$ ) or ionic ( $i$ ). The  $2p$  orbitals are defined so that the direction  $z$  is along the internuclear axis from  $a$  to  $b$ .

The secular determinant therefore is

$$\begin{vmatrix} H_{cc} - E & H_{ci} - ES_{ci} \\ H_{ic} - ES_{ic} & H_{ii} - E \end{vmatrix} = 0,$$

where

$$H_{cc} = E_c = \int \phi_c \mathcal{H} \phi_c d\tau, \quad H_{ii} = E_i = \int \phi_i \mathcal{H} \phi_i d\tau,$$

$$H_{ci} = H_{ic} = \int \phi_c \mathcal{H} \phi_i d\tau, \quad \text{and} \quad S_{ci} = S_{ic} = \int \phi_c \phi_i d\tau,$$

$\mathcal{H}$  is the complete Hamiltonian operator of the molecule.

All the one-electron integrals and the Coulomb two-electron integrals were computed from the analytical expressions given by Coulson<sup>11</sup> and Roothaan,<sup>12</sup> respectively. The last-mentioned integrals were also checked by four and six point interpolation from Roothaan's<sup>13</sup> numerical tables. The numerical values for the exchange and resonance two-electron integrals were made available to us.<sup>14</sup> Atomic units (a.u.) are used throughout the calculations, the unit of length being  $a_0 = 0.5292$  A and the unit of energy  $e^2/a_0 = 27.206$  ev.

Calculations were made for internuclear distances  $\rho$ , varying from 1.6 to 7.0 a.u. with a fairly small interval in the neighborhood of the equilibrium internuclear distance  $\rho_e$  which has been taken equal to 1.293 A ( $\rho_e = 2.4433 a_0$ ). The effective nuclear charges for both canonical structures were varied from 0.6 to 1.4 in steps of 0.2 and in some cases of 0.1. Final results of the energy are given in ev.

Results of the present work are given in Table I, Table II, Table III, and Fig. 1. Table I gives the values of the effective nuclear charges  $Z_c$  and  $Z_i$  which minimize the covalent and ionic energy, respectively, and  $\bar{Z}_c$  and  $\bar{Z}_i$  which minimize the total energy. In Fig. 1 energies are plotted against the internuclear distances. The potential energy curves calculated by Phillipson and Mulliken<sup>6</sup> are also shown in order to compare their results with ours. Table II gives the best values obtained for the covalent, ionic, and total energies. Table III gives the values of the approximate weights of the covalent and ionic functions. They were calculated for

<sup>11</sup> C. A. Coulson, Proc. Cambridge Phil. Soc. **38**, 210 (1942).

<sup>12</sup> C. C. J. Roothaan, J. Chem. Phys. **19**, 1445 (1951).

<sup>13</sup> C. C. J. Roothaan, "Tables of two center coulomb integrals between  $1s$ ,  $2s$  and  $2p$  orbitals," Special Technical Report, University of Chicago (1955).

<sup>14</sup> These integrals were computed in the Laboratory of Molecular Structure and Spectra at the University of Chicago on a general program for the Univac Scientific WADC, Dayton, Ohio, computing machine. We wish to thank Professor C. C. J. Roothaan and especially Dr. B. Ransil for making available the computation of these integrals.

<sup>8</sup> S. Huzinaga, Progr. Theoret. Phys. (Kyoto) **17**, 162 (1957).

<sup>9</sup> S. Weinbaum, J. Chem. Phys. **1**, 593 (1933).

<sup>10</sup> C. W. Scherr, J. Chem. Phys. **22**, 149 (1954).

the set of values of effective nuclear charges nearest to the ones that minimize the total energy.

