

THE PROBLEM OF THE NORMAL HYDROGEN MOLECULE
IN THE NEW QUANTUM MECHANICS*

BY S. C. WANG

ABSTRACT

The solution of Schroedinger's equation for the normal hydrogen molecule is approximated by the function $C[e^{-z(r_1+p_2)/a} + e^{-z(r_2+p_1)/a}]$ where $a = \hbar^2/4\pi^2mc^2$, r_1 and p_1 are the distances of one of the electrons to the two nuclei, and r_2 and p_2 those for the other electron. The value of Z is so determined as to give a minimum value to the variational integral which generates Schroedinger's wave equation. This minimum value of the integral gives the approximate energy E . For every nuclear separation D , there is a Z which gives the best approximation and a corresponding E . We thus obtain an approximate energy curve as a function of the separation. The minimum of this curve gives the following data for the configuration corresponding to the normal hydrogen molecule: the heat of dissociation = 3.76 volts, the moment of inertia $J_0 = 4.59 \times 10^{-41}$ gr. cm², the nuclear vibrational frequency $\nu_0 = 4900$ cm⁻¹.

CONSIDERABLE work has been done by the various authors¹⁻⁸ in finding the energy value of specific atoms or molecules as prescribed by Schroedinger's wave equation. It is well known that the wave equation has not been rigorously solved for any other atoms or molecules beside hydrogen. Consequently some kind of an approximate method has to be introduced to make the energy calculation. While some of the authors use ordinary perturbational methods as given by Schroedinger⁹ or the equivalent as given by Born, Heisenberg and Jordan,¹⁰ others devise special schemes to solve particular problems. One such scheme was introduced in a paper by Kellner⁸ who calculated the energy values of normal He by trying to solve directly the variational problem corresponding to the wave equation. The present

* A preliminary note appeared in the Bulletin of the American Physical Society, Chicago meeting, November, 1927. When the paper was near completion, a recent issue of the Zeitschrift für Physik arrived containing a paper by Dr. Y. Sugiura (Zeits. f. Physik **45**, 484, 1927) who continued the work of Heitler and London (Zeits. f. Physik **44**, 455 (1927) by evaluating the integral referred to in the present paper in footnote 18 and calculated in Eq. (13). As is to be expected, Sugiura made calculations of the different atomic constants such as we do here. However, the present paper is still submitted here for the reason that we used a new method of calculation and arrived at some results in a little better agreement with the experimental data than Sugiura's.

¹ Unsöld, Ann. d. Physik **82**, 355 (1927); Zeits. f. Physik **43**, 563 (1927).

² Heisenberg, Zeits. f. Physik **39**, 499 (1926).

³ Sugiura, Zeits. f. Physik **44**, 190 (1927).

⁴ Heitler and London, Zeits. f. Physik **44**, 455 (1927).

⁵ Burrau, Danske Vidensk. Selskab, Math-fys. Meddel. **7**, 14, Copenhagen, (1927).

⁶ Condon, Proc. Nat. Acad. Sci. **13**, 466 (1927).

⁷ Slater, Proc. Nat. Acad. Sci. **13**, 423 (1927).

⁸ Kellner, Zeits. f. Physik **44**, 91 (1927).

⁹ Schroedinger, Ann. d. Physik **80**, 437 (1926).

¹⁰ Born, Heisenberg and Jordan, Zeits. f. Physik **35**, 557 (1926).

paper will be chiefly concerned with the problem of the normal hydrogen molecule investigated along similar lines.

When the two hydrogen atoms are at a great distance apart, the problem has been treated in the quantum mechanics in a recent paper by the author.¹¹ In that case, the two atoms more or less retain their individuality and, according to a perturbation calculation, the total energy of the two-atom problem is, to a first approximation, the sum of the energies of two single atoms plus a mutual term which can be ascribed to the polarizability of the atoms. When the atoms are close together, such a procedure is no longer valid and we shall have to resort to a different method.

