Isotope Shift in the (2^1S_0-2^1P_1) Line of Atomic Helium

James M. Burger and Allen Lurio
IBM Watson Laboratory, Columbia University, New York, New York 10025
(Received 17 July 1970)

A measurement of the isotope shift in the (2^1S_0-2^1P_1) line of atomic helium has been made and is in excellent agreement with theory. Both He^4 and He^3 2^1S_0 metastable beams were irradiated in a magnetic field with 20 582-Å (2^1S_0-2^1P_1) radiation from He^3 and He^4 resonance lamps, respectively. In each case, a magnetic sublevel of the 2^1P_1 state was Zeeman shifted so as to scan the resonance-lamp profile. The 584-Å (2^1P_1-1^1S_0)-decay photons served to monitor the excitation. A shift $\nu(He^3)-\nu(He^4)=0.1408\pm0.0019$ cm^{-1} was obtained.

I. INTRODUCTION

In a previous publication, a preliminary measurement of the (2^1S_0-2^1P_1) isotope shift was reported.[1] This work has been extended and these results are now described. The (2^1S_0-2^1P_1) isotope shift is of interest, in that it permits a measurement of the mass-polarization contribution to the binding energy and hence provides a test of the atomic wave functions. Recently developed wave functions[2,3] have permitted a calculation of great accuracy but no direct measurement has been made. A shift of 0.11 cm^{-1} had been inferred by extrapolation from the results of spectroscopic measurements in the higher members of the (2^1S_0-n^1P_1) lines,[4,5] whereas the predicted value is 0.1419 cm^{-1} with an estimated error of no more than 0.0001 cm^{-1}.

In the present paper, a complete description of the experiment is given and a new and improved measurement is reported. The experimental technique may be briefly described as follows. A beam of 2^1S_0 metastable atoms was first produced by electron bombardment of a ground-state helium beam. The 2^1S_0 beam then passed through a uniform variable magnetic field where the 2^1P_1 state was excited by 20 582-Å (2^1S_0-2^1P_1) resonance radiation. Both He^4 and He^3 beams were irradiated with He^3 and He^4 resonance lamps, respectively. By means of the applied field, a magnetic sublevel of the optically excited 2^1P_1 state was Zeeman shifted so as to scan the resonance-lamp profile. The 584-Å photons, resulting from the dominant 2^1P_1 decay to the 1^1S_0 ground state, served as a monitor of the (2^1S_0-2^1P_1) excitation.

II. THEORY

Because the nuclear motion about the center of mass contributes slightly to the binding energy of an atom, the mass difference of isotopes gives rise to small shifts in their energy levels and consequently in their emission and absorption spectra. In the simplest case of one-electron atomic systems, particularly hydrogen, the effect of nuclear motion on the binding energy may be described by replacing the electron mass m by a reduced mass $\mu = mM_N/(m+M_N)$, where M_N is the nuclear mass. The binding energy E is related to E_∞, the Schrödinger solution for an infinitely heavy nucleus, through $E=(\mu/m)E_\infty$; the resulting isotopic energy differences are generally referred to as reduced-mass or normal shifts. In the case of N electrons and one nucleus, the effect of nuclear motion on the binding energy can be described in terms of a reduced-mass shift, analogous to the above, and a mass-polarization term.[6] As both these contributions are present in a two-electron atom, helium provides a quite general system for the investigation of the effect of nuclear motion on binding energy.

The reduced-mass and mass-polarization contributions can be demonstrated in a straightforward manner[6] for helium by a transformation of the two-particle nonrelativistic Schrödinger equation to center-of-mass coordinates, i.e., with the transformation

$$M\vec{X} = M_N\vec{r}_N + m\vec{r}_1 + m\vec{r}_2 \ , \quad M = M_N + 2m \ ,$$

$$\vec{x}_k = \vec{r}_k - \vec{r}_N \ , \quad k = 1,2 \text{ for the two electrons,}$$

where $\vec{r}_N$ and $\vec{r}_k$ are the nuclear and electronic positions in the laboratory system. A classical derivation may instead be given. The kinetic energy of a system of particles can be written as the kinetic energy of the entire mass of the center of mass plus the sum of the kinetic energies of the individual particles about the center of mass,[7] i.e.,

$$T = \frac{P^2}{2M} + \frac{p_N'^2}{2M_N} + \frac{p_1'^2}{2m} + \frac{p_2'^2}{2m} \ , \tag{1}$$

