tions due to the self-energy, vacuum polarization, magnetic interaction, and retardation. Nearly all of these corrections have been calculated by expansions in terms of the parameter $Z\alpha$, but experiments are already being conducted in the region where $Z\alpha > 1$. This is a great challenge to the theory. An approach to *ab initio* relativistic many-electron molecular Hartree-Fock calculations is under way.

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New Measurement of the Positronium Hyperfine Interval*

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The hyperfine interval $\Delta\nu$ of the positronium ground state has been measured with significantly improved accuracy. Using a SF_6 buffer gas we obtain $\Delta\nu = 203.3875 \pm 0.0017$ GHz and $(\Delta\nu)^{-1}\partial\Delta\nu/\partial D = (-8.0 \pm 0.4) \times 10^{-5}$ amagat^{-1}. Using a N_2 buffer gas we obtain $\Delta\nu = 203.3854 \pm 0.0029$ GHz and $(\Delta\nu)^{-1}\partial\Delta\nu/\partial D = (-2.1 \pm 0.6) \times 10^{-5}$ amagat^{-1}. No evidence is found for a quadratic dependence of $\Delta\nu$ on density in either gas.

This Letter reports a new measurement of the hyperfine interval $\Delta\nu$ of the ground state of positronium (Ps). The use of a high-efficiency γ-ray detection system has made possible a significant increase in the accuracy of this measurement. The fact that no quadratic density shifts have been observed in this experiment is important in connection with a previous measurement of $\Delta\nu$.[1]

The importance of a precise determination of $\Delta\nu$ as a test of the predictions of quantum electrodynamics is well known.[2] Since Ps is a purely leptonic atom, there should be no fundamental difficulty in calculating its properties. In practice, however, the calculation of the ground-state hyperfine interval is still a challenge. Expressed as an expansion in the Sommerfeld fine-structure

constant, $\alpha = e^2/\hbar c = 1/137.0602 \pm 1.5$ ppm,[3] the most recent calculation gives[4]

$$\Delta\nu_{\rm th} = \tfrac{1}{2} m\alpha^4[\tfrac{7}{6} - (\tfrac{16}{9} + \ln 2)(\alpha/\pi) + \tfrac{1}{2}\alpha^2 \ln\alpha^{-1} + O(\alpha^2)] = 203.4040 \pm 0.0006 \text{ GHz}. \quad (1)$$

While the 3-ppm uncertainty of this value stems principally from the error in α, the neglected terms in the expansion may well represent a much larger uncertainty in $\Delta\nu_{\rm th}$. It is to be noted that if $\Delta\nu_{\rm th}$ were sufficiently well known in terms of α, an experimental value with an accuracy only 3 times better than that presented here would result in one of the most precise determinations of α.

The design of the present experiment is similar to that used in all the previous measurements of $\Delta\nu$.[1,5] Positronium is formed in a buffer gas in a microwave cavity located in a uniform magnetic induction B. The triplet ground state is split into two Zeeman sublevels by the magnetic field, and transitions between the $m = 0$ and the $m = \pm 1$ states may be induced by an rf magnetic field perpendicular to B. The Breit-Rabi formula gives the resonant value of the rf frequency f_{01} in terms of B and $\Delta\nu$:

$$f_{01} = \tfrac{1}{2}\Delta\nu[(1+x^2)^{1/2} - 1], \quad (2)$$

where $x = 2\mu_B g' B/h\Delta\nu$ and g' is the bound-state electron g factor in Ps.[6] If the nuclear magnetic resonance of the protons in a spherical sample of water (proton magnetic moment μ_p') is used to measure B we may write

$$\Delta\nu = (g'/g)^2(\mu_e/\mu_p')^2(f_p^2/f_{01}) - f_{01}, \quad (3)$$

where f_p is the measured proton resonance frequency in the water, and we use $g'/g = 1 - 11.1 \times 10^{-6}$ and $(\mu_e/\mu_p')^2 = 433\,263.56 \pm 0.06$.[3] The resonance condition of B and f_{01} causes an increase in the 2γ annihilation yield and a concomitant decrease in the 3γ yield.[7] Since rather large rf fields are required, the experiments use a tuned microwave cavity; and since it is difficult to change the tuning while holding the power level constant, a resonance curve is obtained by holding the rf frequency fixed and observing the changes in the annihilation yields as a function of B. The value of f_p at the peak of such a resonance is substituted into Eq. (3) to obtain an experimental value for $\Delta\nu$.

