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Sidney Weinbaum

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The Normal State of the Hydrogen Molecule

SIDNEY WEINBAUM, *Gates Chemical Laboratory, California Institute of Technology**

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A simple wave function for the normal state of the hydrogen molecule, in which both the atomic and ionic configurations are taken into account, was set up and treated by a variational method. The dissociation energy was found to be 4.00 v.e. as compared to the experimental value of 4.68 v.e. and Rosen's value of 4.02 v.e. obtained by use of a function involving complicated integrals. It was found that the atomic function occurs with a coefficient 3.9 times that of the ionic function. A similar function with different screening constants for the atomic and ionic parts was also tried. It was found that the best results are obtained when these screening constants are equal. The addition of Rosen's term to the atomic-ionic function resulted in a value of 4.10 v.e. for the dissociation energy.

ATTEMPTS to obtain some of the properties of the normal hydrogen molecule by wave-mechanical methods date to the early days of wave mechanics. Heitler and London[1] applied a first-order perturbation method, and Sugiura,[2] by evaluating an integral whose value Heitler and London had only estimated, obtained results qualitatively comparable with known experimental data. Eisenschitz and London[3] applied a second-order perturbation treatment and obtained results in poorer agreement with experimental values than the results of previous calculations. For example, Heitler-London-Sugiura's value for the dissociation energy is 3.2 v.e. and the experimental value corrected for the zero point energy is 4.68 v.e., while Eisenschitz and London obtained 9.5 v.e. Thus it seems that the perturbation method is not very satisfactory for the treatment of the hydrogen molecule. The variational method, by approaching the value of energy from one side, is safe from the possibility of overshooting the mark. Wang,[4] using a variational method involving the introduction of a shielding constant as a parameter, obtained 3.7 v.e. for the dissociation energy. Rosen,[5] by using the three-parameter function $\psi=\psi^0+\sigma\psi'$, where ψ^0 is the hydrogenic wave function for the lowest state with a shielding constant Z, ψ' is a function symmetrical about the axis but not about a plane through the nucleus perpendicular to it, and σ is a parameter, has obtained 4.02 v.e. for the dissociation energy. The improvement on the previous value is considerable, but the calculations are rather laborious.

All these calculations were based on the assumption that each of the nuclei always has one electron attached to it, these electrons sometimes interchanging their positions, which leads to the interchange energy. It was suggested by Hund and Mulliken[6] that a truer picture would be given by a wave function $(\psi_1+\varphi_1)(\psi_2+\varphi_2)$ which takes account not only of the atomic configuration but also of the ionic configuration, when both electrons are on the same nucleus, the other being completely stripped of electrons. However, a function of the type suggested by Hund and Mulliken would give the hydrogen molecule in the normal state as much ionic character as atomic. There seems to be no reason to assume this, and a logical wave function to take care of the atomic-ionic character of the hydrogen molecule appears to be

$$c(\psi_1\varphi_2+\varphi_1\psi_2)+(\psi_1\psi_2+\varphi_1\varphi_2)$$

where c is a parameter,

$$\psi_1=Ne^{-Zr_{A1}} \quad \text{and} \quad \varphi_1=Ne^{-Zr_{B1}}.$$

* Contribution No. 364.

[1] W. Heitler and F. London, Zeits. f. Physik **44**, 455 (1927).

[2] Y. Sugiura, Zeits. f. Physik **45**, 484 (1927).

[3] R. Eisenschitz and F. London, Zeits. f. Physik **60**, 491 (1927).

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

[5] N. Rosen, Phys. Rev. **38**, 2099 (1931).

[6] F. Hund, Zeits. f. Physik **73**, 1 (1931).

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It has been shown[7] that the integral

$$E=\int \varphi^* H\varphi d\tau / \int \varphi^* \varphi d\tau,$$

where H is the Hamiltonian operator and φ is a function which satisfies certain boundary conditions but is otherwise arbitrary, containing, say, some variable parameters, has the property that the lowest value W obtained from varying the numerical parameters is the best approximation to the value of E, and that $E-W$ is always positive or zero. Hence the variational integral presents, as already mentioned, a satisfactory means for evaluating the energy of the normal state of the hydrogen molecule.

The first test for the wave function

$$\psi=c(\psi_1\varphi_2+\varphi_1\psi_2)+(\psi_1\psi_2+\varphi_1\varphi_2)$$

would be to consider it a two-parameter function. The results obtained by varying c would then be comparable with the Heitler-London-Sugiura results. It is, however, more convenient to treat

$$\psi=c(\psi_1\varphi_2+\varphi_1\psi_2)+(\psi_1\psi_2+\varphi_1\varphi_2)$$

as a three-parameter function, and then, at a certain point in the algebra, to reduce it to a two-parameter function by letting $Z=1$.

