NMR determination of the triton-proton magnetic moment ratio to within $10^{-6}\%$

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An NMR pulse spectrometer has been used to determine the triton and proton free precession frequencies for HT molecules in a gas to within $\pm 2.7\times 10^{-9}$ and the spin-spin interaction energy ($J_{pT}=299.3\pm 0.2$ Hz). A calculation is given of the difference between the screening of the triton and the proton in HT. The calculation is based on the Fraga-Ransil ground-state wave function, and the correction antisymmetric functions are obtained by a variational method subject to the condition that the electric dipole moment of HD should be accurately described. Corrections due to mutual nuclear screening are also taken into account. Calculations have shown that the triton in HT is screened more effectively than the proton by a factor of 20.4×10^{-9}. The corresponding factor for the deuteron in HD is 15.0×10^{-9}. The final result for the magnetic moment of the triton is 1.066 639 908 ± 3 and the magnetic moment of the deuteron is 0.3070121983 ± 8 in units of the proton magnetic moment.

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The two neutrons in the ground s-state of the triton have opposite spins and, therefore, the magnetic moment of ^{3}T is not very different from the magnetic moment of the proton. The difference is about 6.6% and is due to the tensor nature of the nucleon–nucleon forces, the presence of mesonic currents between the nucleons, and relativistic effects. The tensor character of the nucleon–nucleon forces gives rise to an admixture of of the D state and, correspondingly, to a contribution to the magnetic moment due to the orbital motion of the proton in this state.

As the theory of systems with a small number of nucleons continues to develop, theoretical papers begin to appear on the magnitude of the magnetic moment of the triton. For example, we note the paper by Kim, Fischbach, Harper, Tubis, Cheng, and Rho[1] on the contribution of meson exchange to the magnetic moments of ^{3}T and ^{3}He. These calculations have shown that whilst the first two significant figures in the magnetic moments of the triton and helion can be obtained in the single-particle approximation with the inclusion of the D-state admixture, the next two significant figures can be described by considering single-pion exchange between the nucleon pairs. To explain the next significant figures, one must include the less frequent events that are accompanied by an appreciable change in the individual characteristics of nucleons (for example, the coalescence of two nucleons into six-quark systems is being intensively investigated theoretically at present).

Since there are many contributary factors, and the number of physically measurable constants of the triton is small, it is not surprising that there is considerable interest in the derivation of functional dependences (which is possible by studying the angular distribution in nucleon–nucleon scattering), and in increased precision of measurement of the principal constants. High-precision measurements can then be used as a foundation for semiempirical searches.

The present paper is a continuation of our previous work,[2] which was carried out with a specially constructed spectrometer designed for the determination of the ratios of free-precession frequencies of nuclear spins. If the triton and proton free-precession signals are excited and recorded simultaneously for a given region in the specimen, the ratio of the magnetic moments of the triton and proton can be related to the precession-frequency ratio by the formula

$$\mu_T/\mu_p = f_T/f_p[1+(\sigma_T-\sigma_p)], \quad (1)$$

where σ_T and σ_p are the triton and proton screening constants.

Duffy[3] has determined the ratio f_T/f_p in 20% tritium-enriched water. This ratio has been used to determine the magnetic moment of the triton,[3,4] and the difference between the triton and proton screening in water was allowed for through the somewhat arbitrary assumption that $\sigma_T - \sigma_p \approx (1\pm 1)\times 10^{-7}$. The value of f_T/f_p obtained by Duffy was confirmed by more accurate measurements,[5] but the difference $\sigma_T - \sigma_p$ cannot at present be accurately calculated because water is a complicated system.

The most convenient material for the determination of the triton-proton magnetic moment ratio is the gaseous isotopic analog of hydrogen, namely, HT, because the motion of the nuclei and electrons in this molecule is such as to produce only a small asymmetry of the electron cloud. Accordingly, the difference $\sigma_T - \sigma_p$ is small, in this case, and can be estimated with adequate accuracy in view of the simplicity of this chemical compound.

EXPERIMENTAL PART

To obtain the isotopic analog of hydrogen, HT, we used 2.5% tritium-enriched water with an activity of about 35 Ci/mliter. The pressure of the gaseous mix-

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ture $H_2 - HT$ was about 130 atm and this was achieved by the method used previously.[2] However, additional safety measures were introduced because accidental breakage of the ampule would, in this case, result in the release of highly active water.

