

The Polarizability and Related Properties of Molecular Hydrogen and the Diatomic Hydrogen Ion

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oxygen concentration is large K_w is negligible compared to $K_1(\text{O}_2)$, and the above expression reduces to

$$-(d/dt)(R\text{CHO}) = K_1 K_2 (R\text{CHO})^2,$$

in agreement with experiment. On the other hand, we would expect that at low oxygen concentrations K_w would no longer be negligible,

and that the rate would become dependent upon a power of the oxygen concentration lower than the first. Actually the data of Table V show that when the partial pressure of oxygen falls below about 10 cm the rate begins to fall off in the manner indicated above.

The bearing of these results upon the oxidation of acetylene will be discussed in a forthcoming publication.

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The Polarizability and Related Properties of Molecular Hydrogen and the Diatomic Hydrogen Ion

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The polarizability of molecular hydrogen is calculated from both the Rosen and the Wang eigenfunctions by the variational method. The eigenfunctions of the perturbed molecule contain two parameters which are adjusted to give the molecule a minimum energy. The Rosen eigenfunction leads to a parallel polarizability $7.5 \times 10^{-25} \text{ cm}^3$ and a perpendicular polarizability $7.4 \times 10^{-25} \text{ cm}^3$. The Wang eigenfunction gives similar results. When only one adjustable parameter is used in the variational method, the

formula for the polarizability is $\alpha = 8(\bar{q}_1^2 + \bar{q}_1 \bar{q}_2) a_0^3$ where q_1 and q_2 are the coordinates of electrons 1 and 2 in the direction of the applied electric field and a_0 is the radius of the first Bohr orbit of atomic hydrogen. The magnetic susceptibility and the mean square dimensions of the hydrogen molecule are computed. It is found that the Kirkwood formula is applicable to the diatomic hydrogen ion and polarizabilities are obtained for many internuclear separations using the Guillemin and Zener eigenfunction.

THE recent papers of Steensholt¹ have renewed interest in the problem of calculating the polarizability of molecular hydrogen. In 1932, we computed the polarizabilities by applying the variational method of Hylleraas² and Hassé³ upon the Rosen⁴ and Wang⁵ eigenfunctions. The eigenfunctions for the perturbed molecule were considered in both the one parameter form: $\psi_0[1 + A(q_1 + q_2)]$ and the two parameter form: $\psi_0[1 + A(q_1 + q_2) + B(r_1 q_1 + r_2 q_2)]$. Where ψ_0 is the eigenfunction of the unperturbed molecule. A and B are parameters to be varied so as to give the system a minimum energy; q_1 and q_2 are the coordinates of electrons one and two in the direction of the applied electric field as measured from the center of the molecule; r_1 and r_2 are their distances from the center of

the molecule. The numerical results are presented in Table I and compared with the values obtained by Mrowka⁶ and by Steensholt.¹ Mrowka formed approximate eigenfunctions for the excited states of the hydrogen molecule and applied the usual second-order perturbation method. Steensholt used the variational method with the Wang eigenfunction in the one-parameter form as given above. However, he took Wang's effective nuclear charge $Z_{\text{eff}} = 1.166$, while we considered

TABLE I. Polarizabilities in 10^{-25} cm^3 .

	α_{\perp}	α_{\parallel}	$\bar{\alpha}$	$ \alpha_{\parallel} - \alpha_{\perp} $	$\partial \alpha_{\perp} / \partial R$	$\partial \alpha_{\parallel} / \partial R$
Rosen eigenfunc. 2 parameters	7.4	7.5	7.4	0.1	$9.5 \times 10^{-17} \text{ cm}^2$	$11.0 \times 10^{-17} \text{ cm}^2$
Rosen eigenfunc. 1 parameter	6.7	7.1	6.9	.4	8.0	10.8
Wang eigenfunc. 2 parameters	7.3	7.5	7.3	.2	9.8	10.2
Wang eigenfunc. 1 parameter	6.6	7.1	6.8	.5	8.9	10.2
Steensholt using Wang eigenfunc. and 1 parameter	5.2	7.7	6.0	2.5		
Mrowka	8.5	6.1	7.7	2.4		
Experimental			8.0	3.6		

¹ G. Steensholt, *Zeits. f. Physik* **93**, 620 (1935); **94**, 770 (1935).

² E. Hylleraas, *Zeits. f. Physik* **65**, 209 (1930).

³ Hassé, *Proc. Camb. Phil. Soc.* **26**, 542 (1930); **27**, 66 (1931).

⁴ N. Rosen, *Phys. Rev.* **38**, 2099 (1931).

⁵ S. Wang, *Phys. Rev.* **31**, 579 (1928).

⁶ B. Mrowka, *Zeits. f. Physik* **76**, 300 (1932).