Two previous attempts have been made to treat that phase of the H₂ problem. Condon⁶ proposed to regard it as the perturbed problem of the case where we have two non-interacting electrons, each in the configuration of an H₂⁺ ion. The "Eigenfunktion" of such an unperturbed problem is not yet available but the "Eigenwerte" for different nuclear separations has been worked out by Burrau⁵ by a numerical method. To Burrau's results Condon then incorporated his approximate estimate of the perturbation energy curve as a function of the nuclear separation, which arises out of the interaction of the two electrons, from the experimental energy data in the He problem. (However, in view of the recent work of Slater⁷ and of Kellner,⁸ we may say the data are also theoretical.) The resulting energy value for normal H₂ is in remarkably good agreement with the experimental value. It will be referred to again in a table near the end of the present paper.

Heitler and London,⁴ also using a perturbational method, started their calculations from hydrogen-like "Eigenfunktionen." Of course, they recognized the weakness of assigning each of the electrons to only one of the nuclei, which would amount to saying that in the zero-order approximation each electron is not affected by the other nucleus. To remedy this defect, they construct, out of considerations of the degeneracy of the problem, an "Eigenfunktion," consisting of hydrogen-like terms but symmetrical to the two nuclei so far as each of the two electrons is concerned. They did not carry through the numerical part in the calculation of the first order perturbation energy; that was done in a later paper by Sugiura, already referred to at the beginning of the present article.

In the calculations here presented, we propose to attack the problem from a slightly different angle. Schroedinger¹² has shown that the wave equation for an atomic system of k degrees of freedom with a Hamiltonian $T(q_k, p_k) + V(q_k)$ is nothing more than Euler's differential equation for the minimizing of the following generalized volume integral

$$I = \int \left\{ \frac{\hbar^2}{4\pi^2} T \left(q_k, \frac{\partial \psi}{\partial q_k} \right) + \psi^2 V(q_k) \right\} \Delta_p^{-1/2} dx \quad (1)$$

¹¹ Wang, Phys. Zeits. **28**, 663 (1927).

¹² Schroedinger, Ann. d. Physik **79**, 734 (1926).

subject to the condition

$$J = \int \psi^2 \Delta_p^{-1/2} dx = 1 \tag{2}$$

where $\int dx$ is an abbreviation for $\int \dots \int dq_1 \dots dq_k$, and $\Delta_p^{-1/2}$ is the reciprocal of the square root of the determinant belonging to the quadratic form T . Besides, what is perhaps of more importance here, the minimum values of the volume integral are just the "Eigenwerte" of the wave equation.

To solve the variational problem directly, we can use what is commonly called the Ritz method.¹³ It consists of first setting up an infinite sequence of functions of the coordinates (known functions of the independent variables), satisfying certain requirements regarding completeness, and so forth, which we shall not go into here, and then approximating the unknown function ψ by a linear combination of a finite number of the selected coordinate functions with constant coefficients to be determined later. When this approximate ψ is substituted into the integral I and the integration performed, I reduces to a homogeneous quadratic function of the coefficients. The latter are then so determined as to minimize this quadratic function, subject to the restriction that condition (2) is always satisfied. The calculation made in this paper corresponds, though only roughly, to a Ritz approximation of two terms; the approximate ψ function used involves the two constants in a quite complicated way instead of linearly.

We shall first set up the variational integral connected with the problem of the hydrogen molecule. Let r_1 and p_1 be the distances of the first electron to the two nuclei and r_2 and p_2 those for the second electron. Let s be the distance between the two electrons and ϕ_1 be the azimuthal angle of one of the electrons, say the first, referred to the line joining the nuclei as the polar axis. We shall use these six quantities r_1, p_1, r_2, p_2, s and ϕ_1 as independent variables; the separation between the nuclei, which we shall designate by D enters into the problem as a fixed parameter. We may also have occasion to use the ordinary spherical coordinates r_1, ϑ_1, ϕ_1 and r_2, ϑ_2, ϕ_2 for the two electrons referred to one and the same nucleus.

Now let us first remark that if we try on the wave equation of the hydrogen molecule the substitution $\psi = U\Phi$ where Φ is a function of ϕ_1 alone and U of the remaining variables, it is found that the part involving ϕ_1 can be separated from the rest. For the lowest "Eigenwerte," we therefore need only to take $\Phi = \text{constant}$ so that the solution ψ is actually a function of five variables.