To prevent such breakage, the specimen was prepared in accordance with the following strictly-adhered-to sequence of operations. The glass capillary was first etched in hydrofluoric acid. The resonance coil was wound on the capillary (six turns) which was then fixed with the aid of epoxy resin in the lower copper cylinder (Fig. 1). The capillary was then filled with radioactive water in a specially ventilated fume chamber and the upper part of it was separated from the water by a teflon insert on which a crystal of LiH was placed. A gas burner was used to seal off the upper end of the capillary, and the system was carefully annealed. The upper copper tube was placed on top of the lower tube, and the interior of the cylinders containing the capillary was filled with epoxy resin (Fig. 1). When the solidification of the epoxy resin was complete, the specimen was inverted and the chemical reaction involving the release of the gaseous mixture of $H_2 + 2.5\%$ HT was initiated by shaking. The net result of this was that the hydrogen-containing part of the capillary, free of fluid, was in the receiving coil of the radiospectrometer.

The proton-triton resonance frequency ratio was determined for the HT molecule with the aid of the pulse spectrometer tuned to the magnetic resonance of the nuclei of hydrogen, tritium, and deuterium. All three resonance frequencies were derived from the same quartz oscillator, using dividers and multipliers.

Stabilization of the resonance conditions was carried out by reference to deuteron resonance in an external specimen. The stabilization signal was obtained from an ampule containing heavy water (D_2O). To reduce the deuteron relaxation time, a saturated solution of $CuSO_4$ in the heavy water was employed. The pickup coil of the deuteron channel was attached to the copper cylinder surrounding the main specimen. The resonance stabilization channel was operated under time separation conditions.

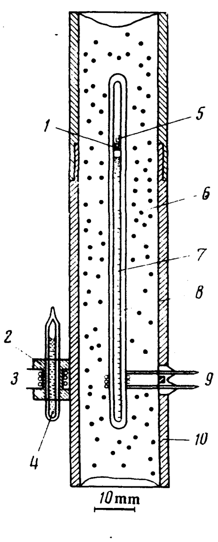

FIG. 1. The sealed specimen: 1—teflon plug; 2, 3—deuteron channel coil for the stabilization of resonance conditions; 4—ampule filled with D_2O; 5—LiH used to start the chemical reaction; 6—expoxy resin; 7—$H_2O + 2.5\%$ TOH; 8—glass capillary; 9—resonance coil in the triton and proton channels; 10—copper cylinder.

The frequency of excitation of the free-procession signals for tritons was greater than the corresponding frequency for protons by a factor of 16/15. The ratio of the free-precession frequencies was therefore determined from the formula

$$\frac{f_T}{f_p} = \frac{{}^{16}/_{15} f_p{}^0 - \Omega_T}{f_p{}^0 + \Omega_p} \approx \frac{16}{15} - \frac{1}{f_p{}^0}\left(\Omega_T + \frac{16}{15}\Omega_p\right), \tag{2}$$

where Ω_p and Ω_T are the frequencies isolated with the aid of phase detectors and corresponding to the proton and triton procession frequencies of the HT molecules in the magnetic field ($F \sim 15$ kG, $f_p^0 = 63.501\ 585$ MHz) relative to the reference set of quartz frequencies.

The spin-spin interaction of the nuclei in the HT molecule produces a splitting of the NMR signals into doublets for both types of nuclei. The frequencies Ω_p and Ω_T in (2) should, therefore, correspond to the doublet centers. The components of the proton doublet should be weaker by more than two orders of magnitude as compared with the intensity of the singlet due to the H_2 molecule (the latter was observed directly on an oscillograph, and was used to adjust the homogeneity of the magnetic field).

The proton-triton spectra were recorded with the aid of the Élektronika-100 computer, which produced the pulses used to excite the free-procession signals at intervals of 0.1 sec and recorded 520 signal amplitudes at the output of the proton and triton channel amplifiers within this interval. Each spectrum was recorded for 12 min and then, after each 0.1 sec, the pickup coil was switched from proton to triton resonance with the aid of a D 901B varicap. The preamplifier was based on the low-noise field effect transistor KP 305 and was common to both signals.

Whilst the spectrum was being acquired, two data sets of 520 numbers each containing information on the positions of the proton and triton doublets, were formed in the memory of the Élektronika-100 computer. These data sets were then transferred along a communications link to the Minsk-32 computer, where they were subjected to a Fourier transformation and the results were printed out in graphic form for preliminary inspection. The homogeneity of the magnetic field was adjusted in the intervals between the acquisition of the spectra.

