and Es I do correspond to $J_{max}-1$, whereas Fm I and Md I correspond to $J_{max}-3$. Only Bk I with its value corresponding to $J_{max}-2$ appears to be anomalous; presumably it arises from a competition about exchange and direct interactions as noted above in connection with Ce III.

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[1]F. Hund, Z. Physik 43, 788 (1927).

[2]B. H. Flowers, Proc. Roy. Soc. Lond. A212, 248 (1952).

[3]A. R. Edmonds and B. H. Flowers, Proc. Roy. Soc. Lond. A214, 515 (1952).

[4]B. Wybourne, Spectroscopic Properties of Rare Earths (Wiley, New York, 1965).

[5]M. Hammermesh, Group Theory (Addison-Wesley, Palo Alto, Calif., 1962).

[6]B. R. Judd, Operator Techniques in Atomic Spectroscopy (McGraw-Hill, New York, 1963).

[7]E. U. Condon, and G. H. Shortley, The Theory of Atomic Spectroscopy (Cambridge U. P., Cambridge, 1935).

[8]J. Sugar, J. Opt. Soc. Am. 55, 33 (1964).

[9]I. P. Grant, Adv. Phys. 19, 747 (1970).

[10]W. R. Callahan, J. Opt. Soc. Am. 53, 695 (1963).

[11]A. de Shalit and I. Talmi, Nuclear Shell Theory (Academic, New York, 1963).

[12]P. Schuurmans, Physica 11, 419 (1946).

[13]B. R. Judd, Phys. Rev. 125, 613 (1962).

[14]J. G. Conway, in Proceedings of the Robert Welch Foundation Conference, XIII Transuranic Elements (Robert Welch Foundation, Houston, 1970), p. 430.

[15]L. Brewer, J. Opt. Soc. Am. 61, 1101 (1971); J. Opt. Soc. Am. 61, 1666 (1971).

[16]J. Mann, 1972 (private communication).

Neutrality of Molecules by a New Method*

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We report a new experimental technique for testing the electrical neutrality of molecules. An alternating electric field applied to an acoustic cavity containing SF_6 gas will generate sound at the electric field frequency if the gas has a charge. With a suitably calibrated microphone in the cavity the sound pressure can be measured yielding an upper limit for the charge per molecule ϵ. Dividing by the mass number of the molecule (146) yields an upper limit for an electron-proton charge difference. (This last result assumes that the electron-proton charge difference equals the neutron charge.) The results: $|\epsilon| \leq 2 \times 10^{-19}e$ and $|\epsilon|/M \leq 1 \times 10^{-21}e$, where e is the magnitude of the electronic charge, are consistent with the fundamental belief of zero charge imbalance. The measurement is less affected by the presence of ions than other macroscopic neutrality measurements and has an estimated maximum sensitivity of $|\epsilon| \leq 10^{-22}e$.

I. INTRODUCTION

The assumed equality of the electron and proton charges represents a symmetry in nature which corresponds to no known conservation law, but is based directly on a series of sensitive experimental measurements dating from 1925 (see Table I). These measurements have involved three different experimental techniques: (1) the gas-efflux method, (2) the isolated-body method (analogous to the Millikan oil-drop experiment), and (3) the molecular-beam method. We report a new experimental technique for testing the electrical neutrality of molecules.

One must recognize that all measurements become difficult as one approaches the limit of sensitivity imposed by noise. The sensitivity of methods (1) and (2) is high, because the experiments are bulk measurements using large numbers of molecules. Particular care must be taken to eliminate the effects of ions and other charged particles. The gas-efflux method involves the measurement of the change in potential of an electrically insulated container as the enclosed volume of gas

is allowed to escape. Considerable effort is required to minimize the spurious charging effects which result from the flow of the gas through an insulated pipe. In the molecular-beam method the deflection of a beam of molecules by a homogeneous electric field is measured. In such experiments, an asymmetrical reversal of the electric field and the interaction of induced electric multipoles in the molecule with electric field gradients can produce deflections which mimic a charge imbalance. The isolated-body method, which is a refinement of the Millikan oil-drop experiment, also suffers from such electric-field-gradient problems.

