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The Normal State of the Hydrogen Molecule-Ion*

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A variation function somewhat similar to that applied by Rosen to H_2 is used in the discussion of the normal state of H_2^+ .

IN treating the normal state of the hydrogen molecule by the variational method, N. Rosen¹ used an eigenfunction involving the one-electron function

$$\psi = \psi^0 + \sigma\psi',$$

in which $\psi^0 = (\alpha^3/\pi)^{1/2} e^{-\alpha r_a}$ is a hydrogen-like $1s$ wave function for nucleus a , with effective nuclear charge (in units e) $Z = \alpha a_0$, and $\psi' = (\alpha^5/\pi)^{1/2} r_a e^{-\alpha r_a} \cos \theta_a$ is a hydrogen-like $2p$ function for nuclear charge $2Z$, θ_a being the angle between the nuclear axis and the radius vector from nucleus a to the electron, and σ a parameter. In order to see to what extent this method of treatment of molecules could be expected to be satisfactory in other cases, and whether or not pronounced improvement could be obtained by varying the ratio of the effective nuclear charges in ψ^0 and ψ' , we have treated the hydrogen molecule-ion (which has previously been well investigated) by methods similar to Rosen's.

For this purpose we replace Z by $Z' = \epsilon Z$ in ψ' . ψ^0 and ψ' satisfy the equations

$$H_a^0 \psi^0 = Z^2 E_0 \psi^0 \quad \text{and} \quad H_a' \psi' = \epsilon^2 Z^2 E_0 \psi',$$

where

$$H_a^0 = \frac{-\hbar^2}{8\pi^2 m} \nabla^2 - \frac{Ze^2}{r_a} \quad \text{and} \quad H_a' = \frac{-\hbar^2}{8\pi^2 m} \nabla^2 - \frac{2Z\epsilon e^2}{r_a},$$

and are normalized and mutually orthogonal.

$$\begin{aligned} I_{01} &= (8\epsilon^{5/2}/(1-\epsilon^2)^4 \rho^2) [e^{-\rho} \{ (\epsilon^2 - 1)4\epsilon\rho^2 - 24\epsilon\rho - 24\epsilon \} + e^{-\epsilon\rho} \{ (1-\epsilon^2)^2 \rho^3 - 8\epsilon\rho^2(1-\epsilon^2) + 24\epsilon^2\rho + 24\epsilon \}], \\ RJ_{01} &= (4\epsilon^{5/2}/(1-\epsilon^2)^3 \rho) [-8\epsilon e^{-\rho}(\rho+1) + e^{-\epsilon\rho} \{ (1-\epsilon^2)^2 \rho^3 - 4\epsilon(1-\epsilon^2)\rho^2 + 8\epsilon^2\rho + 8\epsilon \}], \\ RJ_{10} &= (8\epsilon^{5/2}/(1-\epsilon^2)^3 \rho) [e^{-\rho} \{ (1-\epsilon^2)\rho^2 + 4\rho + 4 \} + e^{-\epsilon\rho} \{ (1-\epsilon^2)\rho^2 - 4\epsilon\rho - 4 \}], \\ RG_{01} &= (4\epsilon^{5/2}/(1+\epsilon)^5 \rho) [-e^{-(1+\epsilon)\rho} \{ (1+\epsilon)^3 \rho^3 + 4(1+\epsilon)^2 \rho^2 + 8(1+\epsilon)\rho + 8 \} + 8]. \end{aligned}$$

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¹ N. Rosen, Phys. Rev. **38**, 2099 (1931).

We write

$$\chi = \psi^0 + \phi^0 + \sigma(\psi' + \phi')$$

as the complete eigenfunction for the molecule-ion, with ϕ^0 and ϕ' replacing ψ^0 and ψ' for the nucleus b . The Hamiltonian for this problem is

$$H = \frac{-\hbar^2}{8\pi^2 m} \nabla^2 + e^2 \left(\frac{1}{R} - \frac{1}{r_a} - \frac{1}{r_b} \right).$$

The integrals arising from the expression for the energy

$$W = \int \chi H \chi d\tau / \int \chi^2 d\tau$$

are listed below using Rosen's notation.