### DISCUSSION

Table I shows that for the *B* state of the hydrogen molecule,  $Z_c$  is greater than one, while as already shown by Brackman,<sup>5</sup> the  $Z_i$  is less than one, for the equilibrium internuclear distance. We also conclude that as the internuclear distance increases both  $Z_c$  and  $Z_i$  decrease, approaching the values given by Slater's rules as  $\rho$  tends to infinity. This is also true for the ground state, as pointed out by Hirschfelder and Linnett.<sup>15</sup> According to an empirical formula given by Musulin,<sup>16</sup> the dependence of  $Z_c$  on the internuclear distance can be expressed approximately by an exponential function that approaches the values for the united and separated atoms, according to Slater rules. It follows then that  $Z_c$  depends on: (i) the values of the effective nuclear charge for the united and separated atoms, and (ii) the internuclear distance. Then it is not surprising to find  $Z_c=1.166$  for the ground state<sup>17</sup> and  $Z_c=1.16\pm 0.02$  for the state *B*. In fact, effect (i) tends to increase the value of  $Z_c$  when going from the ground to the *B* state, for the values of  $Z_c$  for the united atoms corresponding to the two states are 1.7 and 2.0, respectively. But effect (ii) is just the opposite because the large equilibrium internuclear distance of the state *B* relative to that of the ground state tends to decrease  $Z_c$ , so that both effects are just balanced.

The variation of  $Z_i$  with the internuclear distance is almost linear and very slow and the Slater rules are approximately valid in this case. For the ground state and the equilibrium internuclear distance, the value of  $Z_i$  is greater than 1.0. Altmann and Cohan<sup>5</sup> suggested that the difference in symmetry of the two states is responsible for this difference in behavior. Due to the antisymmetry of the wave function of the *B* state, which involves the existence of a node between the nuclei, the electron cloud tends to be outside this region, the attraction of one nucleus upon the electron cloud attached to the other is small compared with the

TABLE I. Values of the effective nuclear charges which minimize the covalent, ionic, and total energies.<sup>a</sup>

| $\rho$ (a.u.) | $Z_c$ | $Z_i$ | $\bar{Z}_c$ | $\bar{Z}_i$ |
|---------------|-------|-------|-------------|-------------|
| 1.6           | 1.33  | ...   | 1.33        | ...         |
| 2.1           | 1.22  | 0.81  | 1.22        | 1.15        |
| 2.4433        | 1.16  | 0.80  | 1.15        | 1.04        |
| 2.8           | 1.12  | 0.78  | 1.12        | 1.00        |
| 3.1           | 1.09  | 0.77  | 1.10        | 0.91        |
| 4.0           | 1.03  | 0.74  | 1.06        | 0.84        |
| 7.0           | 1.00  | 0.69  | 1.00        | 0.76        |

<sup>a</sup> All values have an estimated error of  $\pm 0.02$ .

<sup>15</sup> J. O. Hirschfelder and J. W. Linnett, *J. Chem. Phys.* **18**, 130 (1950).

<sup>16</sup> R. Musulin, *J. Chem. Phys.* **25**, 801 (1956).

<sup>17</sup> C. Wang, *Phys. Rev.* **31**, 579 (1928).

