

Magnetic Susceptibility of the Hydrogen Molecule*

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The effects of the nuclear motion on the magnetic susceptibility $\langle \xi \rangle_{0,1}$ of H_2 in the $v=0, J=1$ vibrational-rotational level of its electronic ground state are investigated. The dependence of $\langle \xi \rangle_{0,1}$ on the orientation of the molecule in the applied magnetic field is also considered. The effects of the nuclear motion are found to be of the order of 2–4 parts in 10^2 .

THE magnetic susceptibility of H_2 in the $v=0, J=1$ vibrational-rotational level of its electronic ground state was measured by Havens¹ to be²

$$\langle \xi \rangle_{0,1} = -(4.486 \pm 0.002) \times 10^{-5} \text{ a.u.} \quad (1)$$

The dependence of $\langle \xi \rangle_{0,1}$ on the orientation of the molecule in the applied magnetic field was investigated experimentally by Harrick and Ramsey³ who obtained²

$$\langle \xi_0 \rangle_{0,1} - \langle \xi_{\pm 1} \rangle_{0,1} = (0.247 \pm 0.014) \times 10^{-5} \text{ a.u.}, \quad (2)$$

where the subscript 0, ± 1 indicates the value of the rotational magnetic quantum number m_J .

In the Born-Oppenheimer approximation the second-order perturbation theory estimates of $\langle \xi \rangle_{0,1}$ and $\langle \xi_0 \rangle_{0,1} - \langle \xi_{\pm 1} \rangle_{0,1}$ may be written, in atomic units, as^{4,5}

$$\langle \xi \rangle_{0,1} = -(\alpha^2/3)[\langle z^2(r) \rangle_{0,1} + 2\langle x^2(r) \rangle_{0,1}] + \langle \xi^{hf} \rangle_{0,1}, \quad (3)$$

and

$$\begin{aligned} \langle \xi_0 \rangle_{0,1} - \langle \xi_{\pm 1} \rangle_{0,1} \\ = (\alpha^2/5)[\langle z^2(r) \rangle_{0,1} - \langle x^2(r) \rangle_{0,1}] - (3/5)\langle \xi^{hf} \rangle_{0,1}, \end{aligned} \quad (4)$$

where α is the fine structure constant, $\langle \xi^{hf} \rangle_{0,1}$ is the high-frequency (second order perturbation) term, r is the internuclear distance, and $\langle z^2(r) \rangle_{0,1}$ and $\langle x^2(r) \rangle_{0,1}$ are the second moments of the electron distribution in the direction of the molecular axis and in a direction perpendicular to the molecular axis, respectively.

Theoretical values of $z^2(r)$ and $x^2(r)$ were recently calculated by Kolos and Roothaan⁶ for a series of values of r . Using these values and a few additional extrapolated values for small and large r , the present author has determined $\langle z^2(r) \rangle_{0,1}$ and $\langle x^2(r) \rangle_{0,1}$. Averaging over the nuclear motion was done by an accurate

numerical procedure⁷ in which the effective internuclear potential $V(r)$ was taken to be (in atomic units)

$$V(r) = E(r) + 1/r + 1/\mu r^2, \quad (5)$$

where $E(r)$ is the electronic energy⁸ and μ is the reduced nuclear mass. The results were

$$\begin{aligned} \langle z^2(r) \rangle_{0,1} &= 1.062 \pm 0.001 \text{ a.u.}, \\ \langle x^2(r) \rangle_{0,1} &= 0.775 \pm 0.001 \text{ a.u.} \end{aligned} \quad (6)$$

The term $\langle \xi^{hf} \rangle_{0,1}$ in Eqs. (3) and (4) is difficult to evaluate.⁹ As shown by Ramsey¹⁰ however, an approximate value for it may be obtained by expressing it in the form

$$\langle \xi^{hf} \rangle_{0,1} = (4/3)f_e \langle r^l \rangle_{0,1}, \quad (8)$$

where the constants f_e and l may be determined using the relation

$$\langle \mu_R \rangle_{0,J} = J[1 - (16/\alpha^2)f_e \langle r^{l-2} \rangle_{0,J}], \quad (9)$$

in which $\langle \mu_R \rangle_{0,J}$ is the rotational magnetic moment (in nuclear magnetons) and J is the rotational quantum number. Substituting in Eq. (9) the experimental values^{3,11} of $\langle \mu_R \rangle_{0,1}$ and $\langle \mu_R \rangle_{0,2}$ and using the procedure referred to above for averaging over the nuclear motion, one obtains

$$\langle \xi^{hf} \rangle_{0,1} = (0.116 \pm 0.001) \times 10^{-5} \text{ a.u.}, \quad (10)$$

in agreement with the result previously obtained by Ramsey *et al.*¹²

Substituting in Eqs. (3) and (4) the values (6) and (10) and taking $\alpha = (7.29726 \pm 0.00008) \times 10^{-3}$ gives

$$\langle \xi \rangle_{0,1} = -(4.520 \pm 0.004) \times 10^{-5} \text{ a.u.}, \quad (11)$$

and

$$\langle \xi_0 \rangle_{0,1} - \langle \xi_{\pm 1} \rangle_{0,1} = (0.237 \pm 0.001) \times 10^{-5} \text{ a.u.} \quad (12)$$

These values may be compared with the values

$$\xi = -(4.422 \pm 0.004) \times 10^{-5} \text{ a.u.}, \quad (13)$$

⁷ J. W. Cooley, *Math. of Comp.* **15**, 363 (1961).

⁸ The best available theoretical $E(r)$ [see reference 6] was used in this calculation.

⁹ See, for instance, J. Tillieu and G. Guy, *Compt. rend.* **239**, 1203 (1954); **240**, 1402 (1955).