where $\vec{P} = M\dot{\vec{X}}$, and $\vec{p}_i' = m\dot{\vec{x}}_i'$, $\vec{x}_i' + \vec{X} = \vec{r}_i$ for $i = k, N$. The classical nuclear momentum $\vec{p}_N'$ may be eliminated by the condition $\vec{p}_1' + \vec{p}_2' + \vec{p}_N' = 0$ in the center-of-mass system. Furthermore, from the canonical formalism or by comparison with the quantum-mechanical transformation $(\vec{p}_k', \vec{P})$ can readily be shown to be conjugate to $(\vec{x}_k, \vec{X})$. Hence, introducing the gradient operators for these momenta into the kinetic energy and expressing the electrostatic po-

tential in terms of $\vec{x}_k$, one obtains the Hamiltonian

$$H=-\frac{\hbar^2}{2M}\nabla^2-\frac{\hbar^2}{2\mu}(\nabla_1^2+\nabla_2^2)-\frac{\hbar^2}{M_N}\nabla_1\cdot\nabla_2 - \frac{2e^2}{x_1}-\frac{2e^2}{x_2}+\frac{e^2}{x_{12}}\ , \tag{2}$$

where $\mu=mM_N/(m+M_N)$. The first term, which describes the translational motion of the atom as a whole, can be ignored as it does not contribute to the binding energy. The second term gives rise to the reduced-mass shift through the nuclear mass contained in μ. The third term is the mass polarization. The dependence of this Hamiltonian on nuclear mass (excluding translational motion) can be seen to arise from the kinetic-energy term of the nucleus in the center-of-mass system.

The reduced-mass and mass-polarization shifts can both be calculated by use of the energy eigenvalues E_∞ and corresponding wave functions Ψ_∞, obtained from the above Hamiltonian for an infinitely heavy nucleus, i.e., $\mu=m$ and no mass-polarization term. The reduced-mass effect, resulting from the introduction of μ in place of m in the infinite-nuclear-mass Hamiltonian, gives rise to a shift in the energy eigenvalue from E_∞ to $E=(\mu/m)E_\infty$. This result follows immediately from the coordinate transformation $\vec{x}_k\rightarrow(\mu/m)\vec{x}_k$.[6] Hence, to calculate the reduced-mass effect in a state only the energy is needed. The mass-polarization term, treated by first-order perturbation theory, contributes a shift to the energy $-(\hbar^2/M_N)\int\Psi_\infty\nabla_1\cdot\nabla_2\Psi_\infty$ and is seen to be inversely proportional to the nuclear mass. A knowledge of atomic wave functions is necessary for its evaluation.

The reduced-mass corrections to the binding energy E_∞ for both He^4 and He^3 were calculated from theoretical values[2,3] for the nonrelativistic ionization energy of He^4, ν. This shift in the energy level, $\delta E_{rm}=E-E_\infty$, is for the two isotopes

$$\delta E_{rm}(He^4)=\frac{m}{M_4}\nu+4\frac{m}{m+M_4}R_\infty\ ,$$
$$\delta E_{rm}(He^3)=\frac{m}{M_4}\frac{m+M_4}{m+M_3}\nu+4\frac{m}{m+M_3}R_\infty\ , \tag{3}$$

where M_4 and M_3 are the He^4 and He^3 nuclear masses, respectively, and R_∞ is the Rydberg constant (electron mass). The terms $4mR_\infty/(m+M_N)$, corresponding to the reduced-mass shifts of He^+, do not contribute to a shift in emission or absorption spectra of neutral helium but should properly be included in δE_{rm}(cf., Ref. 1). The mass-polarization corrections δE_{mp} to E_∞ were calculated directly from the tabulated[2,3] mass-polarization contributions to the He^4 ionization energy $(-\epsilon_M)$ and are

$$\delta E_{mp}(He^4)=\epsilon_M\ ,\quad \delta E_{mp}(He^3)=(M_4/M_3)\epsilon_M\ . \tag{4}$$