The results of these experiments are consistent with the assumption that the charge per molecule is zero within the experimental error. We describe an experimental technique, free of many of the difficulties of the other methods, with a sensitivity capable of reducing the upper limit on the charge per molecule lower than any established result.

II. DESCRIPTION OF METHOD

The experiment depends on the effect of an alternating electric field on a gas contained within a high-Q acoustic cavity. If the gas has a charge density because of a small charge ϵe ($\epsilon \ll 1$, $e = 4.8 \times 10^{-10}$ esu) on each molecule, and a molecular

polarizability α, then the force per unit volume of the gas in the presence of the field is given by

$$F_v = n\epsilon eE + (n/8\pi)\alpha\nabla E^2 . \tag{1}$$

If the applied electric field has the frequency ω_0, the volume force will have a component at ω_0 attributable to the first term in Eq. (1), and a component at $2\omega_0$ because of the second term. Such alternating volume forces will generate sound waves in the gas.

The apparatus is designed to detect the presence of sound waves in the cavity at the same frequency as the applied electric field. If care is taken to prevent coupling between the electric driving and detection circuits, and if harmonic distortion in the electric field is minimized to prevent coupling of the polarization signal at $2\omega_0$, then the detected sound pressure at ω_0 is proportional to the charge on the molecule. The sensitivity of the experiment is limited by the inherent noise sources, primarily Johnson noise in the detection circuit, and by background sound and spurious signals from the driving field. The experiment gains sensitivity by adjusting the frequency of the applied electric field to coincide with a cavity resonance, and by discriminating against all but this single frequency in the detection circuitry.

The acoustic cavity chosen for the experiment was a sphere of 20-cm radius. A radial electric

TABLE I. Comparison of neutrality measurements.

	Method	Molecule	Upper limit[a] for ϵ	Upper limit[b] for ϵ/M	Ref.
Millikan	(2)	•••	•••	$\pm 10^{-16}$	1
Stover, Moran, and Trischka	(2)	•••	•••	$\pm 0.8 \times 10^{-19}$	2
Piccard and Kessler	(1)	CO_2	$\pm 2 \times 10^{-19}$	$\pm 5 \times 10^{-21}$	3
Hillas and Cranshaw	(1)	Ar	$(4 \pm 4) \times 10^{-20}$	$(1 \pm 1) \times 10^{-21}$	4
		N_2	$(6 \pm 6) \times 10^{-20}$	$(2 \pm 2) \times 10^{-21}$	
King	(1)	H_2	$(1.8 \pm 5.4) \times 10^{-21}$	$+(0.9 \pm 2.7) \times 10^{-21}$	5
		He	$(-0.7 \pm 4.7) \times 10^{-21}$	$(-0.2 \pm 1.2) \times 10^{-21}$	
		SF_6	$(0 \pm 4.3) \times 10^{-21}$	$(0 \pm 3.0) \times 10^{-23}$	
Hughes	(3)	CsI	4×10^{-13}	2×10^{-15}	6
Zorn, Chamberlain, and Hughes	(3)	Cs	$(1.3 \pm 5.6) \times 10^{-17}$	$(1.0 \pm 4.2) \times 10^{-19}$	7
		K	$(-3.8 \pm 11.8) \times 10^{-17}$	$(-1.0 \pm 3.0) \times 10^{-18}$	
		H_2	$\pm 2 \times 10^{-15}$	$\pm 1 \times 10^{-15}$	
		D_2	$\pm 2.8 \times 10^{-15}$	$\pm 7 \times 10^{-16}$	
Fraser, Carlson, and Hughes	(3)	Cs	$\pm 1.7 \times 10^{-18}$	$\pm 1.3 \times 10^{-20}$	8
		K	$\pm 1.3 \times 10^{-18}$	$\pm 3.3 \times 10^{-20}$	
Shapiro and Estulin	(3)	n	6×10^{-12}	6×10^{-12}	9
Shull, Billman, and Wedgwood	(3)	n	$(-1.9 \pm 3.7) \times 10^{-18}$	$(-1.9 \pm 3.7) \times 10^{-18}$	10

[a]Measured charge per molecule in units of the electronic charge.