¹⁰ N. F. Ramsey, *Phys. Rev.* **87**, 1075 (1952).

¹¹ R. G. Barnes, P. J. Bray, and N. F. Ramsey, *Phys. Rev.* **94**, 893 (1954).

¹² See reference 11. The method used in the present calculation for averaging over the nuclear motion differs from the one used by these authors. See also J. P. Auffray and J. W. Cooley, *Phys. Rev.* **122**, 1203 (1961).

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¹ G. G. Havens, *Phys. Rev.* **43**, 992 (1933).

² Converted from the original data to atomic units (a.u.) using $1 \text{ a.u.} = (0.148179 \pm 0.000003) \times 10^{-24} \text{ erg gauss}^{-2}$.

³ N. J. Harrick and N. F. Ramsey, *Phys. Rev.* **88**, 228 (1952).

⁴ J. H. Van Vleck, *Electric and Magnetic Susceptibilities* (Oxford University Press, New York, 1932); see also N. F. Ramsey, *Phys. Rev.* **87**, 1075 (1952).

⁵ N. F. Ramsey, *Phys. Rev.* **78**, 221 (1950).

⁶ W. Kolos and C. J. Roothaan, *Revs. Modern Phys.* **32**, 219 (1960); see also M. Karplus, *Revs. Modern Phys.* **32**, 455 (1960).

and

$$\xi_0 - \xi_{\pm 1} = (0.219 \pm 0.001) \times 10^{-5} \text{ a.u.}, \quad (14)$$

obtained by neglecting the effects of the nuclear motion.

The comparison indicates that these effects are of the order of 2 parts in 10^2 and 4 parts in 10^2 , respectively, and thus must be considered in accurate work.

The differences remaining between the theoretical

values (11) and (12) and experimental values (1) and (2), particularly in the case of $\langle \xi \rangle_{0,1}$, may be attributed, in part, to the neglect of the effects of small interactions between the electronic and nuclear motions.¹³ These effects would tend to cancel out for $\langle \xi_0 \rangle_{0,1} - \langle \xi_{\pm 1} \rangle_{0,1}$ [see Eq. (4)].

¹³ J. H. Van Vleck, *J. Chem. Phys.* **4**, 327 (1936); see also J. P. Auffray and J. W. Cooley, *Phys. Rev.* **124**, 137 (1961).

Elastic Scattering of Low-Energy Electrons by Atomic Hydrogen*

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The differential and total cross sections for elastic scattering of electrons by atomic hydrogen are calculated below the threshold for excitation of the second target quantum level (10.2 eV). A close-coupling approximation is used in which the total wave function is expanded in hydrogen eigenstates, and only terms corresponding to the $1s$, $2s$, and $2p$ states are retained; the wave function is symmetrized or antisymmetrized explicitly.

The coupled set of integro-differential equations resulting from the approximate wave function is integrated numerically on an IBM 709 computer, subject to standard boundary conditions, to yield the phase shift in each total spin and total angular-momentum state. The solution involves an iteration procedure to treat the integral terms, and a specialized integration scheme, including an asymptotic expansion of the solution, to overcome certain numerical difficulties associated with low-incident electron energy.

The results of this calculation agree reasonably well, in regions where comparison is possible, both with previous analyses and with experiment—although in states in which short-range correlation effects are important, the close-coupling expansion is seen to converge very slowly. It is suggested that this situation may be rectified either by including continuum hydrogen eigenstates in

the wave function, or by replacing the close-coupling approximation by some different method, such as the alternative expansion suggested in the present work.

The most striking feature of our results is the appearance in many of the spin and angular-momentum states of pronounced, extremely narrow Breit-Wigner resonances at energies slightly below the second quantum excitation threshold. The resonance lying lowest in energy has been analyzed in most detail; it occurs in the singlet S state. It is found to have a full width at half maximum of 0.109 eV, and to be centered at 9.61 eV.

The long-range polarization effect is found to be dominant only at and very near zero energy for S and P states; for D states it is important up to 6 or 7 eV, and for F states it is of central importance for almost the entire range of energy below threshold.

The results of the calculation differ most from previous calculations at small scattering angles in the differential cross section, and in the existence of resonances near threshold. It is suggested that the former discrepancies can be resolved by differential cross-section measurements at angles of 30 deg and less, whereas the latter phenomenon requires electron-energy resolutions less than, or of the order of, 0.1 eV for experimental verification.

I. INTRODUCTION

IN this paper we describe our investigation of elastic electron-hydrogen collisions. This work was undertaken to bring to bear upon this problem calculational opportunities placed at the disposal of theorists by modern computing facilities, in the hope that certain discrepancies between theory and experiment may be resolved by the more nearly exact solutions now possible. These discrepancies are most serious for certain reaction processes¹ but here we examine the less complicated case of elastic scattering, which we intend to be

the first of several investigations of problems of increasing complexity. Further, improvements in experimental techniques now make possible more complete and accurate data.² Our calculation is intended to make use of the data already available, as well as to point out where, and what kind of, new data would be useful.

In what follows we shall regard the proton as infinitely massive and therefore stationary during the interaction. Under such circumstances, the wave function for the electron-hydrogen system will depend only upon the coordinates of the bound and free electrons.

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¹ See, for example, A. E. Kingston, B. L. Moiseiwitsch, and B. G. Skinner, *Proc. Roy. Soc. (London)* **A258**, 245 (1960), and D. G. Hummer and M. J. Seaton, *Phys. Rev. Letters* **6**, 471 (1961).

² High-resolution electron-hydrogen scattering experiments have been proposed by Stephen Smith at the National Bureau of Standards, Washington, D. C.