The shifts obtained from these expressions are summarized in Fig. 1. For these computations, the nuclear mass was obtained as the atomic mass minus twice the electron mass.[8] The predicted shift in the $(2^1S_0-2^1P_1)$ line is

$$\nu(He^3)-\nu(He^4)=0.1419\ cm^{-1}(4254\ MHz)\ .$$

The peaks of the scanning profiles obtained in the measurement were easy to interpret due to the absence of effects from fine and hyperfine structure. With regard to fine structure, no splittings occur in the singlet states of the helium atom.[9] Other contributions to the energy, such as relativistic corrections, have been calculated[2,3] but are independent of nuclear mass and only give rise to level displacements independent of the isotope. He^4 has no hyperfine structure as its nuclear spin is zero. In the case of He^3, which has a finite moment, the hyperfine energy vanishes in the $^1S_0$ state.[10] A splitting in the $^1P_1$ state due to orbital motion is small (19 MHz in a hydrogenic approximation) as compared with the natural linewidth (287 MHz) and would have a negligible effect in these measurements since the center of gravity of the line is not displaced.

A shift does result from the different nuclear dimensions of isotopes. The consequent difference in electrostatic potential within the nucleus gives rise to a shift in binding energy when a finite electron density at the nucleus exists. This nuclear

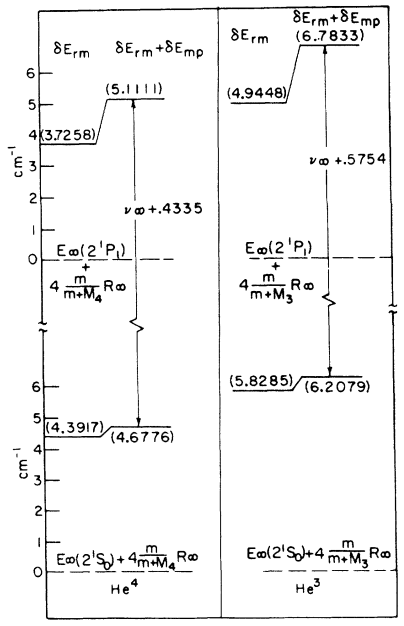

FIG. 1. Energy-level diagram showing the reduced-mass and mass-polarization contributions relative to the infinite nuclear-mass solution of the Schrodinger equation [see Eq. (2) of text]. The reduced-mass contribution of the He^+ ion is included in the dotted baselines.

volume effect δE_{nv}, increasingly more important in heavier nuclei, is small in the present case in comparison with experimental resolution. For purposes of an estimate consider the 2^1S_0 and 2^1P_1 states as a $2s$ and $2p$ electron, respectively, moving in an effective Coulombic potential. The shift arises primarily from the $2s$ electron due to its greater density at the nucleus. Under the assumption of a uniform distribution of charge throughout the nuclear volume, the energy difference in cm^{-1} of the $2s$ electron is

$$\delta E_{nv}(He^3) - \delta E_{nv}(He^4) = \tfrac{2}{5} ZR_\infty 4\pi a_0^3 \psi_{2s}^2(0) \times \frac{r_0}{a_0}\left(\frac{r_0(He^3) - r_0(He^4)}{a_0}\right) , \quad (5)$$

where a_0 is the Bohr radius, r_0 the nuclear radius, and $\psi_{2s}(0)$ the hydrogenic wave function for a $2s$ electron evaluated at the nucleus, with $Z = 2$ for simplicity. With the experimental nuclear radii,[11] we have

$$\delta E_{nv}(He^3) - \delta E_{nv}(He^4) = 6.6 \times 10^{-5}\ cm^{-1}\ (2.0\ MHz) .$$

This is a factor of 30 smaller than our quoted experimental error.

III. APPARATUS

The equipment used in these measurements will be briefly summarized as a detailed description has been given elsewhere.[12] The 2^1S_0 (and unavoidably 2^3S_1) metastable beam was produced by electron bombardment in the source chamber of a two-chamber brass vacuum system. The operating helium pressure in the source chamber was 1.7×10^{-5}- mm Hg with a corresponding helium partial pressure in the interaction chamber of 4×10^{-7}- mm Hg. Excitation of the 2^1S_0 metastable beam with 20 582-Å radiation occurred between the 7.3-cm-diam poles (0.93-cm gap) of an iron electromagnet in the interaction chamber. A brass spacer for these poles had two orthogonal apertures, one 0.93×0.93 cm^2 for the beam to enter and exit, the other 0.93 cm high by 5 cm long (along the beam) for excitation and detection. The directions of magnetic field, atomic beam, and incident (or detected) radiation were mutually perpendicular. A Bendix channeltron electron multiplier was used to detect the 584-Å-decay photons. This electron multiplier was totally insensitive to the incident 20 582-Å radiation and hence, the excitation and detection directions could be colinear. The channeltron, located 15 cm from the magnet center and shielded with mu-metal, was unaffected by our magnetic field scan as verified by the absence of any field dependence in the signal resulting from irradiation with a Hg Osram lamp. A number of parallel, alternately biased, electric field plates were located in front of the channeltron to remove ions.