[b]Measured charge per molecule divided by the total number of nucleons.

field could be produced within the cavity by a spherical electrode located at the center. When excited in its first radial mode $[P(r) = P_0 j_0(k_0 r)]$, the cavity exhibited Q's greater than 10^3 at 1 atm.

The solution of the wave equation with a source term given by the product of the charge density, $\rho = n_e e$, and an electric field alternating at the resonant frequency yields the following expression
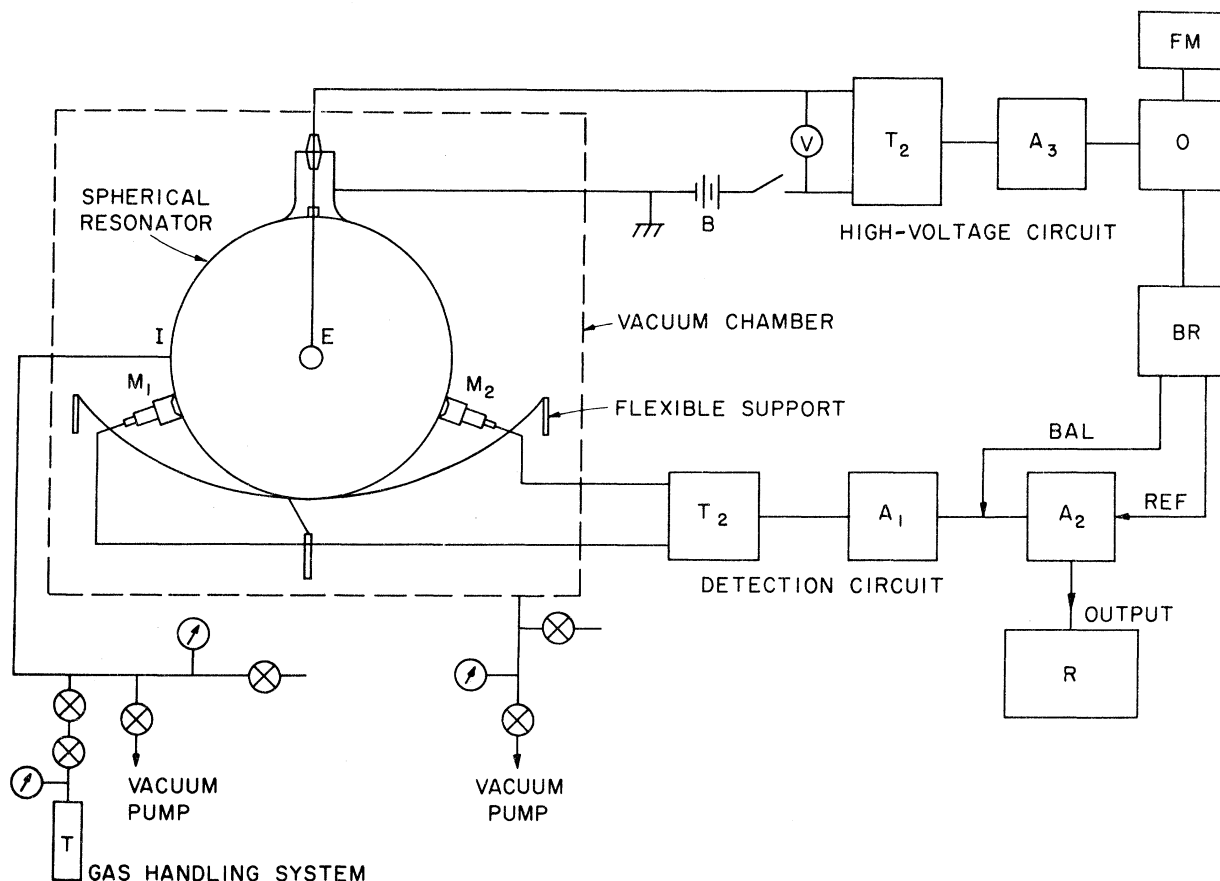