The present experiment uses an electromagnet with 15.2-cm-diam pole faces and 4.44-cm gap to produce the induction $B \cong 9.25$ kG. Ps is formed from positrons emitted by a 300-μCi Na^{22} source in the wall of a silver-plated 11.25-cm-i.d.$\times$1.27-cm-wide TM_{110} cavity. The positrons are collimated by a Au shield and emerge into the center of the cavity after passing through a 0.000 25-cm-thick Cu window. Since this is more than a skin depth thick, the electrical properties of the cavity are not disturbed by the presence of the source. Annihilation photons pass through the 0.025-cm-thick outer walls of the cavity and are detected by ten 2.54-cm$\times$2.54-cm NaI(Tl) scintillation detectors with faces located 12.7 cm from the center of the cavity and spaced at 36° in a plane perpendicular to B. Magnetic shielding for the RCA 8575 photomultiplier tubes is provided by 1.9-cm-thick Armco iron shields and by additional concentric Mu-metal shields; each detector is gain stabilized.[8] The singles (1γ) counting rates, two-photon-annihilation ($2\gamma''$) rates, 511-keV photopeak ($2\gamma'$) rates, photopeak-gated two-photon-annihilation (2γ) rates, and three-photon-annihilation (3γ) rates are all recorded by a set of forty scalers printing on paper tape. The 1γ rate is approximately 50 000 sec^{-1} for each counter.

The microwave power is provided by an injection-locked 4J64 magnetron with a current-regulated high-voltage supply at 120 mA and a dc filament supply. The magnetron is not always locked on frequency because of variations in operating conditions; however, the microwave frequency is recorded by one of the forty scalers, and it is thus possible to make use of the data whether the frequency is locked or not. The magnetic induction at any of several locations in the cavity wall can be measured by a pulsed NMR technique. The probe in the wall nearest to the center of the cavity (probe No. 1) is used to lock the frequency f_p of the protons in the oil at that point to the 39–40-MHz frequency of a programmable synthesizer. The amplitude of the frequency excursions of f_p is approximately ± 16 Hz peak to peak, or ± 0.4 ppm. A set of shim coils between the outside walls of the cavity and the magnet pole faces is used to minimize the variations in B near the center of the cavity. The central magnetic induction B_0 is measured relative to probe No. 1 before and after each 1-week run using a removable probe without disturbing the apparatus in any way except to turn off the microwave power. This probe has an outer case of 6061T6 Al tubing with a 0.635 cm diam and 0.061 cm wall, is filled

with mineral oil, and uses an 8-turn coil of No. 28 wire. The thickness of the wall is chosen so that the external perturbation of B from the paramagnetic Al cancels that of the diamagnetic oil and copper inside. The induction in the oil is $2\pi\chi/3 \approx 1.6$ ppm lower than it would be in a spherical sample of oil and 5.3 ± 0.6 ppm lower than it would be in a spherical water sample.

Since the inhomogenieties in B could lead to an error in our measurements of $\Delta\nu$, we have measured the spatial distributions of both B and the positrons stopping in the buffer gas. Using another removable probe with an unshielded spherical mineral-oil sample of radius 0.20 cm, the gradients of B at the center of the cavity were found to be $\partial B/\partial x = -1.8$, $\partial B/\partial y = -8.3$, and $\partial B/\partial z = -4.0$ in ppm/cm, where $\hat{z}$ is the direction of $\vec{B}$ and $\hat{x}$ and $\hat{y}$ are transverse directions; $\partial^2 B/\partial x^2 = -14$, $\partial^2 B/\partial y^2 = -28$, and $\partial^2 B/\partial z^2 = +44$ in ppm/cm^2. No higher gradients were measured and we have assumed that a Taylor expansion of B to second order is sufficient. The transverse distribution of positrons in the cavity was measured using a pair of counters with long slits parallel to the direction of B, and was found to be $\exp\{-y^2/2\sigma^2\}$ with $\sigma = 0.244$ cm. The distribution is assumed to be the same in the x direction. The longitudinal distribution of positrons stopping in the gas was found to be approximately e^{-az} with $a = (D/3.04)$ cm^{-1}, where D is the SF_6 density in amagats. For N_2, a is expected to be ~5 times smaller.