Channeltron pulses were counted in a multichannel analyzer (Tech. Meas. Corp. CAT 1000, North Haven, Conn.), while the magnetic field was varied synchronously with channel address. With 256 channels and an address rate of 0.080 sec/channel, each sweep took a little over 20 sec. Typically, 300 sweeps were made in a run, so each curve represented about 1 h and 40 min of data accumulation. The varying magnetic field was read with a temperature-compensated Hall probe (T6010) and a Bell 640 gaussmeter (F. W. Bell, Columbus, Ohio), which could be read into the multichannel analyzer with an analog to digital converter. The CAT 1000 data in digital form was read directly into an IBM 1130 computer.

The Hall element was located radially 1.9 cm from the magnet gap center. For the tapered pole pieces used (5 cm pole diameter), the magnetic field was constant to within 0.3% over the central 2.5-cm-diam portion of the gap, but was down by 0.75% at the position of the Hall element. As the resonance radiation was reasonably well focused into the gap center (~3 cm image length along the beam), the magnetic field was calculated as 1.0075 times the observed field. The gaussmeter itself was calibrated against proton resonance, and the magnetic field measurement technique checked against known static fields. The error in magnetic field measurement is estimated as 1%.

The He^3 used for both the atomic beam and the resonance lamps was produced by the Monsanto Company and contained a He^4 impurity of 0.05%. For the beam production, a total of about 0.3 liters STP of He^3 was used; it was collected by an auxilliary mechanical pump backing the diffusion pumps. Little He^3 was needed to make the resonance lamps since a He^3 gas-handling system with a Toepler pump for recovery was available in the laboratory. The quartz lamp bulbs were evacuated to a pressure of 10^{-6}- mm Hg and baked overnight at 1000 °C before the He^3 gas was admitted. These He^3 lamps were operated identically to the similar He^4 lamps previously discussed.[12]

IV. MEASUREMENT

A measurement with both a He^3 and a He^4 beam (with He^4 and He^3 lamps, respectively) allowed an estimate and a correction for certain possible systematic errors. Such errors could result from any displacement in the central frequency of the resonance lamps (pressure shifts, etc.) from the natural atomic frequency or from the excitation of the beam atoms by slightly Doppler-shifted incident radiation. With regard to the latter, while no Doppler shifts occur for the average direction of the incident radiation perpendicular to the beam, the lamps and optics were only aligned to within a degree or two; furthermore, the Hall probe in the

magnet spacer introduced a slight asymmetry.

The use of the He^3 and He^4 beams to minimize such errors can be formally expressed by considering the resonance condition at the 584-Å-photon signal maximum. In the case of a He^4 beam in which a 2^1P_1 magnetic sublevel has been Zeeman shifted, we find that

$$\nu(He^4) \pm (g_1\mu_B H_4/h) = \nu(He^3) + \delta\nu_3 \ , \qquad (6)$$

where ν represents the $(2^1S_0\text{-}2^1P_1)$ pure atomic transition frequency and $\delta\nu_3$ the real or Doppler displacement from $\nu(He^3)$ of the He^3 lamp. The $\pm$ sign is written because it is experimentally not known whether the $m_J = +1$ or $m_J = -1$ sublevel scans the lamp profile, even for a known direction of magnetic field. Similarly, for the He^3 beam, we have

$$\nu(He^3) \mp (g_1\mu_B H_3/h) = \nu(He^4) + \delta\nu_4 \ . \qquad (7)$$

Combining, we obtain

$$\nu(He^3) - \nu(He^4) = \pm (g_1\mu_B/h)\tfrac{1}{2}(H_3 + H_4) + \tfrac{1}{2}(\delta\nu_4 - \delta\nu_3) \ . \qquad (8)$$

The Doppler-shift contribution to $\delta\nu_3$ and $\delta\nu_4$ should be related by the expression $\delta\nu_3/\delta\nu_4 = \sqrt{\frac{4}{3}} = 1.15$, provided the velocity distribution in the beam is Maxwellian. The assumption of a Maxwellian velocity distribution in the metastable beam is probably not valid,[13] but nevertheless, the ratio of equivalent velocities on the He^3 and He^4 velocity distributions should certainly be close to $\sqrt{\frac{4}{3}}$. We might therefore expect in Eq. (8) that the term $\frac{1}{2}(\delta\nu_4 - \delta\nu_3)$ will yield a net correction of $-0.075\delta\nu_3$ from the Doppler contribution. In view of the small size of this correction (~5 G) and our lack of knowledge of how much $\frac{1}{2}(\delta\nu_4 - \delta\nu_3)$ is due to Doppler effects, we will take the experimentally determined isotope shift to be given by the average of H_3 and H_4.