FIG. 1. Experimental apparatus. The spherical resonator consisted of two 20-cm-radius copper hemispheres from a liquid-N_2 Dewar soft soldered together. Two microphones (M_1, M_2) and a gas intake (I) were positioned on the periphery of the sphere, and the high-voltage electrode (E), consisting of a 1-in. brass sphere, was supported at the center of the sphere. The sphere was mounted on flexible supports within a large iron vacuum chamber for acoustic isolation. A gas-handling system enabled the sphere to be evacuated or pressurized with any gas from standard high-pressure cylinders (T). All connections to the sphere were made flexible to minimize the transmission of vibrations. The microphones (Lafayette PA-74) were wired in series with the primary of a matching transformer (T_1), such that common-mode sound signals added and electrostatic pickup from the electrode canceled. The resultant signal was first preamplified (A_1, Hewlett-Packard 466A) and then amplified by a lock-in amplifier (A_2, PAR JB-5) referenced to the electric field frequency. The dc output of the lock-in was displayed on a strip chart recorder (R). The initial driving signal for the electrode was supplied by an audio oscillator (O, Hewlett-Packard 202C). This signal was amplified (A_3, McIntosh MC75) and then fed into the primary of a high-voltage transformer (T_2, N.E. Transformer Co. No. 8142). A switched 300-V battery (B) in the high-voltage secondary circuit was used (1) for tuning the resonator to resonance by coupling a fraction of the second-harmonic polarization signal to the fundamental and (2) for sweeping ions from the resonator. The high voltage was measured with a voltmeter across the secondary (V, Simpson 260), and the driving frequency was measured with a digital frequency meter (FM, General Radio 1138) at the oscillator output. The frequency stability of the entire system (over a period of one run) was limited by temperature variations in the resonator gas to ± 0.1 Hz. Incomplete cancellation of electrostatic pickup in the microphone circuit, and stray magnetic fields from the high-voltage transformer and amplifier, resulted in a residual pickup at the lock-in input that was typically 10^{-5} V (corresponding to the signal that a gas carrying a charge per molecule of $10^{-19} e$ would produce). An equivalent amount of signal of the same frequency, but opposite phase, was obtained from the balance circuit (BR), and added to the lock-in input to cancel the residual pickup. A signal in the lock-in could be distinguished as electrical pickup or a true acoustic signal by virtue of the frequency dependence of the respective signals. This same circuit provided a convenient isolated reference voltage for the lock-in.
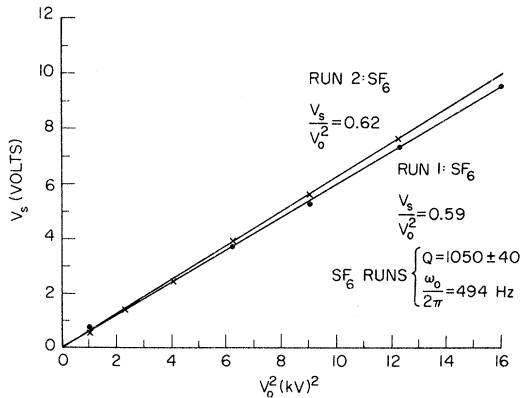
FIG. 2. Polarization signal measurements.

for the molecular charge in terms of the sound pressure at the cavity walls:

$$\epsilon \leq \frac{P_D kT}{QPeV_0} \frac{\pi k_0/2r_0}{[(\sin k_0 r_0)/k_0 r_0^3 + (\sin k_0 a)/k_0 a^3]} \quad, \tag{2}$$

where a is the radius of the cavity and r_0 is the radius of the electrode. The sensitivity of the experiment is seen to depend linearly on the detected sound pressure P_D and the electrode voltage V_0, and depend faster than linearly on the cavity gas pressure P, since the cavity Q also increases with pressure. Taking reasonable values for the parameters, the maximum sensitivity obtainable should be of the order of $|\epsilon| \leq 10^{-22}$.

The apparatus is calibrated at its resonant frequency ω_0, by driving the electrode at $\frac{1}{2}\omega_0$, thereby generating sound at ω_0 because of the polarizability of the molecules. In this case the sound pressure is given by the solution to the wave equation with the second term of Eq. (1) as the source term:

$$\frac{P_D}{V_0^2} \approx 1.02 \frac{Q k_0 n \alpha r_0^2}{a^3 j_0(k_0 a)} \quad. \tag{3}$$

There is also sound produced at twice the driving frequency because of electromechanical forces on the cavity walls, but this signal is three orders of magnitude smaller than the polarization signal in the present apparatus.