For accurate analysis, the data sets were transferred to a BÉSM-6 computer and were processed along the time scale by the method of least squares. The triton signals were approximated by the following expression:

$$f(t) = A \exp(-bt)\{\cos[2\pi(\Omega_T - J_{pT}/2)(t+\varphi_1)] + \cos[2\pi(\Omega_T + J_{pT}/2)(t+\varphi_2)]\}, \tag{3}$$

where A, b, φ_1, φ_2 are auxiliary variational variables, J_{pT} is the triton-proton interaction energy, and Ω_T is the required position of the center of the doublet. A similar expression was used for the proton data for which, in addition, the presence of the strong singlet due to H_2 had to be taken into account.

The ratio of the signal amplitude due to the nuclei in the HT molecule to the random noise level can be

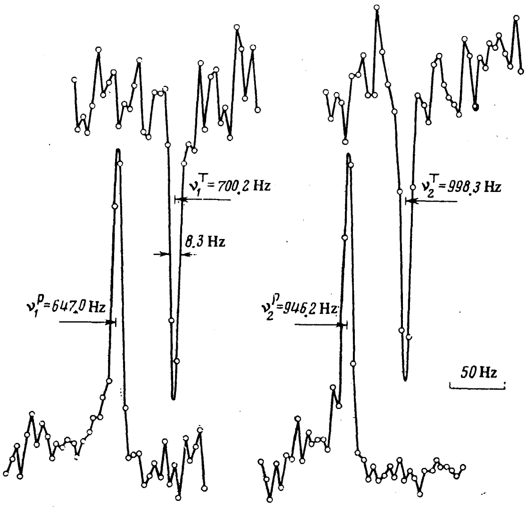

FIG. 2. NMR signals due to the HT molecules, obtained by a Fourier transformation of one pair of data sets. The linewidth of 8.3 Hz and the position of the doublets were determined by an optimization procedure based on 300 experimental points on the time scale.

estimated from one of the spectra (Fig. 2) that was specially printed out for illustration. The points were obtained by fast Fourier transformation of a pair of data sets consisting of up to 1024 numbers. The components of the proton doublet lie on the slopes of the broad signal due to H_2. However, in Fig. 2, the doublet is given after subtraction of the singlet due to H_2, whose parameters were first optimized by the method of least squares (see Note added in Proof).

Only 300 out of the 520 values in the data set (between the 70th and 370th) were used for optimization of the parameters. The spread among the last 50 numbers of the data set was used to determine the random noise level, and this was then used to determine the uncertainty in each spectrum. This uncertainty was ~ 1.2 $\times 10^{-8}$ for each pair. The final result for the 20 processed pairs of spectra was

$$f_T/f_p=1.0666398866\pm 29$$

with a relative uncertainty of $\pm 2.7\times 10^{-9}$. The systematic uncertainty due to the time instability of the quartz oscillator in Élektronika-100 is of the order of 1 MHz and its deviation from the reference frequency, estimated from the position of the peak, is lower by an order of magnitude than the random uncertainty. Another source of systematic uncertainty was due to the error introduced by fitting the function given by (3) to the numerical experimental data. The closeness of the fit was monitored with the aid of the χ^2 criterion (its average reduced value was $\chi^2=1.1$) and by comparing external and internal uncertainties. The ratio of the root mean square uncertainty in the individual pairs to the root mean square spread among the 20 values of f_T/f_p is ~ 0.9.

Table I shows the results obtained for the 20 pairs of spectra. The increase in the uncertainty in f_T/f_p for certain pairs is due to changes in the temperature of the magnets. These temperature changes produce a drift in the magnetic field gradients and, consequently, an inferior signal-to-noise ratio during the acquisition of the spectra.

As an additional check on the validity of the function (3) in the description of the experimental data, we used the following procedure. The number of processed points and the number of the experimental point after which this approximation was employed were varied during the processing of the spectrum. This was accompanied by a variation in only the phase parameters φ_1 and φ_2 and the size of the uncertainty. The stability of the results confirmed, to within the limits of uncertainty, the absence of systematic errors which could have appeared as a consequence of incorrect processing of the experimental data.

The magnitude of the doublet splitting was used to determine the proton-triton interaction energy in HT simultaneously with the measurement of the free-precession frequency ratio. Analysis of the triton spectra yielded $J_{pT}^T=299.3\pm 0.2$ Hz (see Table I). The result obtained from the proton spectra was $J_{pT}^T=299.3\pm 0.4$ Hz. The agreement between these two results is a further indication of the reliability of the experimental data.