It is useful to set up the following scheme, devised by Slater:

	I	II	III	IV
ψ	+	−	+−	
φ	−	+		+−

and rewrite our wave function as

$$\psi=c(\psi_{\mathrm{I}}-\psi_{\mathrm{II}})+\psi_{\mathrm{III}}+\psi_{\mathrm{IV}}, \tag{1}$$

where $\psi_{\mathrm{I}}-\psi_{\mathrm{II}}$ is the atomic Heitler-London term and $\psi_{\mathrm{III}}+\psi_{\mathrm{IV}}$ is the ionic term. The variational integral

$$W=\int \psi^* H\psi d\tau / \int \psi^* \psi d\tau \tag{2}$$

then takes the form

$$W=\frac{W_N}{d}=\frac{\int H[c(\psi_{\mathrm{I}}-\psi_{\mathrm{II}})+\psi_{\mathrm{III}}+\psi_{\mathrm{IV}}]^2 d\tau}{\int [c(\psi_{\mathrm{I}}-\psi_{\mathrm{II}})+\psi_{\mathrm{III}}+\psi_{\mathrm{IV}}]^2 d\tau}. \tag{2a}$$

The wave equation for a hydrogen-like atom, in a system of units where unit of length $a_0=0.52845$A and unit of energy $e^2/a_0=27.06$ volt-electrons, is

$$\nabla^2\psi+2(W-V)\psi=0 \tag{3}$$

or, in a rewritten form,

$$W\psi=-\tfrac{1}{2}\nabla^2\psi+V\psi, \tag{3a}$$

where $W=-Z^2/2$. The general wave equation may be written as

$$W\psi=H\psi, \tag{4}$$

with

$$H=-\tfrac{1}{2}\nabla^2+V \quad \text{and} \quad V=\Sigma\Sigma(Z_iZ_j/r_{ij}), \tag{5}$$

the Hamiltonian function for the case of a hydrogen molecule being

$$H=-\tfrac{1}{2}(\nabla_1{}^2+\nabla_2{}^2)-\frac{1}{r_{A1}}-\frac{1}{r_{A2}}-\frac{1}{r_{B1}}-\frac{1}{r_{B2}}+\frac{1}{r_{12}}+\frac{1}{r_{AB}}. \tag{6}$$

In subsequent calculations the letter I with a subscript will be used to indicate the different integrals occurring. The integral $\int \psi\varphi d\tau$ will be denoted by s.

Leaving out for the present the term $1/r_{AB}$ in the Hamiltonian we can now set up the following expressions:

$$\int \psi_1 H_1 \psi_1 d\tau_1 = \int \psi_1\left(-\frac{\nabla_1{}^2}{2}-\frac{1}{r_{A1}}-\frac{1}{r_{B1}}\right)\psi_1 d\tau_1$$

$$=\int \psi_1\left(-\frac{Z^2}{2}+\frac{Z-1}{r_{A1}}-\frac{1}{r_{B1}}\right)\psi_1 d\tau_1$$

$$=-[Z^2/2+(1-Z)Z+I_1]=A \tag{7}$$

$$\int \psi_1 H_1 \varphi_1 d\tau_1 = -[(Z_2/2)s+(2-Z)I_2]=B. \tag{7a}$$

Let us denote integrals of the type $\int \psi_{\mathrm{I}} H \psi_{\mathrm{II}} d\tau$ by $H_{\mathrm{I\,II}}$. These integrals may be represented also by $\Sigma_p(-)^p(\psi\varphi/H/\psi\varphi)$, where p stands for the number of permutations of the signs of the spin that are necessary to obtain the same spin for functions pertaining to the same electron. Then, in terms of A and B, we obtain

$$H_{\mathrm{I\,I}}=H_{\mathrm{II\,II}}=2A+I_4;\ H_{\mathrm{IV\,III}}=H_{\mathrm{IV\,IV}}=2A+I_3,$$
$$H_{\mathrm{I\,II}}=H_{\mathrm{II\,I}}=-2Bs-I_6;H_{\mathrm{III\,IV}}=H_{\mathrm{IV\,III}}=2Bs+I_6,$$
$$H_{\mathrm{I\,III}}=H_{\mathrm{III\,I}}=H_{\mathrm{I\,IV}}=H_{\mathrm{IV\,I}}=-H_{\mathrm{II\,III}}=-H_{\mathrm{III\,II}}$$
$$=-H_{\mathrm{II\,IV}}=-H_{\mathrm{IV\,II}}=As+B+I_5. \tag{8}$$

[7] C. Eckart, Phys. Rev. **36**, 878 (1930).

