quired in a precision measurement. The results are for αf,

$$\mathcal{S} = 4198 \pm 20 \text{ Mc/sec};$$

for βe,

$$\mathcal{S} = 4167 \pm 20 \text{ Mc/sec}.$$

The quoted uncertainties are twice the statistical fluctuations in the data and are thought to allow for the neglected corrections. Clearly no large discrepancy, i.e., greater than 1%, with theory has been found. The quality of the data indicates that a much higher precision measurement should be possible. This will be attempted in the near future utilizing computer techniques to perform a detailed treatment of the resonance line shape, and it is believed that a sensitive test of quantum electrodynamics will be provided.

†Research supported in part by the U. S. Air Force Office of Scientific Research.

[1]S. Triebwasser, E. S. Dayhoff, and W. E. Lamb, Jr., Phys. Rev. 89, 98 (1953) (H, D, $n=2$).
[2]R. T. Robiscoe, Phys. Rev. 138, A22 (1965) (H, $n=2$).
[3]L. R. Wilcox and W. E. Lamb, Jr., Phys. Rev. 119, 1915 (1960) (H, D, $n=3$).
[4]H. Kleinpoppen, Z. Physik 164, 174 (1961) (H, $n=3$).
[5]E. Lipworth and R. Novick, Phys. Rev. 108, 1434 (1957) (He^+, $n=2$).
[6]G. W. Series, Proc. Roy. Soc. (London) A226, 377 (1954) (He^+, $n=3,4$).
[7]G. Herzberg, Z. Physik 146, 269 (1956) (He^+, $n=3,4$).
[8]C. Y. Fan, M. Garcia-Munoz, and I. A. Sellin, Phys. Rev. Letters 15, 15 (1965) (Li^{++}, $n=2$).
[9]12% of the $3\,^2P_{1/2}$ ions decay via the $2\,^2S_{1/2}$ level.
[10]W. E. Lamb, Jr., and M. Skinner, Phys. Rev. 78, 539 (1950).
[11]W. E. Lamb, Jr., and T. M. Sanders, Jr., Phys. Rev. 119, 1901 (1960).
[12]G. W. Erickson, Phys. Rev. Letters 15, 338 (1965).

ELECTRON-COUPLED PROTON DEUTERON COUPLING CONSTANT IN HD†

Jeremy I. Musher*

Rockefeller University, New York, New York
(Received 7 June 1965)

The coupling of nuclear spins by second-order perturbation mechanisms was first proposed and discussed by Ramsey and Purcell[1] in explanation of experimental results obtained by Hahn and Maxwell.[2] Ramsey[3] showed that the dominant contribution to the scalar coupling constant, J, defined in terms of the coupling energy by

$$E = hJ\vec{I}_H \cdot \vec{I}_D + h\vec{I}_H \cdot \mathcal{J} \cdot \vec{I}_D$$

arises from the second-order perturbation theory energy of the Fermi contact Hamiltonian. We have calculated the first term in a perturbation-theory expansion for the Fermi contact contribution, J_F, to the indirect scalar coupling between the nuclear spins in hydrogen deuteride.

In the presence of the dominant spin interactions, the total Born-Oppenheimer Hamiltonian for the HD molecule can be written as

$$H = H_0 + \lambda H_{100} + \vec{I}_H \cdot \vec{H}_{010} + \vec{I}_D \cdot \vec{H}_{001}, \tag{1}$$

where

$$H_0 = -\frac{\hbar^2}{2m}(\nabla_1^2 + \nabla_2^2) - \frac{e^2}{r_{1H}} - \frac{e^2}{r_{2D}}, \tag{2a}$$

$$\lambda H_{100} = -\frac{e^2}{r_{2H}} - \frac{e^2}{r_{1D}} + \frac{e^2}{r_{12}} + \frac{e^2}{R}, \tag{2b}$$

$$\vec{I}_H \cdot \vec{H}_{010} = (16\pi\beta\hbar\gamma_H/3) \times [\delta(\vec{r}_{1H})\vec{S}_1 + \delta(\vec{r}_{2H})\vec{S}_2] \cdot \vec{I}_H, \tag{2c}$$

$$\vec{I}_D \cdot \vec{H}_{001} = (16\pi\beta\hbar\gamma_D/3) \times [\delta(\vec{r}_{1D})\vec{S}_1 + \delta(\vec{r}_{2D})\vec{S}_2] \cdot \vec{I}_D, \tag{2d}$$

and where $r_{kN} \equiv r_k - R_N$, S_k and I_N are the electron and nuclear spins, respectively, and λ is a dummy parameter. The nonsymmetrical separation of the purely electronic Hamiltonian into H_0 and λH_{100} has been discussed elsewhere[4] where it has been shown that other properties of the hydrogen molecule to zeroth order in λ are in good agreement with experiment. The rapid convergence of such an electronic unsymmetrical perturbation theory—which only exists when the exact wave function is separable in space and spin coordinates—has recently been demonstrated by Bailey[5] for H_2^+.