In the measurements, He^4-lamp-filling pressures ranged from 3- to 6-mm Hg, and He^3 lamps at 5- and 7-mm Hg were used. Typical observed 584-Å-photon signals at the scanning curve maxima were of the order of 70 counts/sec. These signals are consistent with expectations from the level-crossing work with this apparatus.[12] Because of the smaller magnet gap in the present study, the beam and focused intensity were each down by a factor of 2 and only one magnetic sublevel ($|m_J| = 1$) was excited. This above 70 counts/sec is about equal to one-eighth the observed signal (0 G) with a linear polarizer in the level-crossing work.

The observed background, i.e., no resonance-lamp excitation, was typically 20–25 counts/sec. An increase in counting rate equal to about 15% of the peak 584-Å-photon signal (due to 20 582-Å radiation) was however observed near 0 G when the beam was irradiated with the resonance lamp. This signal, observed with both He^3 and He^4 beams, was presumably due to the tail of the exciting-light profile.

In the data analysis, the number of counts stored in each CAT channel address was plotted as a function of magnetic field as shown in Figs. 2 and 3. A curve was drawn through the data by eye, and center points then determined for several values of relative signal. The theoretical shape of this curve is not known since the lamp-intensity profile is not known, but it is expected to be symmetric about the maximum. The curves were indeed symmetric within experimental uncertainty about the magnetic field at which the signal peaked. No assumptions about the shape of the lamp profile other than the experimentally verified symmetry were made. The He^3 profiles were wider than the He^4 ones roughly in the expected ratio for Doppler broadening, i.e., the inverse square root of the atomic masses. However the observed half-widths were too wide for pure Doppler broadening, as previously noted.[1] Typical results are shown in Figs. 2 and 3. The average values obtained from a number of independent runs for the He^4 and He^3 beams, respectively, were

$$\bar{H}_4 = 2980 \text{ G}, \quad \bar{H}_3 = 3049 \text{ G} \ .$$

The value of $\bar{H}_4$ can be seen to be less than $\bar{H}_3$, indicating the presence of a systematic shift. No dependence of H_3 or H_4 on lamp-filling pressure,

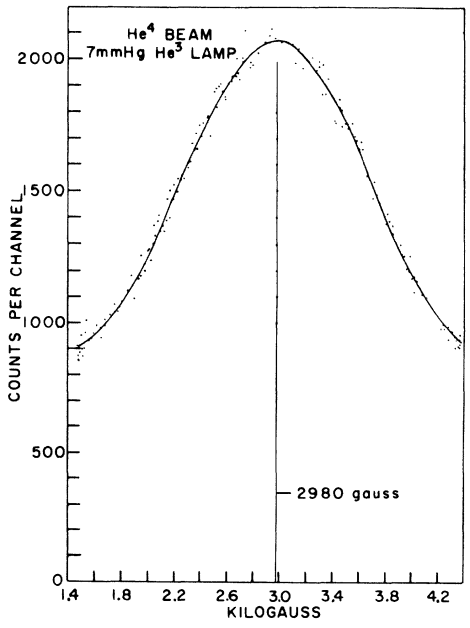

FIG. 2. Typical experimental curve where a He^4 beam Zeeman scanned a He^3 lamp profile. Solid curve through the data points was drawn by eye. Solid vertical line was drawn through the center of symmetry points.