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Making use of the relations (8), we find

$$\tfrac{1}{2}W_N = c^2H_{\mathrm{I\,I}} + H_{\mathrm{III\,III}} - c^2H_{\mathrm{I\,II}} + H_{\mathrm{III\,IV}} + 4cH_{\mathrm{I\,III}}$$
$$= c^2(2A+I_4) + 2A + I_3 + c^2(2Bs+I_6) + 2Bs + I_6 + 4c(As+B+I_5) \quad (9)$$

and putting $I = ZF$, where F is a function of $\rho(=Zr_{AB})$ only, this becomes

$$\tfrac{1}{2}W_N = Z^2[(c^2+1)(1+2sF_2-s^2)+4cF_2] + Z[(c^2+1)(F_6-2-2F_1-4sF_2)$$
$$+F_3+c^2F_4-4c(s+F_1s+2F_2-F_5)] = \lambda Z^2+\mu Z, \quad (9a)$$

where

$$\lambda = (c^2+1)(1+2sF_2-s^2)+4cF_2 \quad (10)$$

$$\mu = (c^2+1)(F_6-2-2F_1-4sF_2)+F_3+c^2F_4-4c(s+F_1s+2F_2-F_5). \quad (10a)$$

The denominator in the expression for W has the value

$$d = \int \psi^*\psi d\tau = 2d_{\mathrm{I\,I}} + 2d_{\mathrm{III\,III}} - 2d_{\mathrm{I\,II}} + 2d_{\mathrm{III\,IV}} + 8d_{\mathrm{I\,III}}$$
$$= 2c^2+2+2c^2s^2+2s^2+8cs = 2[(c^2+1)(1+s^2)+4cs] = 2\nu. \quad (11)$$

As $\rho = Zr_{AB}$, introducing the term $1/r_{AB}$ that we left out of the calculations, we have

$$W = (\lambda Z^2+\mu Z)/\nu + Z/\rho = (\lambda/\nu)Z^2 + (\mu/\nu+1/\rho)Z. \quad (12)$$

Substituting $Z=1$ in (12) we obtain W as a function of parameters c and ρ:

$$W = \frac{\lambda+\mu}{\nu} + \frac{1}{\rho} = \frac{(c^2+1)(-1-s^2-2F_1-2F_2s+F_6)+F_3+c^2F_4-4c(s+F_1s+F_2-F_5)}{(c^2+1)(1+s^2)+4cs} + \frac{1}{\rho}. \quad (13)$$

Minimizing (13) with respect to c, $dW/dc=0$ yields a quadratic in c. Substituting the value of c obtained from this quadratic back in (13) and varying ρ, the lowest value of W was found to be $W=-1.1187$ with $\rho=1.67$ and $c=6.322$. The Sugiura value for W is $W=-1.1156$, so that the inclusion of the ionic term gives an improvement in the dissociation energy of 0.0031 or 3 percent.

Going back to (12), we can improve the treatment by minimizing (12) with respect to Z, which is equivalent to Wang's treatment plus an ionic term. We get

$$dW/dZ = (2\lambda/\nu)Z + \mu/\nu + 1/\rho \quad (14)$$

and

$$Z_{\min} = -(\nu/2\lambda)(\mu/\nu+1/\rho). \quad (15)$$

Substituting (15) into (12) we have

$$W_{Z=\min} = -(\nu/4\lambda)(\mu/\nu+1/\rho)^2. \quad (16)$$

Expression (16) is a function of c and ρ, as was the case for (13). But while in the case of (13) $dW/dc=0$ gave a quadratic in c, in the case of (16) $dW/dc=0$ gives an equation of the fifth degree in c. However, to evaluate c by direct substitution of different values of c for a given ρ involves very little labor. The procedure employed was as follows: the best value of c was first obtained for $\rho=1.67$; then ρ was varied to get the best value for the obtained c; then c was varied again, and so on, until the variation in either c or ρ would result in a lower value of W. The lowest value of W obtained from (16) is $W=-1.148$, with $\rho=1.69$, $c=3.9$ and $Z=1.193$.