In spherical coordinates the integral to be minimized is

$$I = \int \left\{ \frac{\hbar^2}{8\pi^2 m} \left[\left(\frac{\partial \psi}{\partial r_1} \right)^2 + \frac{1}{r_1^2} \left(\frac{\partial \psi}{\partial \vartheta_1} \right)^2 + \frac{1}{r_1^2 \sin^2 \vartheta_1} \left(\frac{\partial \psi}{\partial \phi_1} \right)^2 + \left(\frac{\partial \psi}{\partial r_2} \right)^2 + \frac{1}{r_2^2} \left(\frac{\partial \psi}{\partial \vartheta_2} \right)^2 + \frac{1}{r_2^2 \sin^2 \vartheta_2} \left(\frac{\partial \psi}{\partial \phi_2} \right)^2 \right] + \psi^2 V \right\} d\Omega_1 d\Omega_2 \tag{3}$$

¹³ See Riemann-Webers Differentialgleichungen der Physik, 7th ed., vol. I, p. 678 or Ritz, Ann. d. Physik **28**, 737 (1909).

where

$$d\Omega_1 d\Omega_2 = r_1^2 r_2^2 \sin \vartheta_1 \sin \vartheta_2 dr_1 dr_2 d\vartheta_1 d\vartheta_2 d\phi_1 d\phi_2 \quad (4)$$

and

$$V = -\frac{e^2}{r_1} - \frac{e^2}{p_1} - \frac{e^2}{r_2} - \frac{e^2}{p_2} + \frac{e^2}{s} + \frac{e^2}{D}.$$

We now make the following change of independent variables for the integrand

$$\begin{aligned} r_1 &= r_1, & r_2 &= r_2, \\ p_1^2 &= r_1^2 + D^2 - 2r_1 D \cos \vartheta_1, & p_2^2 &= r_2^2 + D^2 - 2r_2 D \cos \vartheta_2 \\ s^2 &= r_1^2 + r_2^2 - 2r_1 r_2 [\cos \vartheta_1 \cos \vartheta_2 + \sin \vartheta_1 \sin \vartheta_2 \cos(\phi_1 - \phi_2)], & \phi_1 &= \phi_1. \end{aligned}$$

Noting that $\partial\psi/\partial\phi_1 = 0$, we find

$$\begin{aligned} I = \int \left\{ \frac{h^2}{8\pi^2 m} \left[\left(\frac{\partial\psi}{\partial r_1} \right)^2 + \left(\frac{\partial\psi}{\partial p_1} \right)^2 + \left(\frac{\partial\psi}{\partial r_2} \right)^2 + \left(\frac{\partial\psi}{\partial p_2} \right)^2 + 2 \left(\frac{\partial\psi}{\partial s} \right)^2 \right. \right. \\ + \frac{r_1^2 + p_1^2 - D^2}{r_1 p_1} \frac{\partial\psi}{\partial r_1} \frac{\partial\psi}{\partial p_1} + \frac{r_2^2 + p_2^2 - D^2}{r_2 p_2} \frac{\partial\psi}{\partial r_2} \frac{\partial\psi}{\partial p_2} + \frac{s^2 + r_1^2 - r_2^2}{r_1 s} \frac{\partial\psi}{\partial s} \frac{\partial\psi}{\partial r_1} \\ + \frac{s^2 + r_2^2 - r_1^2}{r_2 s} \frac{\partial\psi}{\partial s} \frac{\partial\psi}{\partial r_2} + \frac{s^2 + p_1^2 - p_2^2}{p_1 s} \frac{\partial\psi}{\partial s} \frac{\partial\psi}{\partial p_1} \\ \left. \left. + \frac{s^2 + p_2^2 - p_1^2}{p_2 s} \frac{\partial\psi}{\partial s} \frac{\partial\psi}{\partial p_2} \right] + \psi^2 \Delta \right\} d\Omega_1 d\Omega_2 \quad (5) \end{aligned}$$

while the restricting condition remains formally

$$J = \int \psi^2 d\Omega_1 d\Omega_2 = 1 \quad (6)$$

As for the volume element $d\Omega_1 d\Omega_2$ we can either preserve its meaning in Eq. (4), or we can write it in the new variables. In the latter case, we find that the expression is in general very complicated. But, in case the integrand is independent of s as well as ϕ_1 so that we can integrate with respect to these two variables at the very beginning, then the volume element expressed in the remaining four variables has the very simple form

$$d\Omega_1 d\Omega_2 = \frac{4\pi^2}{D^2} r_1 p_1 r_2 p_2 dr_1 dp_1 dr_2 dp_2 \quad (7)$$

In the subsequent work we shall interpret $d\Omega_1 d\Omega_2$ either by (4) or by (7) as occasion demands.