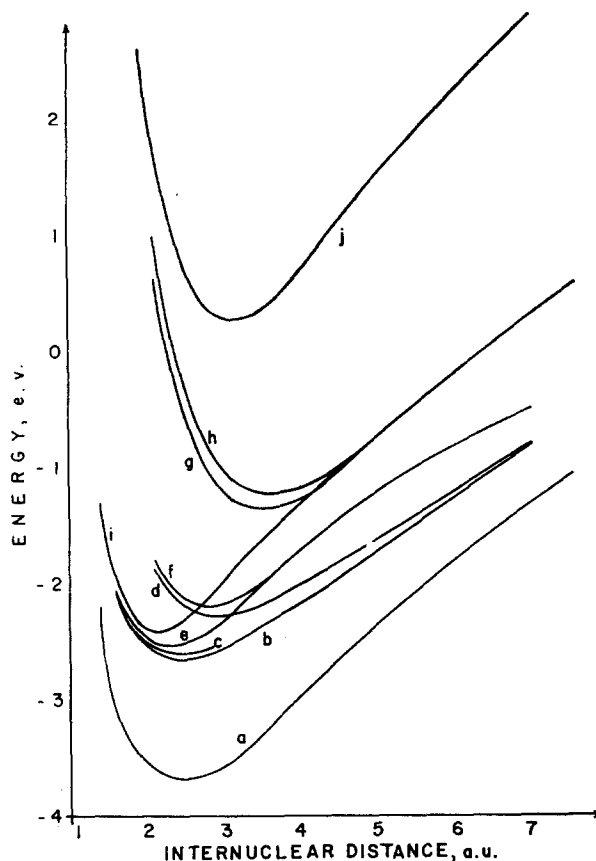


FIG. 1. Potential energy curves. (a) Experimental, according to the data given by Phillipson and Mulliken; (b) using the best total wave function of the present calculation; (c) using the total wave function with  $\bar{Z}_c = \bar{Z}_i$  [curve (c) is only approximate because we had not calculated enough values of  $E$  so as to be able to make a full variational treatment. The only important feature for the following discussion is that curve (c) lies just above curve (b) as indicated]; (d) using the total wave function with  $\bar{Z}_c = 1.0$  and  $\bar{Z}_i = 0.7$  (Slater rules); (e) using the best covalent wave function; (f) using the covalent wave function with  $Z_c = 1.0$  (Slater rules); (g) using the best ionic wave function; (h) using the ionic wave function with  $Z_i = 0.7$  (Slater rules); (i) the curve obtained by Phillipson and Mulliken using different screening constants [Phillipson and Mulliken report 10.98 ev at 4.0 Å; it should be 10.79 ev. This corrected energy value was obtained by the referee from private communication with the authors]; (j) the curve obtained by Phillipson and Mulliken with  $\zeta_0 = \zeta_u = 1.0$  coincident with our ionic wave function when  $Z_i = 1.0$ .

electron repulsion; this causes an expansion of the electron cloud and hence a diminution of the effective nuclear charge  $Z_i$ .

The results of the last two columns of Table I are rather surprising.  $\bar{Z}_c$ , which minimizes the total energy, is practically the same as  $Z_c$ , which minimizes the covalent energy  $E_c$  for each value of the internuclear distance. However the same is not true for  $\bar{Z}_i$ . This effective nuclear charge increases unexpectedly and, for values of  $\rho$  near the equilibrium internuclear distance it is greater than unity. Therefore it seems that the above explanation given by Altmann and Cohan<sup>5</sup> for the ionic function alone does not apply when it mixes with the covalent function.

TABLE II. Best values obtained for the covalent energy  $E_c$ , ionic energy  $E_i$ , and total energy  $E$ . The zero energy is taken as the energy of a ground-state hydrogen atom [H(1s)] plus the energy of an excited hydrogen atom [H(2s)].

| $\rho$ (a.u.)    | $E_c$ (ev) | $E_i$ (ev) | $E$ (ev) |
|------------------|------------|------------|----------|
| 1.6 <sup>a</sup> | -2.07      | ...        | -2.07    |
| 2.1              | -2.55      | 0.64       | -2.57    |
| 2.4433           | -2.54      | -0.44      | -2.64    |
| 2.8              | -2.41      | -1.03      | -2.59    |
| 3.1              | -2.26      | -1.27      | -2.54    |
| 4.0              | -1.71      | -1.26      | -2.18    |
| 7.0              | -0.48      | -0.33      | -0.78    |

<sup>a</sup> The ionic function was not included in the final calculations of the total energy, at this value of the internuclear distance, on account of the extremely small weight of this function.

Several conclusions can be drawn from Fig. 1. First of all, curve (g) indicates that the ionic wave function alone is a poor approximation to the energy of state  $B$ . As pointed out in the introduction, this result was already suggested by Brackman's and Phillipson's and Mulliken's calculations. It is also a poor approximation to the equilibrium internuclear distance (1.9 Å approximately) which is much larger than the experimental value of 1.293 Å. Curve (h) with  $Z_i=0.7$  throughout is not very different from the former while  $Z_i=1.0$  (curve j) tried by Phillipson and Mulliken and recalculated by us gives much worse results.