III. APPARATUS

The details of the apparatus and a block diagram of the electronics are shown in Fig. 1. An audio oscillator driving a transformer with a turns ratio of 2000:1 was used as a source of high voltage. The problem of electrostatic pickup in the detection circuit was minimized by using low-impedance magnetic microphones. Two gases, SF_6 and N_2, were employed in the experiment. The actual neutrality measurements were made with SF_6 be-

cause of its large mass number ($M = 146$) and small acoustic absorption coefficient at the frequency of interest. Polarization signal measurements were made with SF_6 and with N_2. The SF_6 polarization signal was used to calibrate the neutrality measurements, and the N_2 signal served as a check on the calibration procedure, since the microphone free-field response in air was known. No special precautions were taken in purifying the gases. They were used directly from standard tanks in pressures up to 1 atm, which was the pressure limit of the apparatus.

Before a neutrality measurement, a steady potential V_1 was added to the alternating potential $V_0 e^{i\omega t}$ applied to the electrode so that the polarization signal $\sim (V_1 + V_0 e^{i\omega t})^2$ contained a term at the fundamental frequency to be used to set the frequency of the alternating potential ω to the cavity resonance ω_0. This steady potential also served to remove any ions or other stray charged particles from the cavity. For any plausible ion density, calculations show that the ion motion would couple a negligible amount of energy to the acoustic motion of the gas molecules. Thus, the effect of ions in the cavity (resulting from residual radioactivity in the solder joints, cosmic rays, etc.) is probably not important and need be considered only in the event of a non-null result.
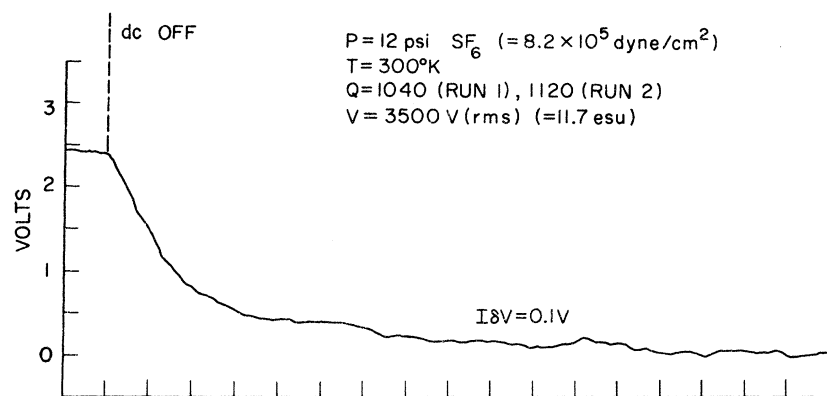
IV. RESULTS

An experimental calibration is obtained from measurements of the slope of the polarization signal of SF_6 (Fig. 2) and Eq. (3):

$$\frac{\Delta V_s}{\Delta P_D} = \frac{V_s}{V_0^2} \frac{V_0^2}{P_D} = 1.9 \times 10^3 \frac{V}{\text{dyn/cm}^2} \quad. \tag{4}$$
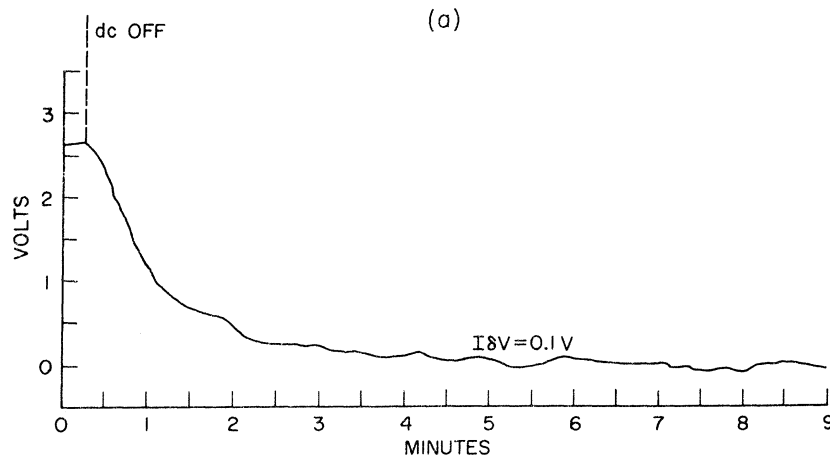
With this result and the quantities $r_0 = 1.27$ cm, $a = 19.7$ cm, and $k_0 = 0.228$ cm^{-1}. Equation (2) yields an expression for the charge per molecule directly in terms of the voltage V_s which deflects the chart recorder trace,