Using straightforward coupled perturbation theory, J_F is given by the energies linear in the scalar product $\vec{I}_H \cdot \vec{I}_D$ to all orders in λ, i.e.,

$$J_F = h^{-1}(E_{011} + \lambda E_{111} + \cdots) = J_F{}^0 + \lambda J_F{}^1 + \cdots,$$

where the subscripts on the E's give the orders in the three perturbations, respectively. $J_F{}^0$ is thus

$$J_F{}^0 = h^{-1}(\tfrac{2}{3})\langle 0|[f_{H1}\delta(\vec{r}_{2D}) + f_{D1}\delta(\vec{r}_{2H})]\vec{S}_1 \cdot \vec{S}_2 + [f_{H1}\delta(\vec{r}_{1D}) + f_{D1}\delta(\vec{r}_{1H})]S_1{}^2|0\rangle, \quad (3)$$

where $\psi_0 \equiv |0\rangle$ is the lowest eigenfunction of H_0,

$$|0\rangle = (\pi a_0{}^3)^{-1}\exp[-(r_{1H} + r_{2D})/a_0],$$

and the f_{N1} are the solutions to the partial differential equations

$$(H_0 - E_0)f_{N1}|0\rangle = -(16\pi\beta\hbar\gamma_N/3) \times [\delta(\vec{r}_{1N}) - \langle 0|\delta(\vec{r}_{1N})|0\rangle]|0\rangle. \quad (4)$$

[Note also that $(f_{H1}\vec{S}_1 + f_{H2}\vec{S}_2)\psi_0$ is the first-order wave function in the perturbation H_{010}, i.e., ψ_{010}. In the traditional notation it would be written as $\sum'(E_0 - E_n)^{-1}|n\rangle\langle n|\vec{H}_{010}|0\rangle$.] The solution to (4) for f_{H1}, as first obtained by Schwartz,[6] is

$$f_{H1} = (m/\pi\hbar^2)\left[-\frac{1}{r_{1H}} + \frac{2}{a_0}\ln\left(\frac{r_{1H}}{a_0}\right) + \frac{2r_{1H}}{a_0{}^2}\right]. \quad (5)$$

The function f_{D1} can be obtained by expanding it and $\delta(\vec{r}_{1D})$ in Legendre polynomials about H as $f_{D1} = \sum f_D{}^l(r_{1H})P_l(\cos\theta_{1H})$ and $\delta(\vec{r}_{1D}) = \sum \delta^l(r_{1H})P_l(\cos\theta_{1H})$ with $\delta^0 = \delta(r_{1H} - R)/4\pi R r_{1H}$. After multiplying both sides of (4) by r_{1H} and taking the Laplace transforms, one obtains the $f_D{}^l$ by direct integration. It is seen, however, from (3) that for $J_F{}^0$ only $f_D{}^0$ is necessary, and furthermore that the method of Schwartz and Tiemann,[7] using directly $\bar{f}_D{}^0$ the Laplace transform of $f_D{}^0$, is applicable, i.e.,

$$\int_0^\infty \exp(-2r_H/a_0)f_D{}^0(r_H)r_H{}^2 dr_H = \frac{1}{4}\frac{\partial^2}{\partial(1/a_0)^2}\bar{f}_D{}^0,$$

where $f_D{}^0 \propto a_0 \exp[-R/a_0]$. Using these solutions and the fact that for a singlet ψ_0, $\langle 0|\vec{S}_1 \cdot \vec{S}_2|0\rangle = -\langle 0|S_1{}^2|0\rangle = -\frac{3}{4}$, we obtain from (3) an exact, closed-form expression for $J_F{}^0$:

$$J_F{}^0 = -h^{-1}(16\beta\hbar/3)^2\gamma_H\gamma_D e^{-2}a_0{}^{-5}\{[\tfrac{5}{2} - C - \ln 2] - [-(R/a_0)^{-1} + 2\ln(R/a_0) + 2(R/a_0)]\exp(-2R/a_0) + \tfrac{1}{2}[(R/a_0)^{-1} + 2 + 2(R/a_0)]\exp(-4R/a_0)\} = -50.3 \text{ cps}, \quad (6)$$

where C is Euler's constant $0.5772\cdots$, and where R has been taken as $R_e = 1.42a_0$. The term in the first square brackets of (6) arises from one of the two-electron terms of (3), $f_{H1}\delta(\vec{r}_{2D})$, and gives the dominant, negative, contribution to $J_F{}^0$. The term in $\exp[-2R/a_0]$ is positive and arises from the one-electron term of (3), and the negative, but negligible, term in $\exp[-4R/a_0]$ arises from the remaining two-electron term of (3). In a symmetrical wave function the two two-electron parts would be equal instead of highly disparate; however, the sums should, of course, be relatively equal for both symmetric and nonsymmetric ψ_0's. The total two-electron contribution to (6) is -58.1 cps, while the total one-electron contribution is $+7.8$ cps.

Had a variable screening parameter for the nuclear charge, Z, been included in the division of $H_0 + \lambda H_{100} + \cdots$, as is often done in describing the helium atom, $J_F{}^0$ would have been roughly proportional to Z^4, and hence the actual $J_F{}^0$ obtained depends critically on the chosen value of Z. A value of $Z = 1.05$ gives the minimum energy at R_e, but since $\partial E/\partial Z$ is terribly small, we have chosen $Z = 1$ for simplicity. When the first-order correction, $J_F{}^1$, is obtained, this extreme Z dependence must disappear.

In order to show how accurately $J_F{}^0$ approximates J_F itself, it is of interest to examine the expression for $J_F{}^1$:

$$J_F{}^1 = h^{-1}E_{111} = (\tfrac{2}{3}h)[\langle 010|\cdot(H_{100} - E_{100})|001\rangle + \langle 0|(H_{100} - E_{100})|011\rangle]. \quad (7)$$

According to the rules of coupled perturbation theory, ψ_{011} is defined as the solution to an equation analogous to (4) with the inhomogeneity $(E_{010} - H_{010})\cdot|001\rangle + (E_{001} - H_{001})\cdot|010\rangle$. Because of the exponentials in ψ_0, and the smallness of f_{H2} and f_{D1} as compared with f_{H1} and f_{D2} the dominant terms in this inhomogeneity are $\propto \vec{S}_1 \cdot \vec{S}_2[f_{2D}\gamma_H\delta(\vec{r}_{1H}) + f_{1H}\gamma_D\delta(\vec{r}_{2D})]$ for which the partial solution is simply $\vec{S}_1 \cdot \vec{S}_2 f_{1H} f_{2D}$, which is identical to the dominant part of $\psi_{010}\psi_{001}$ in the first integral of (7). Thus

$$J_F^{\ 1} \approx (\tfrac{4}{3}h)\langle 0|\vec{S}_1 \cdot \vec{S}_2 f_{1H} f_{D2}(H_{100}-E_{100})|0\rangle. \qquad (8)$$

We have not computed this part of $J_F^{\ 1}$ since it involves a great number of two-center integrals.[8] However, it does not seem unfair to state that from the form of (8), $J_F^{\ 1}$ looks to be smaller than $J_F^{\ 0}$: (1) λH_{100} is itself small as demonstrated by the fact that $\lambda E_{100} \sim 0.1$ eV while each term of λH_{100} contributes ~15 eV to λE_{100}; and (2) there are not unusually large contributions to $J_F^{\ 1}$ despite the fact that λH_1 diverges at $r_{D1} = r_{H2} = 0$, points at which ψ_0 is a poor representation of the electronic wave function. Thus the assumption that $J_F^{\ 0}$ is a good approximation to J_F appears to be justified.

It should be noted that the uniqueness of the present calculation lies in the ability to express $J_F^{\ 0}$ in closed form and to write down an explicit expression for (part of) $J_F^{\ 1}$ for this particular nonsymmetrical ψ_0. No other calculation has come close to giving such a $J_F^{\ 0}$ for its ψ_0—remember that a variational calculation using a symmetrical valence bond or molecular orbital wave function is merely an attempt to find approximate solutions to (4)—much less ever considered the prospect of the $J_F^{\ 1}$.