CALCULATION OF THE NUCLEAR SCREENING DIFFERENCE IN THE HT MOLECULE

In a previous paper,[2] we obtained a preliminary estimate of the nuclear screening difference in the HD molecule. We calculated the "diamagnetic" part of the mutual nuclear screening, and reported a correction for the asymmetry of the electron cloud, based on an approximate simulation of the electron density distribution. In the present paper, we report the results of more rigorous calculations of the various contributions obtained from the resultant Hamiltonian for the system of four particles, taking into account the highest-order correction terms that are antisymmetric under the interchange of the nuclei.

The Hamiltonian for the system of four particles in a magnetic field F has the following form (in the atomic system of units):

TABLE I. Results of measurement.

Number of pair of spectra	Ω_T, Hz	Ω_p, Hz	f_T/f_p	$\pm\delta(f_T/f_p)\cdot 10^9$	J_{pT}, Hz
1	828,1	819,8	1,066639856	10	300.2±1.2
2	820,6	824.3	1.066639897	12	300.4±1.4
3	849.8	797.5	1.066639889	14	304.0±1.7
4	848.6	798.8	1.066639886	12	297.5±1.4
5	849.3	796.5	1.066639913	14	296.7±1.7
6	850.0	797.3	1.066639889	11	297.8±1.2
7	831.2	815.5	1,066639880	14	298.8±1.8
8	842,2	804.3	1,066639893	10	299.4±1.1
9	850.5	797.0	1.066639886	11	299.1±1.2
10	851,9	795.3	1.066639892	13	298.5±1.6
11	856.1	791,8	1,066639885	10	299.5±1.1
12	853.9	793.2	1.066639896	12	300.9±1.4
13	857,9	789.9	1,066639887	12	298.7±1.4
14	845.0	805.9	1.066639814	37	301.2±2.3
15	861.3	786,9	1.066639882	21	300.2±1.9
16	870.7	779.1	1.066639868	65	295.2±3.4
17	852.5	794.4	1.066639900	18	296.5±1.8
18	853.4	794.4	1,066639849	44	299.9±1.9
19	841,4	804.8	1.066639898	16	300.1±1.2
20	859,0	793,2	1,066639817	54	298.9±1.5

Mean values $f_{T/f_p}=1.0666398866\pm 29$; $J_{pT}^T=299.3\pm 0.2$ Hz.

$$H=\frac{1}{2}\sum_{i=1}^{2}(\mathbf{p}_i+\alpha\mathbf{A}_i)^2+\frac{1}{2}\sum_{j=3}^{4}\frac{1}{M_j}(\mathbf{p}_j-\alpha\mathbf{A}_j)^2-\mu_3\mathbf{F}-\mu_4\mathbf{F}+V, \tag{4}$$

where $\mathbf{p}_i$ are the electron momenta, $\mathbf{p}_j$, M_j, and μ_j are the momenta, masses, and magnetic moments of the nuclei, V is the Coulomb interaction energy between the four particles, and

$$\mathbf{A}_i=\frac{1}{2}[\mathbf{F}\times\mathbf{r}_i]+\sum_{j=3}^{4}[\mu_j\times\mathbf{r}_{ij}]\frac{1}{r_{ij}^3}, \quad i=1,\ 2;$$

$$\mathbf{A}_j=\frac{1}{2}[\mathbf{F}\times\mathbf{r}_j]+[\mu_j\times\mathbf{r}_{j\bar{j}}]\frac{1}{r_{j\bar{j}}^3}, \quad j=3,4;\ \bar{j}=4,3.$$

The screening σ is defined as the addition to the energy of the dipole magnetic interaction: $E_F=\mu F(1-\sigma)$. The problem is solved with the aid of perturbation theory, using the small parameters α and $\beta=1/(M_3+M_4)$. The analysis is confined to terms of order $\alpha^2\beta$. To the required accuracy, the Hamiltonian can be written in the form

$$\begin{aligned}H={}&H_0+\beta H_\beta+\alpha\mu_iH_{\mu_i}+\alpha F_iH_{F_i}+\alpha^2\mu_iF_iH_{\mu_iF_i}\\&+\alpha\beta\mu_iH_{\beta\mu_i}+\alpha\beta F_iH_{\beta F_i}+\alpha^2\beta\mu_iF_iH_{\mu_iF_i\beta},\end{aligned} \tag{5}$$