Using this positron distribution and the estimated longitudinal resolution function for detecting 2γ and 3γ events, $1 - b|z|$ with $b = 1.4$ cm^{-1}, we find that the average of B over the observed annihilations is

$$\overline{B} = B_0 + \left(\frac{\partial B}{\partial z}\right)\left(\frac{a}{6b^2}\right) + \frac{\partial^2 B}{\partial z^2}\frac{1}{12b^2} + \frac{1}{2}\left(\frac{\partial^2 B}{\partial x^2} + \frac{\partial^2 B}{\partial y^2}\right)\sigma^2 = B_0(1 - 1.03\times10^{-7}D + 0.44\times10^{-6}). \quad (4)$$

The term linear in D causes a negligible change in the measured density shifts. A 100% change in the second derivatives of B would change $\overline{B}$ by only ± 0.5 ppm because $\nabla^2 B \approx 0$. Assigning 20% errors to σ and b results in a ± 1-ppm contribution to the error in $\overline{B}$, and a ± 0.1-cm uncertainty in the location of the center of the cavity would also imply a ± 1-ppm error in $\overline{B}$. Adding these errors in quadrature and including the ± 0.6-ppm error in $\mu_p^{\text{oil}}/\mu_p'$,[3] we find that the estimated error in $\overline{B}$ is ± 1.7 ppm.

In order to reduce the effects of drift, the data are taken in pairs of 5-min counting periods at a proton frequency $f_p + 36$ kHz and then at a frequency $f_p - 36$ kHz. The numbers of counts obtained are later combined into a logarithmic first-difference signal as shown in Fig. 1. This figure is the average of the results of a 16-day continuous run with a 500-Torr (measured with a mercury manometer with a diffusion-pump-oil barrier) SF_6 buffer gas. The data are fitted to a first-difference Lorentzian with a constant background which is proportional to the slope of the field-dependent background reported by Carlson *et al.*[1] Although the theoretical curve is not strictly a Lorentzian, deviations from this shape are small. A calculation shows that the data fitted in this manner give results for $\Delta\nu$ which are about 1 ppm lower than the correctly fitted value.

Figure 2 shows our $\Delta\nu$ results as a function of SF_6 and N_2 buffer-gas density using the 2γ signals

