

Nuclear Spin-Spin Interaction Energy in the Hydrogen Molecule*

J. P. AUFRAY AND J. W. COOLEY

Institute of Mathematical Sciences, New York University, New York, New York

(Received January 5, 1961)

An accurate theoretical estimate of the interaction energy of the two proton magnetic moments in the $v=0$, $J=1$ vibrational-rotational level of the electronic ground state of H_2 is obtained. Agreement with the experimental value for the nuclear spin-spin interaction energy is found to be within 1 part in 10^3 . This is of the order of magnitude of the experimental error.

THE nuclear spin-spin interaction energy in the $v=0$, $J=1$ vibrational-rotational level of the electronic ground state of H_2 has been measured by Ramsey *et al.*¹ to be

$$d = 72.10 \pm 0.05 \text{ kc/sec.} \quad (1)$$

If one assumes² that this energy arises entirely from the dipole-dipole interaction of the two proton magnetic moments, then the first-order perturbation theory estimate of it is³

$$d = h^{-1} \mu_p^2 \langle r^{-3} \rangle_{0,1}, \quad (2)$$

where μ_p is the proton magnetic moment, and r is the internuclear distance. Taking $\mu_p = 1.52102 \times 10^{-3}$ Bohr magnetons,⁴ and the physical constants given by Townes and Schawlow,⁵ one obtains from (1) and (2)

$$\langle r^{-3} \rangle_{0,1} = 0.3558 \pm 0.0002_4 \text{ a.u.,} \quad (3)$$

for the mean inverse cube of the internuclear distance.

The present authors have obtained theoretical values for $\langle r^{-3} \rangle_{0,1}$ which may be compared with this result. The radial Schrödinger equation for the nuclear motion in the Born-Oppenheimer approximation was solved numerically with the internuclear potential (in atomic units)

$$V(r) = E(r) + 1/r + 1/\mu r^2, \quad (4)$$

where $E(r)$ is the electronic energy, $1/r$ is the mutual

TABLE I. Values of $\langle r^{-3} \rangle_{0,1}$ (in atomic units).

| Potential | $\langle r^{-3} \rangle_{0,1}$ |
|---------------------------|--------------------------------|
| I ^a | 0.3587 |
| II ^b | 0.3551 |
| III ^c | 0.3561 |
| Experimental ^d | $0.3558 \pm 0.0002_4$ |

^a Obtained from a Morse function fitted to the experimental data as described in the text. This Morse function differs slightly from the one used by Ramsey (see reference 2) which does not give the correct value of the force constant.

^b Obtained from a configuration interaction calculation [A. D. McLean, A. Weiss, and M. Yoshimine, *Revs. Modern Phys.* **32**, 211 (1960)].

^c Best available theoretical potential (see reference 6).

^d Value quoted in the text [see Eq. (3)].

electrostatic potential between the two protons, and $1/\mu r^2$ is the potential arising from the $J=1$ rotational motion of the molecule with reduced nuclear mass $\mu = 918.06$ a.u.

For the potentials considered here, the procedure used yielded the vibrational-rotational energy with an accuracy of at least 1 part in 10^6 .

When the best available⁶ theoretical $E(r)$ was used in Eq. (4), the agreement between the predicted and experimental values of $\langle r^{-3} \rangle_{0,1}$ was within 1 part in 10^3 . This is of the order of magnitude of the experimental error. Less accurate potentials, however, led to values which deviate from the experimental result by several parts in 10^3 . In particular, when approximating $E(r) + 1/r$ by a Morse function⁷ fitted to give the correct binding energy,⁸ equilibrium internuclear distance,⁹ and force constant,⁹ the disagreement was 8 parts in 10^3 . The results are summarized in Table I.

⁶ W. Kolos and C. C. J. Roothaan, *Revs. Modern Phys.* **32**, 219 (1960).

⁷ P. M. Morse, *Phys. Rev.* **34**, 57 (1929).

⁸ G. Herzberg, *Spectra of Diatomic Molecules* (D. Van Nostrand Company, Inc., Princeton, New Jersey, 1950).

⁹ G. Herzberg and L. L. Howe, *Can. J. Phys.* **37**, 636 (1959).

* The work presented in this paper was supported by the AEC Computing and Applied Mathematics Center, Institute of Mathematical Sciences, New York University, under contract with the U. S. Atomic Energy Commission.

¹ H. G. Kolsky, T. E. Phipps, N. F. Ramsey, and H. B. Silsbee, *Phys. Rev.* **87**, 395 (1952).

² N. F. Ramsey, *Phys. Rev.* **85**, 937 (1952).

³ N. F. Ramsey, *Phys. Rev.* **85**, 60 (1952).

⁴ R. Beringer and M. A. Heald, *Phys. Rev.* **95**, 1474 (1954).

⁵ C. H. Townes and A. L. Schawlow, *Microwave Spectroscopy* (McGraw-Hill Book Company, Inc., New York, 1955).