where H_0 is the Hamiltonian in the Born–Oppenheimer approximation ($i=x,\ y,\ z$), H_{μ_i} and H_{F_i} are terms corresponding to the classical paramagnetic screening (these were described in our previous paper[2]), and $H_{\mu_iF_i}$ is the Hamiltonian responsible for the diamagnetic contribution. The other terms are discussed below. Accordingly, the wave function can be written in the form

$$\psi=\psi_0+\beta\psi_\beta+\alpha\mu_i\psi_{\mu_i}+\alpha F_i\psi_{F_i}+\alpha^2\mu_iF_i\psi_{\mu_iF_i}+\alpha\beta\mu_i\psi_{\beta\mu_i}+\alpha\beta F_i\psi_{\beta F_i} \tag{6}$$

and, similarly, for the energy E.

Let us begin by considering the first four operators. Following Pack and Hirschfelder,[6,7] it is convenient to split the contributions into adiabatic and nonadiabatic (and similarly for the wave function $\psi_\beta=\psi_\beta^{\mathrm{ad}}+\psi_\beta^{\mathrm{na}}$). In the rotating set of coordinates x, y, z attached to the midpoint of the internuclear distance, with the z axis parallel to the axis of the molecule, we have

$$\begin{aligned}\beta H_\beta={}&\beta_1H_\beta^{ad}+\beta_1H_\beta^{na}=\frac{\beta_1}{2R}[(\mathbf{p}_1+\mathbf{p}_2)_y(\mathbf{J}_1+\mathbf{J}_2)_x\\&-(\mathbf{p}_1+\mathbf{p}_2)_x(\mathbf{J}_1+\mathbf{J}_2)_y]+\frac{\beta_1}{2}(\mathbf{p}_1+\mathbf{p}_2)_zi\frac{\partial}{\partial R},\end{aligned} \tag{7}$$

where $\beta_1=(M_3-M_4)/2M_3M_4\sim\beta$, p_k and J_k are the momentum and angular momentum operators for the first and second electrons, and the subscripts x, y, and z indicate the corresponding components of the vector operators.

It is convenient to split the operator H_β into two parts because the correction for the function ψ_β^{ad} can be written in the adiabatic form, i.e., in the form of a product of the function describing the motion of the electrons and the function describing the motion of the nuclei; the function ψ_β^{na} cannot be represented in this way, and is the sum of the series of such products. To construct the functions ψ_β^{ad}, ψ_β^{na}, ψ_{μ_i}, and ψ_{F_i}, we must solve the inhomogeneous Schrödinger equation

$$(H_0-E_0)\psi_1=-H_1\psi_0,\ \langle\psi_1|\psi_0\rangle=0, \tag{8}$$

where ψ_0 is the ground-state wave function and, instead of the operator H_1 and the correction function ψ_1, we must take one of the operators H_β^{ad}, H_β^{na}, H_μ, or H_{F_i} and the corresponding correction function.

Equations of the form (8) were solved by a variational method in a search for the correction functions in which the convergence criterion was the stabilization of the corresponding energy functional. The precision of the preliminary functions obtained in this way was definitely no better than about 5% because the ground-state wave function ψ_0 was taken to be the Hartree-Fock function given by Fraga and Ransil,[8,9] which reproduced the ground-state energy to within about 5%.

The resulting functions ψ_β (which determined the final result) found in this way were first used to determine the mean value of the center of gravity of the electron cloud relative to the internuclear distance:

$$\delta z=2\langle\psi_\beta|z|\psi_0\rangle=3.92\cdot10^{-4}\ \text{at. units}\ .$$

This quantity exceeds the more accurate value $\delta z=3.04\times10^{-4}$ reported by Kolos and Wolniewicz,[10] who used the exact adiabatic ground-state wave function obtained by them in a previous paper.[11] We must now correct our wave function ψ_β by demanding that δz must be the same as in[10]. The modified wave function is $\psi_\beta'=\varkappa\psi_\beta$, where $\varkappa$ is equal to the ratio of the calculated values of δz, i.e., $\varkappa=0.775$.

The formulas of third-order perturbation theory can be rearranged so that the final expression contains the correction functions of only the first order in α and β. It must then be remembered that the operator H_F is symmetric and H_μ is antisymmetric under the interchange of the nuclei. Correspondingly, the function ψ_μ must be split into two parts, i.e., symmetric ψ_μ^s and antisymmetric ψ_μ^u, relative to interchange of the nuclei.