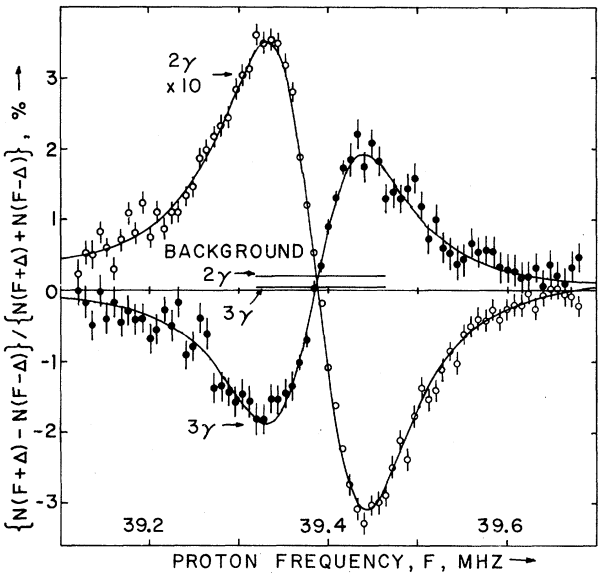

FIG. 1. Positronium Zeeman resonance signal obtained using a 500-Torr SF_6 buffer gas. Each datum point is obtained from a pair of counting rates measured at proton frequencies $f \pm \Delta$, where Δ is 36 kHz, the signal being the difference divided by the sum. The fitted curves are first-difference Lorentzians with constant backgrounds. x^2/ν is 79.0/67 for the 2γ curve and 66.5/67 for the 3γ curve. Using the value $f_{01} = 3252.760$ MHz obtained by averaging f_{01} over the seven central data points and resonant values of f_p obtained from the intersection of the fitted curves and the constant background values yields $\Delta\nu_{2\gamma} = 203.3796 \pm 0.0039$ GHz and $\Delta\nu_{3\gamma} = 203.3647 \pm 0.0082$ GHz.

TABLE I. Zero-density $\Delta\nu$ extrapolations and linear density shifts measured with 2γ and 3γ signals in SF_6 and N_2 buffer gases. The ± 0.0007 GHz uncertainty in $\Delta\nu$ due to the error in $\bar{B}$ is not included in the quoted errors.

Gas	Signal	$\Delta\nu$ (GHz)	$a=(\Delta\nu)^{-1}\partial\Delta\nu/\partial D$ (10^{-5} amagat^{-1})	χ^2/ν
SF_6	2γ	203.3864 ± 0.0018	-8.03 ± 0.38	5.90/5
SF_6	3γ	203.3924 ± 0.0038	-7.92 ± 0.90	6.06/5
SF_6	Mean	203.3875 ± 0.0016	-8.00 ± 0.35	...
N_2	2γ	203.3857 ± 0.0030	-2.25 ± 0.59	0.0006/1
N_2	3γ	203.3832 ± 0.0081	-0.55 ± 1.59	0.23/1
N_2	Mean	203.3854 ± 0.0028	-2.05 ± 0.55	...

only. Most of the data were obtained using only points where the slope of the first difference is greatest to improve the statistical efficiency. For these runs, the background was found from data pairs at proton frequencies ± 308 kHz from the resonant value. Fitting the data to a quadratic expression in the density, $\Delta\nu(D)=\Delta\nu(0)(1+aD+bD^2)$, yields results for the quadratic term b consistent with zero: $b(SF_6)=(+0.21\pm0.59)\times10^{-5}$ amagat^{-2}; $b(N_2)=(+0.3\pm1.3)\times10^{-5}$ amagat^{-2}. Consequently, we have used linear fits to obtain the zero-density extrapolations for $\Delta\nu$ shown in Table I. The $2\gamma'$ and $2\gamma''$ signals have not been used because a statistically significant effect depending on the orientation of B, $\beta\equiv[\Delta\nu(B)-\Delta\nu(-B)]/[\Delta\nu(B)+\Delta\nu(-B)]$, was observed for these signals. At 500 Torr SF_6 we found $\beta(3\gamma)=18\pm30$ ppm, $\beta(2\gamma)=12\pm7$ ppm, $\beta(2\gamma')=35\pm8$ ppm, and $\beta(2\gamma'')=27\pm7$ ppm. This effect is at present unexplained (a calculation of the Zeeman resonance including effects due to the positron polarization implies $\beta<0.2$ ppm). It is interesting however that averaging the $2\gamma'$ and $2\gamma''$ signals over the direction of B yields results consistent with the 2γ and 3γ values.