The next question has to do with the precise form of the two constant approximation for ψ . Let us note in the first place that the lowest "Eigen-

funktion" must be symmetrical¹⁴ with respect to the two electrons and the two nuclei; or more explicitly, it should be invariant to the substitutions

$$\begin{pmatrix} r_1 & r_2 \\ p_1 & p_2 \end{pmatrix} \text{ and } \begin{pmatrix} r_1 & p_1 \\ r_2 & p_2 \end{pmatrix}.$$

Now, if we have two H-atoms so far apart that their mutual influence is negligible and if we assign electron 1 to nucleus 1 and electron 2 to nucleus 2, then the lowest "Eigenfunktion" for the two atom problem would be $Ce^{-(r_1+p_2)/a}$. On the other hand, if we interchange the assignment of the electrons to the nuclei, we would have the "Eigenfunktion" $Ce^{-(r_2+p_1)/a}$. A function which satisfies the properties of symmetry just mentioned and which approaches the one or the other of the above functions as the separation between the atoms becomes greater and greater, is evidently the following: $C[e^{-(r_1+p_2)/a} + e^{-(r_2+p_1)/a}]$.¹⁵ If we had two nuclei of charge Ze each to start with, we would have instead the function

$$C[e^{-Z(r_1+p_2)/a} + e^{-Z(r_2+p_1)/a}]. \quad (8)$$

It is this latter function that we shall use as the approximate solution for our problem. Perhaps, instead of considering our calculation as a modified form of the Ritz process, we had better regard it as one similar to that of Kramers in the He problem¹⁶ (or more recently, that of Hutchisson¹⁷ for H_2) in the classical quantum theory. Roughly speaking, Kramers uses for the unperturbed motion of the He problem a potential due, in part, to a fictitious nuclear charge Ze , the value of Z being determined by the condition that the ratio of the perturbing force to the actual force shall be a minimum on the average. In our work, following the ideas of the new quantum mechanics, we have replaced the latter criterion by the one that Z shall have the "best" value in making the variational integral a minimum.

Returning to our calculations, we first make use of the symmetrical properties of ψ and of $d\Omega_1 d\Omega_2$ and we find that (5) reduces to

$$I = \int \left\{ \frac{\hbar^2}{8\pi^2 m} \left[4 \left(\frac{\partial \psi}{\partial r_1} \right)^2 + 2 \left(\frac{\partial \psi}{\partial s} \right)^2 + \frac{4(s^2 + r_1^2 - r_2^2)}{r_1 s} \frac{\partial \psi}{\partial s} \frac{\partial \psi}{\partial r_1} \right. \right. \\ \left. \left. + \frac{2(r_1^2 + p_1^2 - D^2)}{r_1 p_1} \frac{\partial \psi}{\partial r_1} \frac{\partial \psi}{\partial p_1} \right] - e^2 \psi^2 \left[\frac{4}{r_1} - \frac{1}{s} - \frac{1}{D} \right] \right\} d\Omega_1 d\Omega_2 \quad (9)$$

The above equation holds rigorously for the case of the lowest "Eigenwerte" and the exact solution is that symmetric function of $r_1 p_1 r_2 p_2$ and s that

¹⁴ See Hund, *Zeits. f. Physik* **42**, 93 (1927) and also Heitler and London, loc. cit. In the latter problem the same problem of H_2 was investigated. They were, however, more interested in the general aspect of the formation of the molecule than in the methods of calculating particular energy values.

¹⁵ Heitler and London decided upon this function as the unperturbed Eigenfunktion after considering a modified form of the resonance phenomenon first pointed out by Heisenberg.

¹⁶ Kramers, *Zeits. f. Physik* **13**, 312 (1923).