Since all the orientations of the molecule relative to the external field are equally likely, it can be shown that the corrections to the diamagnetic and paramagnetic screening of a heavy nucleus of mass M_3 are as follows (for light nuclei, the corrections have the same values but opposite signs):

$$\delta\sigma_d^{ad}=\frac{2}{3}\varkappa\alpha^2\beta_1\,\mathrm{Re}\sum_{i=xyz}\langle\psi_\beta^{ad}|H_{\mu_iF_i}|\psi_0\rangle, \tag{9}$$

$$\delta\sigma_d^{na}=\frac{2}{3}\varkappa\alpha^2\beta_1\,\mathrm{Re}\sum_{i=xyz}\langle\psi_\beta^{na}|H_{\mu_iF_i}|\psi_0\rangle, \tag{10}$$

$$\delta\sigma_{1(2)}^{p}=\frac{2}{3}\varkappa\alpha^2\beta_1\,\mathrm{Re}\sum_{i=xyz}\langle\psi_{\mu_i}^{u}|H_{F_i}|\psi_\beta^{ad(na)}\rangle, \tag{11}$$

$$\delta\sigma_{3(4)}^{p}=\frac{2}{3}\varkappa\alpha^2\beta_1\,\mathrm{Re}\sum_{i=xyz}\langle\psi_{F_i}|H_{\mu_i}|\psi_\beta^{ad(na)}\rangle, \tag{12}$$

$$\delta\sigma_{5(6)}^{p}=\frac{2}{3}\alpha^2\beta_1\,\mathrm{Re}\sum_{i=xyz}\langle\psi_{F_i}|H_\beta^{ad(na)}|\psi_{\mu_i}^{u}\rangle. \tag{13}$$

We are thus taking into account two corrections to the diamagnetic screening (adiabatic and nonadiabatic) and six corrections to paramagnetic screening (odd numbers correspond to adiabatic and even to nonadiabatic corrections.

The following values were obtained for the HT molecule:

$$\begin{aligned}&\delta\sigma_d^{ad}=+2.8\cdot10^{-9}, && \delta\sigma_d^{na}=+3.5\cdot10^{-9},\\ &\delta\sigma_1^{p}=+1.6\cdot10^{-9}, && \delta\sigma_2^{p}=+2.9\cdot10^{-9},\\ &\delta\sigma_3^{p}<3\cdot10^{-10}, && \delta\sigma_4^{p}=-0.6\cdot10^{-9},\\ &\delta\sigma_5^{p}<3\cdot10^{-10}, && \delta\sigma_6^{p}<3\cdot10^{-10}.\end{aligned} \tag{14}$$

In view of the accuracy of our calculation, we may neglect $\delta\sigma^{p}_{3,5,6}$.

Let us now consider the corrections due to the operators $H_{\mu_i\beta}$, $H_{F_i\beta}$, and $H_{\mu_iF_i\beta}$. They are conveniently analyzed in the frame attached to the center of gravity of the nuclei. In this frame, we have

$$\begin{aligned}\beta H_{F_j\beta}=\frac{1}{2}\sum_{h=1}^{7}H_{F_j}^{(k)}=\frac{1}{2}\Bigg\{&\frac{1}{M}[(\mathbf{r}_1+\mathbf{r}_2)\times\mathbf{K}]+[\rho\times(\mathbf{p}_1+\mathbf{p}_2)]\\ &\times\left(1+\frac{2}{M-2}\right)-\frac{1}{M}[(\mathbf{r}_1+\mathbf{r}_2)\times(\mathbf{p}_1+\mathbf{p}_2)]-\frac{1}{M-2}\\ &\times\left(\frac{M_3}{M_4}+\frac{M_4}{M_3}\right)[\mathbf{R}\times\mathbf{p}_R]-\frac{M_3-M_4}{(M-2)^2}[\mathbf{R}\times(\mathbf{p}_1+\mathbf{p}_2)]\\ &+\frac{M_3-M_4}{M(M-2)}[\mathbf{R}\times\mathbf{K}]+\frac{M_3-M_4}{M_3M_4}[\rho\times\mathbf{p}_R]\Bigg\}_j,\end{aligned} \tag{15}$$