Experiment[9] gives $J_{HD} = \pm 43$ cps and comparison with the calculated $J_F^{\ 0}$ indicates the likelihood that the sign should be negative. Previous calculations[3,10] have uniformly obtained $J_F^{\ 0}$ positive, so that when in 1963 the author obtained[11] a negative $J_F^{\ 0}$ by a well-defined approximation method, the result was met with great skepticism.

Actually, we regard as relatively obvious the reasons for the apparent failure of the previous calculations to give the correct sign of $J_F^{\ 0}$: (1) The average energy[3] "approximation" only gives the correct sign when the numerator in the excited-state sum is positive-definite;[12] note that it predicts the one-electron contribution to be zero for finite ΔE, whereas in fact this contribution is finite (see also Das and Bersohn[10]) and therefore ΔE must equal zero; and (2) the simple trial functions employed (see Stephan[10] and O'Reilly[10]) if applied[13] to the hydrogen-atom hyperfine interaction would never decently approximate the exact solution [Eq. (5)]; there is no test for "goodness" of a trial function other than degree of convergence. In fact, Das and Bersohn's[10] $J_F^{\ 0}$ appeared to be going negative with an increasing number of terms in the variational function, which shows explicitly the dangers inherent in the use of a simple trial function. Incidentally, the divergence of the Fermi self-couplings (see Das and Bersohn[10]) ($J_{F,HH}^{\ 0}$ and $J_{F,DD}^{\ 0}$) when nuclear-size corrections are neglected is observed trivially from the equations analogous to (3).

The J_{HD} (or J_{HT} or J_{DT}) including the sign is, in principle, experimentally observable, being within the resolution of the best present-day molecular beam techniques. We think that this experiment should be given some priority in molecular spectroscopy.

---

†Preliminary report given in Bull. Am. Phys. Soc. 10, 102 (1965).

*Address after 1 February 1966: Belfer Graduate School of Science, Yeshiva University, New York, New York.

[1]N. F. Ramsey and E. M. Purcell, Phys. Rev. 85, 143 (1952).

[2]E. L. Hahn and D. E. Maxwell, Phys. Rev. 84, 1246 (1951); 88, 243 (1952). H. S. Gutowsky, D. McCall, and C. P. Slichter, Phys. Rev. 84, 589 (1951).

[3]N. F. Ramsey, Phys. Rev. 91, 303 (1953).

[4]J. I. Musher, J. Chem. Phys. 42, 2633 (1965). See also "Approximate Wave Functions for Molecules and Crystals Using Perturbation Theory: A Selected Review" (to be published).

[5]P. B. Bailey, Proc. Phys. Soc. (London) 85, 1127 (1964).

[6]C. Schwartz, Ann. Phys. (N.Y.) 6, 156 (1959).

[7]C. Schwartz and J. J. Tiemann, Ann. Phys. (N.Y.) 6, 178 (1959).

[8]Actually the entire $J_F^{\ 1}$ can be calculated explicitly although with considerable labor using the Laplace transform technique described above.

[9]B. Smaller, E. Yasaitis, E. C. Avery, and D. A. Hutchinson, Phys. Rev. 88, 414 (1952); H. Y. Carr and E. M. Purcell, Phys. Rev. 88, 415 (1952).

[10]M. J. Stephan, Proc. Roy. Soc. (London) A243, 274 (1957); T. D. Das and R. Bersohn, Phys. Rev. 115, 897 (1959); E. Ishiguro, Phys. Rev. 111, 203 (1958); D. E. O'Reilly, J. Chem. Phys. 36, 274 (1962) and others. Ishiguro's procedure uses a limited number of excited hydrogen-molecule bound states, but only two of these contribute to $J_F^{\ 0}$; the contributions are both of large magnitude but of opposite sign.

[11]J. I. Musher, "The Fermi-Contact Contribution to the Proton-Deuteron Coupling Constant in HD" (unpublished). The approximate method is reported in Ann. Phys. (N.Y.) 24, 188 (1963) and can be justified further and iterated by an argument analogous to that in J. Chem. Phys. 41, 2671 (1964).

[12]A. D. McLachlan, J. Chem. Phys. 32, 1263 (1960).

[13]J. I. Musher, in Modern Quantum Chemistry, edited by O. Sinanoglu (Academic Press, Inc., New York, 1965), Vol. 2. Stephan[10] and O'Reilly[10] both used $\delta(\vec{r})$ in their variational functions.