$$\epsilon e \leq \frac{\Delta P_D}{\Delta V_s} \frac{kT(0.45)V_s}{QPV_0} \quad. \tag{5}$$

Recorder plots and other experimental data for two runs are shown in Fig. 3. These plots show the decay of the polarization signal used for tuning the detection circuit to below the inherent noise level, thus revealing no charge signal greater than the noise. This noise voltage is the Johnson noise in the detection circuit, as can be seen by comparing these data with the plots of the background noise shown in Fig. 4. If a signal attributable to a molecular charge were present of 0.1-V magnitude, it could be seen with a signal-to-noise ratio of approximately 1. Substituting the value $V_s = 0.1$ V into Eq. (4) yields an upper limit for the charge on the SF_6 molecule in units of the fundamental

$P = 12$ psi SF_6 $(= 8.2 \times 10^5$ dyne/cm$^2)$
$T = 300°K$
$Q = 1040$ (RUN 1), 1120 (RUN 2)
$V = 3500$ V (rms) $(= 11.7$ esu)

FIG. 3. Neutrality measurements.

charge e:

$$|\epsilon| \leq 1.9 \times 10^{-19} .$$

With the assumption that a fundamental electron-proton charge difference is equal to the charge of the neutron, which follows from the assumption of charge conservation in the β decay of the neutron,[11] $n \to p + e^- + \bar{\nu}$, an upper limit for the electron-proton charge difference is the measured molecular charge divided by the total number of nucleons, $M = Z + N$:

$$|\epsilon| / M \leq 1.3 \times 10^{-21} .$$

V. CONCLUSIONS AND RECOMMENDATIONS

The experiment just described represents a sensitive new method of establishing upper limits on the charge carried by molecules and on the electron-proton charge difference. The results are consistent with the assumption that a molecule carries no charge, thus confirming by an independent technique the results of previous neutrality measurements. The experimental technique avoids the problem of stray ions and stray charged particles, which complicate neutrality measurements by other
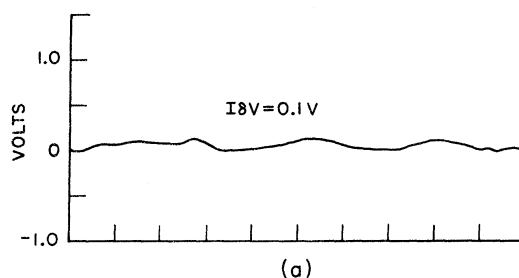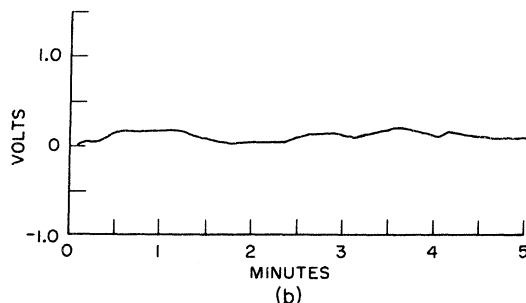
FIG. 4. (a) Total electronic noise with 600-Ω resistor in place of microphones: $\delta V \simeq 1.5 \times 10^{-9}$ V referred to input $(f = 494$ Hz, $\Delta f = 0.1$ Hz). (b) Total noise with 12-psi SF_6 in cavity $(f = 494$ Hz, $\Delta f = 0.1$ Hz).

macroscopic techniques.

The sensitivity could be increased by a factor of 10–100 by using higher pressures, by a factor of 10 by using a higher voltage, and by a factor of 5 with better-quality microphones chosen specifically for the detection of small signals near the thermal limit. With all the improvements that could be made, we estimate that a limit of $|\epsilon| \le 10^{-22}$ could be achieved.