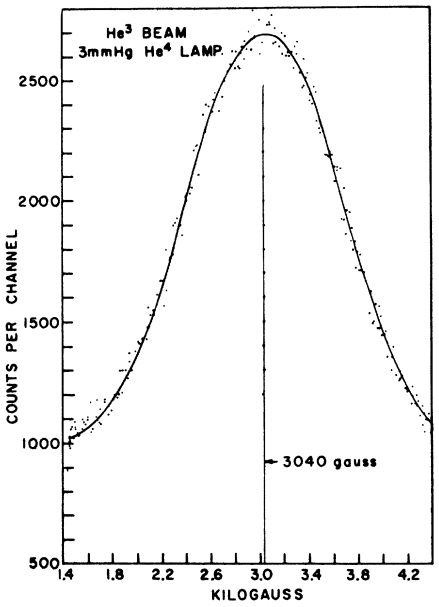

FIG. 3. Typical experimental curve where a He^3 beam Zeeman scanned a He^4-lamp profile. Solid curve through the data points was drawn by eye. Solid vertical line was drawn through the center of symmetry points.

however, was observed.

As indicated above, the sign of the isotope shift could not be determined from a knowledge of the direction of the magnetic field. However, by displacing H_3 or H_4 by a Doppler shift of known direction, this sign could be experimentally determined. The procedure, moreover, gave an indication of the magnitude of possible Doppler contributions to $\delta\nu_3$ and $\delta\nu_4$ in the above data (where no shifts were deliberately introduced). With an additional fixed Doppler shift $\delta\nu^D$, the equations describing the peak scanning signal become

$$\begin{aligned} \pm g_1\mu_B H_4^D/h &= \nu(\mathrm{He}^3) - \nu(\mathrm{He}^4) + \delta\nu_3 + \delta\nu^D , \\ \pm g_1\mu_B H_3^D/h &= \nu(\mathrm{He}^3) - \nu(\mathrm{He}^4) - \delta\nu_4 - \delta\nu^D . \end{aligned} \tag{9}$$

Hence, for a negative value of $\delta\nu^D$ (as actually produced), $|H_4^D| < |H_4|$ and $|H_3^D| > |H_3|$, if $\nu(\mathrm{He}^3) - \nu(\mathrm{He}^4) > 0$, as theoretically predicted.

To produce this Doppler shift $\delta\nu^D$, the optics were tilted about 4° so that the incident radiation was not quite perpendicular to the beam. The direction of tilt was such that the velocity of the beam atoms and the incident radiation direction formed an angle of 86°. The beam atoms hence had a velocity component directed away from the lamp, and hence the 20 582-Å incident radiation appeared to these atoms to have a lower frequency. Roughly, the expected Doppler shift is

$$\delta\nu^D = -(\nu/c)v \sin 4^\circ = -50 \text{ MHz},$$

where $v = 1.5\times10^5$ cm/sec. For $g_J(^1P_1) = 1$, this corresponds to about − 38 G.

With this arrangement, the results with a He^4 and He^3 beam were $H_4^D = 2945$ G and $H_3^D = 3100$ G, respectively, confirming the theoretical prediction. The average of these two values is 3022 G. These Doppler shifts too are of the order of magnitude estimated. Furthermore, it seems plausible that a Doppler shift produced the systematic difference in $\bar{H}_3$ and $\bar{H}_4$ as a result of the Hall-probe mount in the magnet spacer on the downstream side (with respect to the atomic beam). This asymmetry in excitation direction favored a Doppler shift with $\delta\nu^D < 0$, i.e., of the same sign as introduced intentionally, and hence might well account for the observation $\bar{H}_4 < \bar{H}_3$.

The experimental error arose principally from the 1% uncertainty in magnetic field. A net random error of 5 G in picking the symmetry point of the curves is estimated and an allowance of 5 G is made for the uncertainty in the correspondence of $\frac{1}{2}(\bar{H}_3 + \bar{H}_4)$ with the pure atomic isotope shift. No magnetic field dependence was observed in the background over the range where the scanning signal peaked. Hence, the experimental result is

$$\tfrac{1}{2}(\bar{H}_3 + \bar{H}_4) = (3015 \pm 40) \text{ G} .$$

V. CONCLUSIONS

The present experimental value for the isotope shift in the $(2^1S_0\text{-}2^1P_1)$ line is in excellent agreement with theory.[2,3] With $g_J(^1P_1) = 1.000\,00$, the experimental together with the theoretical value is

$$\text{expt: } \nu(\mathrm{He}^3) - \nu(\mathrm{He}^4) = +0.1408 \pm 0.0019 \text{ cm}^{-1};$$

$$\text{theor: } \nu(\mathrm{He}^3) - \nu(\mathrm{He}^4) = +0.1419 \text{ cm}^{-1} .$$