Curve (e) shows the most important feature of the present work, namely, that the covalent structure alone gives a much better result than the ionic wave function with a dissociation energy of 2.56 eV and an equilibrium internuclear distance close to 1.2 Å. That is, *state B seems to be mainly covalent instead of ionic, as was supposed up to now*. The inclusion of an excited  $2p$  orbital is necessary in order to obtain a reasonable value for the dissociation energy. When  $Z_c=1.0$  throughout, only slightly worse results are obtained (curve f). It could be argued that, as suggested by Chandrasekhar<sup>18</sup> and Arai,<sup>19</sup> the ionic wave function used is a rather bad wave function. In fact, it is known that as  $\rho$  tends to infinity it gives an energy of  $-0.472656$  a.u. instead of the best theoretical value of  $-0.52756$  a.u.<sup>20</sup> as calculated by Henrich.<sup>21</sup> Although the ionic wave function could be improved, it seems to us improbably that a different ionic wave function would give a potential energy curve below curve (e). If this is the situation, the mixing of such an ionic wave function with our covalent wave function would be so great as to lower the energy almost to the value of experimental dissociation energy, and this seems highly improbable without

<sup>18</sup> S. Chandrasekhar, *Astrophys. J.* **100**, 176 (1944).

<sup>19</sup> T. Arai, *J. Chem. Phys.* **26**, 451 (1957).

<sup>20</sup> The zero of energy is taken here as the energy of nuclei and electrons at infinite separation.

<sup>21</sup> L. R. Henrich, *Astrophys. J.* **99**, 59 (1944).

TABLE III. Values of the approximate weights of the covalent and ionic functions.

| $\rho$ (a.u.) | $\bar{Z}_c$ | $\bar{Z}_i$ | $ c_c ^2$ | $ c_i ^2$ |
|---------------|-------------|-------------|-----------|-----------|
| 2.1           | 1.2         | 1.2         | 0.92      | 0.01      |
| 2.4433        | 1.2         | 1.0         | 0.80      | 0.03      |
| 2.8           | 1.2         | 1.0         | 0.71      | 0.05      |
| 3.1           | 1.0         | 1.0         | 0.64      | 0.08      |
| 4.0           | 1.0         | 0.8         | 0.41      | 0.19      |
| 7.0           | 1.0         | 0.7         | 0.57      | 0.15      |

explicit introduction of the  $r_{12}$  terms into the wave function.

Curve (b) is our best potential energy curve, and it differs only slightly from curve (e) where only the covalent wave function is used. In fact the weight of the ionic wave function is very small for  $\rho_e$  (of the order of 3% as shown in Table III); it increases considerably for  $\rho$  around  $5 a_0$ , and then decreases again. It is worth noting that a better result is obtained when only one variational parameter  $\bar{Z}_c=\bar{Z}_i$  is used (curve c) than when using the Slater values for the molecule  $\bar{Z}_c=1.0$  and  $\bar{Z}_i=0.7$  (curve d); this is true for the excited as well as for the ground state. As a consequence of the small weight of the ionic wave function at the equilibrium internuclear distance, a small variation of  $\bar{Z}_i$  has a negligible effect on the total energy, while a small variation of  $\bar{Z}_c$  modifies it considerably, in accordance with similar results obtained for the ground state.<sup>5</sup>

Finally, in the present calculation we obtain a dissociation energy of  $2.64 \pm 0.02$  eV and  $\rho_e = 1.30 \pm 0.01$  Å. For comparison, Zener and Guillemin,<sup>4</sup> using a different type of wave function with three parameters,<sup>22</sup> obtained 2.57 eV and with a further variational parameter they improved the calculated energy up to 2.64 eV. Phillipson and Mulliken<sup>6</sup> with their molecular orbital type of wave function with two variational parameters obtained 2.330 eV. Kolos and Roothaan<sup>23</sup> using a 34 term correlated wave function obtained an energy of 3.5130 eV as compared with the experimental value 3.5802 eV. They obtained a value for the equilibrium internuclear distance equal to 1.258 Å compared to the observed value of 1.2926 Å.

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<sup>22</sup> Zener and Guillemin started with five parameters but one turned out to be zero and another infinite.

<sup>23</sup> W. Kolos and C. C. J. Roothaan, Technical Report, part 2, page 169 (1957-9), Laboratory of Molecular Structure and Spectra, The University of Chicago.