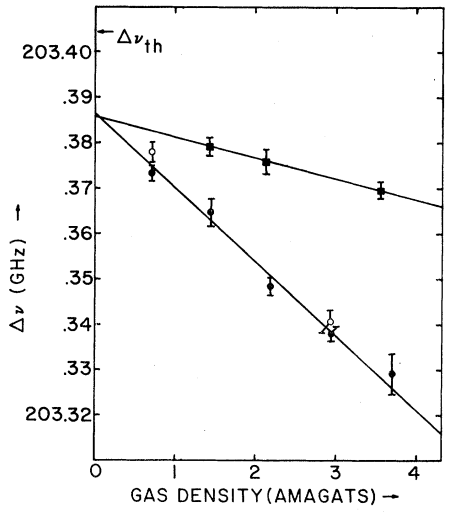

FIG. 2. The positronium hyperfine interval as a function of SF_6 and N_2 buffer-gas density using the 2γ signals only. Corrections have been made for the nonlinear density of SF_6 versus pressure. The SF_6 data (○, field normal; ●, field reversed) were accumulated in ~123 days, the N_2 data (■, field reversed) in ~32 days. The lines show the linear fits to the data used to obtain the zero-density $\Delta\nu$ extrapolations in Table I. 1 amagat $=2.687\times10^{19}$ molecules cm^{-3}.

Using the data of Table I we find that the average of the SF_6 and N_2 zero-density extrapolations for $\Delta\nu$ is 203.3870 ± 0.0016 GHz, where the error includes the uncertainty in $\bar{B}$. This value agrees better with the linear extrapolation in Ref. 1, $\Delta\nu=203.384\pm0.004$ GHz, than with the quadratic extrapolation 203.396 ± 0.005 GHz. The $\Delta\nu_{th}$ value predicted by Eq. (1) is at variance with the results reported here by 10 standard deviations: $\Delta\nu_{th}-\Delta\nu_{expt}=0.0170\pm0.0017$ GHz. This discrepancy might be attributed to the neglected $O(\alpha^2)$ terms in Eq. (1) ($\alpha^2\Delta\nu=0.0108$ GHz). Some but not all of these terms have been calculated[9] and are the right order of magnitude.

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Concentration Gradients in Nitroethane+3-Methylpentane near the Liquid-Liquid Critical Solution Point*

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Precise measurements of density profiles in the system nitroethane + 3-methylpentane near the critical solution point demonstrate that concentration gradients form rapidly, but true equilibrium is not achieved even after long times. The data are in qualitative agreement with computer calculations of the behavior of a critical mixture in a gravitational field which show that the initial gradients form by sedimentation. Thus, effects due to gravity may affect careful experiments in critical mixtures.

It is well known that large density gradients due to gravity exist in substances in the vicinity of the gas-liquid critical point and that these gradients can result in systematic errors in the determination of the properties of critical systems.[1] Thermodynamic considerations lead to the conclusion that density (or concentration) gradients of the same shape and magnitude should likewise be present in mixtures in the vicinity of a critical solution point.[2] Near T_c the equilibrium concentration profile is expected to be sigmoid in shape, with the largest gradient near the midpoint of the sample.

It has been suggested that such concentration gradients are of little significance to the experimenter because they form at a negligibly slow rate. This argument is based on the assumption that the rate of gradient formation is controlled by concentration diffusion: In a mixture of critical composition the diffusion rate falls to zero as the critical temperature is neared.[3] Recently, however, Dickinson *et al.*,[4] in a discussion of the effect of high gravitational fields on critical mixtures, showed that sedimentation (pressure diffusion) plays an essential role in the dynamics of the formation of concentration gradients. In contrast to concentration diffusion, the flux due to sedimentation *diverges* near the critical point.

Attempts by earlier workers to measure concentration gradients gave negative results[5] or were difficult to interpret.[6,7] We describe here precise measurements of the density profile in the system nitroethane + 3-methylpentane in the neighborhood of the upper-critical-solution temperature. Our data show that a significant gradient of the shape expected from sedimentation forms rapidly, but that the time to reach an equilibrium gradient is indeed very long. We show that the time evolution of the profile is in qualitative agreement with calculations based on the mechanism previously proposed.[4]

Nitroethane (99.95%) and 3-methylpentane (99.99%) were dried over silica gel. The mixture was prepared on a vacuum line, degassed twice by freezing and pumping, and sealed in the glass cell. The total sample was 0.086 51 mole, the mole fraction of nitroethane was 0.4990, and T_c was 26.445 ± 0.002°C. These critical parameters are in good agreement with Wims, McIntyre, and Hynne,[8] who reported $x_c = 0.500$