$$\begin{aligned}\beta H_{\mu_{3j}\beta}=\sum_{k=1}^{5}H_{\mu_{3j}}^{(k)}=\Bigg\{&\frac{[\mathbf{r}_{13}\times\mathbf{K}]}{Mr_{13}^3}+\frac{[\mathbf{r}_{12}\times\mathbf{K}]}{Mr_{23}^3}-\frac{1}{M_4}\frac{[\mathbf{R}\times\mathbf{p}_R]}{R^3}\\ &-\frac{1}{M-2}\frac{[\mathbf{R}\times(\mathbf{p}_1+\mathbf{p}_2)]}{R^3}+\frac{1}{M}\frac{[\mathbf{R}\times\mathbf{K}]}{R^3}\Bigg\}_j;\end{aligned}$$

$$\begin{aligned}\beta H_{\mu_{3i}F_j\beta}=\sum_{k=1}^{4}H_{\mu_{3i}F_j}^{(k)}=\Bigg[&\left(\frac{\delta_{ij}\rho\mathbf{r}_{13}-\rho_ix_i^{(13)}}{r_{13}^{3}}+(1\leftrightarrow2)\right)\\ &-\frac{1}{M}\left(\frac{\delta_{ij}(\mathbf{r}_1+\mathbf{r}_2)\mathbf{r}_{13}-(x_j^{(1)}+x_j^{(2)})x_i^{(13)}}{r_{13}^{3}}+(1\leftrightarrow2)\right)\\ &+\frac{M_3}{M_4(M-2)}\frac{\delta_{ij}R^2-R_iR_j}{R^3}-\frac{1}{M_4}\frac{\delta_{ij}\rho\mathbf{R}-\rho_iR_j}{R^3}\Bigg].\end{aligned} \tag{16}$$

In these expressions, $M=M_3+M_4+2$ is the total mass of the molecule, and $\mathbf{K}$ and ρ are the momentum and position vectors of the center of gravity of the molecule in the laboratory frame, respectively.

When these operators were investigated, we took into account the symmetry properties of the unperturbed wave function and the small magnitudes of the correlation corrections to the ground-state Hartree-Fock wave function. The procedure used to calculate the corrections from perturbation theory was the same as for the first operators. However, we were able to solve the corresponding inhomogeneous Schrödinger equation (8) without recourse to numerical methods, and the final formulas are elementary in form. The correction to the screening of a heavy nucleus of mass M_3 (ground state) is

$$\begin{aligned}\delta\sigma_{\mu F\beta}=\frac{\alpha^2}{3}\left\langle\psi_0\left|\frac{1}{R}\right|\psi_0\right\rangle(M_3-M_4)\left(\frac{1}{2M_3M_4}-\frac{1}{M^2}\right)\\ +\sigma^g(M_3-M_4)\frac{1}{M^2}\left(\frac{M_3}{M_4}+\frac{M_4}{M_3}\right),\end{aligned} \tag{17}$$

$$\sigma^g=\frac{\alpha^2}{3}\left\langle\psi_0\left|\frac{Rz}{r^3}\right|\psi_0\right\rangle, \tag{18}$$

where $\sigma^g=-6.15\times10^{-6}$ is the gauge noninvariant part of the classical screening calculated in our previous paper.[2] On the other hand, Wolniewicz[12] has reported $\langle\psi_0|1/R|\psi_0\rangle=0.6997$. The two terms in (17) have different signs and cancel each other out. For the triton in the HT molecule, we have $\delta\sigma_{\mu F\beta}<1\times10^{-10}$.

The final value for the nuclear screening difference in the HT molecule was found to be

$$\sigma_T-\sigma_p=2\left[\sum_{i=1}^{2}\delta\sigma_i^{d}+\sum_{i=1}^{6}\delta\sigma_i^{p}+\delta\sigma_{\mu F\beta}\right]=20.4\cdot10^{-9}. \tag{19}$$

The above expressions can be used to calculate the nuclear screening difference in the HD molecule. Bearing in mind the change in the mass, we find that $\sigma_d-\sigma_p=15.0\times10^{-9}$. When this more accurate correction is used together with our previous results,[2] we obtain the following more accurate value for the ratio of the deuteron and proton magnetic moments:

$$\mu_d/\mu_p=0.3070121983\pm8.$$

We can now calculate the ratio of the triton and proton magnetic moments. Using the correction given by (19) and the expression given by (1), we obtain

$$\mu_T/\mu_p=1.066639908\pm3.$$

We recall that Duffy's value[3] for this ratio was 1.066 639 98 ± 11.