An interesting application of the experimental method (as suggested by Dr. S. G. Kukolich) would be the measurement of the magnetic susceptibilities of gases. Preliminary experimental

work for such measurements was performed by Gleitsman.[12]

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[1] R. A. Millikan, *Electrons (+and −), Protons, Photons, Neutrons, and Cosmic Rays* (University of Chicago Press, Chicago, 1935); R. A. Lyttleton and H. Bondi, Proc. R. Soc. Lond. 252, 313 (1959).

[2] R. W. Stover, T. I. Moran, and J. W. Trischka, Phys. Rev. 164, 1599 (1967).

[3] A. Piccard and E. Kessler, Arch. Sci. Phys. Nat. 7, 340 (1925).

[4] A. M. Hillas and T. E. Cranshaw, Nature (Lond.) 184, 892 (1959); Nature (Lond.) 186, 459 (1960); H. Bondi and R. A. Lyttleton, Nature (Lond.) 184, 974 (1959).

[5] J. G. King (unpublished).

[6] V. W. Hughes, Phys. Rev. 76, 474 (1949); Phys. Rev. 105, 170 (1957).

[7] J. C. Zorn, G. E. Chamberlain, and V. W. Hughes, Phys. Rev. 129, 2566 (1963).

[8] L. J. Fraser, E. R. Carlson, and V. W. Hughes, Bull. Am. Phys. Soc. 13, 636 (1968).

[9] I. S. Shapiro and I. V. Estulin, Zh. Eksp. Teor. Fiz. 30, 579 (1956) [Sov. Phys.-JETP 3, 626 (1957)].

[10] C. G. Shull, K. W. Billman, and F. A. Wedgwood, Phys. Rev. 153, 1414 (1967).

[11] This requires the additional assumption of zero charge carried by the antineutrino.

[12] R. Gleitsman, B. S. thesis (Department of Physics, M.I.T.) (unpublished).

Hyperfine Structure of the 2²P, 3²P, and 4²P States of Lithium

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The hyperfine interactions in the $2\,^2P$, $3\,^2P$, and $4\,^2P$ states of Li[7] are studied, using the spin-optimized self-consistent-field (SO-SCF) and unrestricted Hartree–Fock methods. It is found that the use of a single $\langle r^{-3} \rangle$ parameter to describe all three hyperfine interactions is inadequate for all states considered, as has previously been found for the $2\,^2P$ state. The experimental results for $3\,^2P$ and $4\,^2P$ states are reanalyzed and the following values are obtained: $3\,^2P$: $a_{\text{orb}} = 2.58 \pm 0.05$ MHz, $a_{\text{dip}} = -0.57 \pm 0.02$ MHz, $a_c = -2.98 \pm 0.06$ MHz; $4\,^2P$: $a_{\text{orb}} = 1.10 \pm 0.03$ MHz, $a_{\text{dip}} = -0.24 \pm 0.01$ MHz, $a_c = -1.27 \pm 0.03$ MHz. The lifetimes of the $2\,^2P$ and $3\,^2P$ states are calculated using the SO-SCF method, showing good agreement with experimental values for the $2\,^2P$ state, but giving a lifetime for the $3\,^2P$ state which is about 20% too long.

I. INTRODUCTION

Accurate experimental results for the hyperfine structure (hfs) in the ^2P states of atomic lithium have been available for some time, for the $2\,^2P$ state[1,2] as well as the $3\,^2P$ and $4\,^2P$ states.[3] The $2\,^2P$ state has been the subject of numerous theoretical treatments,[4-15] some of which using very accurate computational methods.[9-11] The $3\,^2P$ state has however been treated only briefly in some of

these papers[7,8,14] and so far no calculations of the hfs in the $4\,^2P$ state have been reported. One of the purposes of the present investigation is therefore to supplement the experimental data with results obtained from calculations, which hopefully will give some additional aspects on the approximations used in the analysis of the experimental results.[3] In this connection one is greatly helped by the extensive material on the $2\,^2P$ state, as well as a wealth of hfs calculations for other systems, which