¹⁷ Hutchisson, *Phys. Rev.* **29**, 270 (1927).

minimizes (9) among the entire class of such symmetric functions. We now substitute the approximate form for ψ as given by (8) into Eqs. (9) and (6), we find they become

$$I = C^2 \int \left\{ \frac{h^2 Z^2}{8\pi^2 m a^2} \left[4e^{-2Z(r_1+p_2)/a} + \frac{2(r_1^2 + p_1^2 - D^2)}{r_1 p_1} e^{-Z(r_1+p_1+r_2+p_2)/a} \right] - e^2 \left[\frac{4}{r_1} - \frac{1}{s} - \frac{1}{D} \right] [e^{-2Z(r_1+p_2)/a} + e^{-2Z(r_2+p_1)/a} + 2e^{-Z(r_1+p_1+r_2+p_2)/a}] \right\} d\Omega_1 d\Omega_2 \quad (10)$$

$$J = C^2 \int [e^{-Z(r_1+p_2)/a} + e^{-Z(r_2+p_1)/a}]^2 d\Omega_1 d\Omega_2 = 1 \quad (11)$$

The condition (11) evidently just determines the value of C . We can therefore dispose of it by dividing (10) by (11). The function to be minimized then becomes

$$E = I/J \quad (12)$$

We will have to simplify this expression by actually carrying out the integration. Most terms in the above expression can be readily integrated by a judicious choice of one form or the other of $d\Omega_1 d\Omega_2$. In the integration of the terms of the type $(1/s)e^{-Z(r+p_2)/a}$, use was made of the well known theorems concerning the averages of a harmonic function over a sphere.

The only integral that gives rise to some difficulty is due to the term $(1/s)e^{-Z(r_1+p_1+r_2+p_2)/a}$.¹⁸ It is the total Newtonian potential energy of that distribution of mass which consists of homogeneous confocal ellipsoidal layers of revolution with the density falling off as $e^{-\kappa\lambda}$ where κ is a constant and λ is the major axis, the fixed foci being in all cases the two nuclei. The result of the integration process gives:

$$\int \frac{1}{s} e^{-Z(r_1+p_1+r_2+p_2)/a} d\Omega_1 d\Omega_2 = \frac{a^5 \pi^2}{60Z^5} \left\{ \frac{1}{Q} \left[e^{-Q}(Q^2+6Q+12)^2 \left(\log \frac{Q}{2} + \gamma \right) + 2\text{Ei}(Q) \times (Q^2+6Q+12)(Q^2-6Q+12) - e^Q \text{Ei}(2Q)(Q^2-6Q+12)^2 \right] - e^{-Q} \left(\frac{Q^3}{2} + 9Q^2 + \frac{69}{2}Q - \frac{75}{2} \right) \right\} \quad (13)$$

where Q is the abbreviation for $2ZD/a$, γ is the Euler's constant and $\text{Ei}(x) = \int_x^\infty (1/u)e^{-u} du$, the numerical values of which can be found in tables in a paper by Glaisher.¹⁹

¹⁸ Essentially the same integral came up in the calculation of Heitler and London (*loc. cit.*) but they did not attempt to evaluate it exactly. See, however, the note after the asterisk on the first page of this paper.

¹⁹ Glaisher, *Phil. Trans.* **160**, 367 (1870).

Collecting the different integrals in (12), we find it finally reduces to

$$\begin{aligned} \frac{E}{R} = & \left\{ 64 + \frac{4}{9} e^{-Q} (Q^2 + 6Q + 12)^2 \right\}^{-1} \left\{ 128 + \frac{8}{9} e^{-Q} (Q^2 + 6Q + 12) (-Q^2 + 6Q + 12) \right\} \\ & \frac{Q^2 a^2}{4D^2} - \left\{ 64 + \frac{4}{9} e^{-Q} (Q^2 + 6Q + 12)^2 \right\}^{-1} \times \left\{ 128(1+Q) - \frac{16}{15} \left[(Q^2 + 6Q + 12)^2 e^{-Q} \right. \right. \\ & \left. \left. \left(\log \frac{Q}{2} + \gamma \right) + 2\text{Ei}(Q)(Q^2 + 6Q + 12)(Q^2 - 6Q + 12) \right. \right. \\ & \left. \left. - e^Q \text{Ei}(2Q)(Q^2 + 6Q + 12)^2 \right] + e^{-Q}(11.2Q^4 + 97.6Q^3 + 316.8Q^2 + 176Q \right. \\ & \left. \left. - 128) \right\} \left(\frac{a}{D} \right) + \frac{a}{D} \end{aligned} \tag{14}$$

where R is the Rydberg constant. For every separation D we choose a value of Z which minimizes E ; or, equally well, since D is a fixed parameter in each case, we may choose the Q that makes E a minimum. The energy curve of two H-atoms expressed as a function of the nuclear separation D is therefore obtained by eliminating Q between the following two equations:

$$E = E(Q, D) \tag{14'}$$

$$\partial E / \partial Q = 0 \tag{15}$$

The minimum of this energy curve gives the data for the equilibrium configuration, which corresponds to the normal hydrogen molecule.