The antisymmetric screening corrections which we have calculated must also be taken into account in the interpretation of the experimental isotopic differences[2] of the form $\sigma(\mathrm{HT})-\sigma(\mathrm{H}_2)$, etc. However, in this case one must also take into account the symmetric corrections which also arise because of the interdependence of the motions of the nuclei and electrons. The symmetric and antisymmetric contributions add with different signs and, therefore, partially cancel each other in the case of the isotopic differences. The net result of this is that the calculated and experimental isotopic effects agree to within about 10^{-9}. Our calculated screening differences for HT and HD are probably subject to the same uncertainty. The experimental and calculated isotopic screening effects will be compared in a separate publication.

Note added in proof (March 21, 1977). To indicate the sensitivity of our instrument and the yield of the HT molecules in the chemical reaction

$$\mathrm{HOT+LiH}\to(1-\eta)(\mathrm{LiOT+H_2})+\eta(\mathrm{LiOH+HT}),$$

we note that the area under the signals corresponding to the two components of the proton doublets was 0.0014 of the area under the signal due to H_2. Consequently, the protons are much more mobile in water than the tritons, and participate more actively in the chemical reaction resulting in the formation of the hydrogen molecules ($\eta\approx0.05$). The partial pressure of the HT gas in our specimen was ~0.3 atm.

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Schrödinger perturbation theory in the adiabatic representation of the three-body problem

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A perturbation theory for the calculation of the binding energy and the wave functions of a three-body system is developed for the problem of three bodies with Coulomb approximation. The zeroth approximation used was an adiabatic basis, i.e., solutions and terms of the two-center problem of quantum mechanics, and the kinetic energy of the relative motion of like charged particles is regarded as a perturbation. The method is illustrated with the calculation of the binding energy of the $pd\mu$ mesic molecule as an example.

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1. INTRODUCTION

To calculate the binding energy of three particles with charges and masses (Z_a, M_a), (Z_b, M_b) and $(-1, m_\mu)$ several methods have been proposed and realized.[1–3] They were used to calculate the energies of the mesic molecules $pp\mu$, $pd\mu$, etc., and also that of the electron-positron system $e^+e^-e^+$.

In the calculation of the binding energy of the ground state of a three-body system, the most accurate result seems to be obtained by different modifications of variational calculation methods,[1,2] but on going over to the excited states these methods become much more complicated. The advantage of adiabatic calculation is their simplicity and lucidity, both in the case of the ground state and in the case of excited states. A classical example of an adiabatic calculation is the Born–Oppenheimer method in the theory of molecular spectra.[4]

It is known[3,4] that in the adiabatic representation of the three-body problem there appears a small parameter $(2M)^{-1}$, where $M \approx M_a M_b/(M_a + M_b)m_\mu$. The Born-Oppenheimer approximation consists of discarding from the equations for the relative motion of the nuclei all the terms $\sim(2M)^{-1}$. The need for this approximation was dictated by insufficient knowledge of the adiabatic basis, i.e., of the solutions of the two-center problem of quantum mechanics.[5] This was also one of the reasons for the loss of interest in the adiabatic method altogether.[1)] By now these difficulties have been overcome to a considerable degree,[7] so that the scope of the Born-Oppenheimer approximation can be expanded and a consistent scheme can be developed for calculations in the adiabatic basis, using the small parameter $(2M)^{-1}$.

We describe here a simple algorithm for the calculation of the binding energy of a three-body system, accurate to terms $\sim(2M)^{-3}$ inclusive.

We recall that in the adiabatic approximation the wave function $|\Psi\rangle$ of a system of three bodies is expanded in the complete set $|\Phi\rangle$ of the eigenfunctions of the Hamiltonian $\hat W$ of the two-center problem:

$$\hat W|\Phi\rangle = W|\Phi\rangle, \tag{1}$$

$$|\Psi\rangle = |\Phi\rangle\langle\Phi|\Psi\rangle. \tag{2}$$

The initial Schrödinger equation for the three-body system

$$(\hat T+\hat W)|\Psi\rangle = E|\Psi\rangle \tag{3}$$

then goes over into an equivalent infinite system of homogeneous integro-differential equations for the functions $\langle\Phi|\Psi\rangle$[4]:

$$\langle\Phi|\hat T+\hat W|\Phi\rangle\langle\Phi|\Psi\rangle = E\langle\Phi|\Psi\rangle. \tag{4}$$

Here $\hat T = -(2M)^{-1}\Delta_R$ is the operator of the kinetic ener-

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