$$\begin{aligned} I_{00} &= \int \psi^0 \phi^0 d\tau, & F_1 &= \int \frac{(\psi')^2}{r_a} d\tau, & J_{00} &= \int \frac{\psi^0 \phi^0}{r_a} d\tau, \\ I_{01} &= \int \psi^0 \phi' d\tau, & G_{00} &= \int \frac{(\psi^0)^2}{r_b} d\tau, & J_{01} &= \int \frac{\psi^0 \phi'}{r_a} d\tau, \\ I_{11} &= \int \psi' \phi' d\tau, & G_{01} &= \int \frac{\psi^0 \psi'}{r_b} d\tau, & J_{10} &= \int \frac{\psi' \psi^0}{r_a} d\tau, \\ F_0 &= \int \frac{(\psi^0)^2}{r_a} d\tau, & G_{11} &= \int \frac{(\psi')^2}{r_b} d\tau, & J_{11} &= \int \frac{\psi' \phi'}{r_a} d\tau. \end{aligned}$$

The integrals (I_{01} , G_{01} , J_{01} , and J_{10}) not given in Rosen's paper were evaluated in elliptic coordinates and have the following forms in terms of ϵ and $\rho = \alpha R$:

The energy can be expressed as

$$W = 2Z^2 E_0 A / d + 2Z E_0 B / d,$$

where

$$\begin{aligned} A &= 1 + I_{00} + \sigma(1 + \epsilon^2)I_{01} + \sigma^2 \epsilon^2(1 + I_{11}) - (2/\rho)[RF_0 + RJ_{00} + \sigma(RJ_{01} + 2\epsilon RJ_{10}) + 2\epsilon \sigma^2(RF_1 + RJ_{11})], \\ B &= (2/\rho)[RF_0 + RG_{00} - I_{00} - 1 + 2RJ_{00} + 2\sigma(RJ_{01} - I_{01} + RG_{01} + RJ_{10}) + \sigma^2(RF_1 - I_{11} + RG_{11} + 2RJ_{11} - 1)], \\ d &= 2[1 + I_{00} + 2\sigma I_{01} + \sigma^2(1 + I_{11})]. \end{aligned}$$

This expression for the energy can be minimized with respect to Z , giving

$$Z = -B/2A,$$

which when combined with the expression for W gives

$$W = -E_0 B^2 / 2dA.$$

RESULTS

On placing $\epsilon=1$ and minimizing the energy relative to Z , σ , and ρ , the values $\epsilon=1$, $\rho=2.50$, $\sigma=0.1605$, $Z=1.2537$, and $W=-16.242$ volt-electrons were obtained. The value given for W by Burrau's² and Hylleraas's³ exact treatments is -16.30 volt-electrons. Consequently the Rosen-type function leads to an error of 0.06 volt-electron, which is rather unsatisfactory, in view of the fact that Guillemin and Zener⁴ obtained the value $W=-16.30$ volt-electrons by using a two parameter function no more complicated than the Rosen-type function.

It was thought that the error of 0.06 volt-electron in W might be removed by varying ϵ . On carrying out this variation for the values of σ , Z , and ρ given above, then varying σ , and finally

varying ϵ again, there were obtained the values

$$\begin{aligned} \rho &= 2.50, & \epsilon &= 1.15, & \sigma &= 0.145, \\ Z &= 1.247, & Z' &= 1.434, & r_0 &= 1.06A, \end{aligned}$$

and $W = -16.257$ volt-electrons. The discrepancy in the energy has, it is seen, been reduced by only one-third by the variation of ϵ , being still 0.04 volt-electron. (The value of r_0 obtained is the same as that found by Burrau and Hylleraas and also found experimentally for excited states of H_2 .) We accordingly conclude that the Rosen-type function for the hydrogen molecule-ion is not so satisfactory as the Guillemin-Zener-type function of equivalent complexity, and that no pronounced improvement results from a variation of ϵ from 1. Change of Rosen's treatment for the hydrogen molecule by introducing ϵ in his function and varying it can hence be expected to lead to little improvement over his results.

It must be mentioned that the error in W of 0.04 volt-electron is only about 8 percent as great as that for a function with $\sigma=0$, i.e., involving 1s functions alone, for which Finkelstein and Horowitz⁵ obtained $Z=1.228$, $r_0 \cong 1.06A$, and $W = -15.75$ volt-electrons, so that very marked improvement in the wave function is obtained by introducing the Rosen-type term ψ' .

² An account of this work is given by Linus Pauling, *Chem. Rev.* **5**, 173 (1928).

³ E. A. Hylleraas, *Zeits. f. Physik*, **71**, 739 (1931).

⁴ V. Guillemin and C. Zener, *Proc. Nat. Acad.* **15**, 314 (1929).

⁵ B. N. Finkelstein and G. E. Horowitz, *Zeits. f. Physik* **48**, 118 (1928).