However, there does not seem to be any feasible way of making the general elimination between Eqs. (14) and (15), either analytically or graphically. We can only give the solution of the most interesting case of the equilibrium configuration which can be treated in the following manner. The set of values E_0 , Q_0 and D_0 for this case is evidently the solution of the simultaneous equations:

$$E = E(Q, D) \tag{14'}$$

$$\partial E / \partial Q = 0 \tag{15}$$

$$(dE/dD = 0) \text{ or } \partial E / \partial D = 0 \tag{16}$$

where the total differentiation denotes the one on E as a function of D alone obtained by elimination of Q between Eqs. (14) and (15). It turns out to be a very simple matter to eliminate analytically the quantity D between Eqs. (14) and (16). If we then plot the resulting as a function of Q alone, the minimum of this curve evidently just gives the E_0 and Q_0 for the equilibrium case. They are thus found to be $E_0 = -2.278R$, and $Q_0 = 3.28$. The value D_0 can now also be computed from one of the equations. We find $D_0 = 1.406a$,

which corresponds to a moment of inertia $J_0 = 4.59 \times 10^{-41}$ gr. cm². From the relation $Q = 2ZD/a$ we also find $Z_0 = 1.166$.

By using this same value of Z_0 found for the equilibrium separation to calculate the approximate energy values for separations in its neighborhood, we obtain an approximate value for the nuclear vibrational frequency $\nu_0 = 4900$ cm⁻¹ from the curvature of the resulting energy curve.

For comparison, we tabulate below the values found in the above calculation and the values obtained by Condon⁶ and Sugiura* of the various atomic constants and those values determined experimentally, mostly from band spectra data:

Calculated values	E_0	J_0	ν_0	Z
This paper	$-2.278R$	4.59×10^{-41} gr.cm ²	4900 cm ⁻¹	1.166 ²²
Condon	$-2.325R$	4.26×10^{-41}	5300	
Sugiura	$-2.24R$	5.2×10^{-41}	4800	
Observed value	$-2.326R$ ²⁰	4.67×10^{-41} ²¹	4360 ²⁰	

Finally as a check on the calculations leading to the energy equation (14), the latter equation is examined for very large and very small values of D . In the first case, we have two independent H-atoms and it is found that the optimum value of Z is unity, giving $E = -2R$ as we should expect. In the second case we have the normal helium atom; the value of Z found is 1.6875 and that of E is -77.4 volts. They are in complete agreement with the results obtained by Kellner²³ for the helium atom.

I take this opportunity to thank Professor A. P. Wills for his encouragement and his kindness in going over the manuscript.

DEPARTMENT OF PHYSICS,
COLUMBIA UNIVERSITY,
December 12, 1927.

²⁰ Witmer, Proc. Nat. Acad. Sci. **12**, 238 (1926); also Phys. Rev. **28**, 1223 (1926).

²¹ Hori, Zeits. f. Physik **44**, 834 (1927); Dennison, Proc. Roy. Soc. **A115**, 483 (1927).

²² Hutchisson (loc. cit.) obtained the value $Z = 0.823$ from the classical quantum theory calculations. It must be mentioned, however, that he introduced another term of the form $\beta e^2/s^2$ in his unperturbed problem. Our value of Z is also to be compared with those given by Van Vleck (Proc. Nat. Acad. Sci. **12**, 662 (1926)), who, using the new quantum mechanics obtained for the Z of H₂ the values 1.08, 1.14 and 1.11 from the experimental values of the energy, the dielectric constant and the diamagnetic susceptibility of H₂ respectively.

²³ Kellner, loc. cit.⁸, see especially Eq. (9) of that paper.