$Z_{\text{eff}}=1.18$ which is more suited to the Rosen eigenfunction. This accounts for part of the discrepancy between our values. Mrowka found, in direct contradiction to the classical theory of Silberstein,⁷ that the parallel polarizability of H_2 was smaller than the perpendicular. However, both Steensholt and this work find the parallel polarizability to be the larger. Van Vleck⁸ has pointed out that the Hylleraas method is not strictly applicable to approximate eigenfunctions and may give results either too small or too large. The values for the polarizability therefore provide a very sensitive test of the eigenfunctions.

The polarizability using one parameter reduces to the simple form:

$$\alpha = 8(\overline{q_1^2} + \overline{q_1 q_2})^2 a_0^3, \quad (1)$$

where the bars indicate the mean value. Since the electrons repel each other, $q_1 q_2$ should be negative. Actually, the Rosen and Wang eigenfunctions make this quantity zero for directions perpendicular to the line of nuclei and appreciable for the parallel direction. The dimensions of the hydrogen molecule may be calculated readily from the eigenfunctions. (z = direction parallel to line of nuclei, x and y are perpendicular.)

Eigenfunction	$\overline{z^2}$	$\overline{y_1^2} = \overline{x_1^2}$	$\overline{z_1 z_2}$	$\overline{r_1^2}$
Rosen	$0.95a_0^2$	$0.76a_0^2$	$-0.17a_0^2$	$2.47a_0^2$
Wang	1.11	0.75	-0.33	2.61

Wang⁹ made a direct calculation of $\overline{r_1^2}$ using his eigenfunction with the effective nuclear charge as discussed in the previous paragraph. He obtained: $\overline{r_1^2} = 2.95a_0^2$ where a_0 is the "radius of the first Bohr orbit." The mean square values for the electronic radius may be used to calculate the diamagnetic susceptibility: $-Le^2 \overline{r_1^2} / 3mc^2$. Including the paramagnetic term as calculated by Van Vleck and Frank,¹⁰ the total magnetic susceptibility is:

Eigenfunction	Magnetic Susceptibility
Rosen	-3.4×10^{-6} per mole
Wang	-3.6
Wang (calculation by Wang)	-4.2
Experimental	-3.9 to -4.0.

⁷ Silberstein, Phil. Mag. **33**, 92, 215, 521 (1917).

⁸ J. H. Van Vleck, *Electric and Magnetic Susceptibilities* (Oxford Press, 1932), p. 205; also footnote at end of paper by Atanasoff, Phys. Rev. **36**, 1242 (1930).

⁹ S. Wang, Proc. Nat. Acad. Sci. **13**, 798 (1927).

¹⁰ Van Vleck and Frank, Proc. Nat. Acad. Sci. **15**, 579 (1929).

POLARIZABILITY OF THE DIATOMIC HYDROGEN ION

We have also calculated the polarizability of the diatomic hydrogen ion for various internuclear distances, using the Guillemin and Zener eigenfunction.¹¹ Steensholt¹ has recently carried through the calculation for the equilibrium distance. The method of Hylleraas and Hassé with one parameter leads directly to the Kirkwood¹² formula:

$$\alpha = 4(\overline{q^2})^2 a_0^3. \quad (2)$$

The following are our results: (in 10^{-25} cm^3)

R/a_0	α_x	$\alpha_{ }$	$\bar{\alpha}$	R/a_0	α_x	$\alpha_{ }$	$\bar{\alpha}$
0.1	0.4	0.4	0.4	2.0	2.5	7.2	4.0
1.0	1.1	1.7	1.3	3.0	4.1	26.7	11.6
				4.0	5.4	79.5	30

Steensholt obtained for $R=2.0$, the equilibrium distance:

$$\alpha_{||} = 7.7 \times 10^{-25} \text{ cm}^3, \quad \alpha_x = 2.4 \times 10^{-25} \text{ cm}^3, \\ \bar{\alpha} = 4.2 \times 10^{-25} \text{ cm}^3.$$

When the nuclei become close, the polarizability approaches that of the helium ion. At large internuclear separations, the polarizability should become that of the hydrogen atom. However, the Guillemin and Zener eigenfunction does not approach the atomic eigenfunction and the parallel polarizability, as calculated from it, increases indefinitely as the nuclear separation increases. This is a striking example of the inadequacy of molecular orbital eigenfunctions at large internuclear distances. The dimensions of the diatomic hydrogen ion may be readily calculated:

R	$\overline{z^2}$	$\overline{x^2} = \overline{y^2}$	$\overline{r^2}$
$0.1a_0$	$0.26a_0^2$	$0.26a_0^2$	$0.78a_0^2$
1.0	.53	.43	1.40
2.0	1.11	.65	2.41
3.0	2.13	.83	3.80
4.0	3.68	.96	5.60

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¹¹ V. Guillemin and C. Zener, Proc. Nat. Acad. Sci. **15**, 4, 314 (1929).

¹² J. Kirkwood, Physik. Zeits. **33**, 2, 57 (1932).