This result compares very favorably with the result of Wang's treatment (improvement of 8 percent in dissociation energy) and is just very slightly lower than Rosen's result, which requires very elaborate calculations. Thus the results of this calculation show that the ratio of the coefficients of the atomic and ionic parts of the wave function is about four and not one as was suggested by Hund and Mulliken.

So far it has been assumed that the effective nuclear charge Z is the same for both the atomic and ionic parts. The next step is to introduce a

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new parameter $\epsilon = Z'/Z$, where Z' is the effective nuclear charge in the ionic term. On carrying out the calculations* it was found that the value $\epsilon = 1$ gives the lowest energy. This interesting fact shows that the screening constants for the atomic and ionic contributions to the normal state of the hydrogen molecule are the same.

The ionic term and the Rosen term giving independently an improvement in Wang's result, a function including both these terms was set up. As both the Wang-ionic and the Rosen treatment give the same internuclear distance, it is a good approximation to use $\rho = 1.7$ for the Rosen-ionic treatment. With $\rho = 1.7$, c and σ were varied until the combination of c and σ giving the lowest value for W was obtained.* The results obtained are $W = -1.1515$, $c = 5.7$, $\sigma = 0.07$ and $Z = 1.190$; ρ has not been varied as such a variation would require very long computations and the expected improvement in the value for W was small.

The comparison of the results of the different calculations can be seen from Fig. 1 and from Table I.

TABLE I.

	W	ΔE(v.e.)	J_e(g-cm^2)	ν_e(cm^{-1})
Present paper				
Wang-ionic	−1.148	4.00	4.65×10^{41}	4750
Rosen-ionic	−1.1515	4.10		
Heitler-London-Sugiura	−1.116	3.14	5.2	4800
Wang	−1.138	3.76	4.59	4900
Rosen	−1.1485	4.02	4.65	4260
Observed	−1.173	4.68	4.537[8]	4418[8]

The fundamental frequency ν_e was calculated by means of a Morse[9] function

$$\Delta E = De^{-2a(\rho_0-\rho_m)} - 2De^{-a(\rho_0-\rho_m)}. \qquad (17)$$

By substituting in (17) three different values of ρ_0 with the corresponding values of ΔE we obtain three simultaneous equations which when solved give $D = 0.1479$ and $a = 1.216$. Then ν_e was calculated from the formula

$$\nu_e = (a/0.1227)(D/M)^{\frac{1}{2}} \qquad (18)$$

where a is in 1/A, D is in wave numbers and $M = M_1M_2/(M_1+M_2)$ is in terms of oxygen = 16.

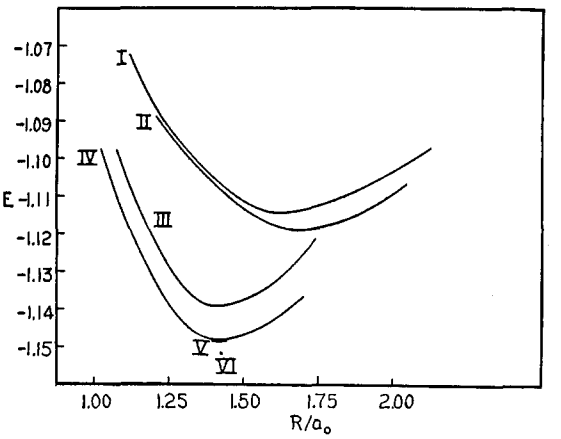

FIG. 1. Calculated energy curves of normal H_2. Curve I, Heitler-London; curve II, Heitler-London-ionic; curve III, Wang; curve IV, Wang-ionic; curve V, Rosen; curve VI, Rosen-ionic.

Table I shows that the introduction of the ionic term in the wave function gives an improvement of 8 percent over Wang's value for the dissociation energy of hydrogen molecule. Thus from a simple wave function results almost equivalent to Rosen's were obtained. It should be noticed that while the ionic term corresponds to a definite physical picture, the physical significance of the Rosen term is not very clear. The addition of the Rosen term to the atomic-ionic wave function gives only about $2\frac{1}{2}$ percent increase in the value of the dissociation energy.†

The writer wishes to thank Professor Pauling for suggesting the problem and for valuable criticism during the progress of the work.

* Details of these calculations are in the author's dissertation.

[8] Private communication from Professor Birge.

[9] P. M. Morse, Phys. Rev. **34**, 57 (1929).

† A. S. Coolidge and H. M. James (Phys. Rev. **43**, 588 (1933)) have recently reported a better value for the energy, obtained by the use of a function involving the distance between the two electrons explicitly.

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