This agreement is consistent with theoretical expectations, as the error in the calculated value, based on its convergence, is no more than 0.0001 cm^{-1}. The present result agrees well with our earlier result.[1]

The experimental results for the isotope shift actually provide a more sensitive test of the mass-polarization contribution than is obvious from the quoted precision. This can be seen by observing that a calculation of the reduced-mass contribution to the isotope shift depends only on the ionization potential, which is known[2,3] experimentally for the states of interest to one part in 10^7. A calculated reduced-mass effect can hence be subtracted with no loss of accuracy from the total measured isotope shift to yield a measured value for the mass polarization. The difference in the $(2^1S_0\text{-}2^1P_1)$ transition frequencies, neglecting the reduced-mass effect, is then

$$\text{expt: } \nu_{mp}(\mathrm{He}^3) - \nu_{mp}(\mathrm{He}^4) = 0.3586 \pm 0.0019 \text{ cm}^{-1};$$

$$\text{theor: } \nu_{mp}(\mathrm{He}^3) - \nu_{mp}(\mathrm{He}^4) = 0.3597 \text{ cm}^{-1} .$$

As the reduced-mass and mass-polarization contri-

butions are of opposite sign, a measured value for the latter with an improved accuracy of 0.5% is obtained.

With regard to other calculations in these states, two independent values[14,15] have been obtained for the 2^1P_1 isotope shift in agreement with the above theory[2,3] to within 0.001 cm^{-1}; none of these calculations could be distinguished in the present experiment. An earlier calculation of the 2^1S_0 isotope shift[16] disagreed considerably with the above theory and with the present experiment.

A brief remark might be made regarding the isotope shift in the higher $(2^1S_0-n^1P_1)$ lines. The isotope shift for the 5016-Å $(2^1S_0-3^1P_1)$ and 3964-Å $(2^1S_0-4^1P_1)$ transitions has been measured spectroscopically, and these values for $\nu(He^3)-\nu(He^4)$ may be compared with the above theory, where the calculation is identical to that for the $(2^1S_0-2^1P_1)$ line (see Table I). The agreement is very good but the shifts are primarily due to the reduced-mass effect. With the reduced-mass contributions excluded, the theoretical shifts would be

TABLE I.

	Spectroscopy[a]	Spectroscopy[b]	Theory[c]
$(2^1S_0-3^1P_1)$	-0.833 ± 0.005	-0.849 ± 0.003	-0.8443 cm^{-1}
$(2^1S_0-4^1P_1)$	-1.150 ± 0.005	-1.165 ± 0.005	-1.1630 cm^{-1}

[a]See Ref. 4. [b]See Ref. 5. [c]See Refs. 2 and 3.

$$(2^1S_0-3^1P_1):\ \nu_{mp}(He^3)-\nu_{mp}(He^4)=0.0497\ cm^{-1};$$

$$(2^1S_0-4^1P_1):\ \nu_{mp}(He^3)-\nu_{mp}(He^4)=0.0320\ cm^{-1}.$$

Hence, of the $(2^1S_0-n^1P_1)$ series, the $(2^1S_0-2^1P_1)$ line is clearly the most sensitive to the mass-polarization term.

ACKNOWLEDGMENTS

We wish to thank Dr. H. Reich and William Yu for supplying and assisting us with the He^3 and Professor W. Happer for his help with the preparation of the resonance lamps.

[1]J. M. Burger and A. Lurio, Phys. Rev. Letters 22, 755 (1969).
[2]C. L. Pekeris, Phys. Rev. 126, 1470 (1962).
[3]B. Schiff, H. Lifson, C. L. Pekeris, and P. Robinowitz, Phys. Rev. 140, A1104(1965).
[4]L. C. Bradley and H. Kuhn, Proc. Roy. Soc. (London) A 209, 325 (1951).
[5]M. Fred, F. S. Tomkins, J. K. Brody, and M. Hamermesh, Phys. Rev. 82, 406 (1951).
[6]D. S. Hughes and C. Eckart, Phys. Rev. 36, 694 (1930).
[7]H. Goldstein, *Classical Mechanics* (Addison-Wesley, Reading, Mass., 1959), Chap. I.
[8]E. R. Cohen and J. W. M. DuMond, Rev. Mod. Phys. 37, 537 (1965); J. H. E. Mattauch, W. Thiele, and A. H. Wapstra, Nucl. Phys. 67, 1 (1965).
[9]H. A. Bethe and E. E. Salpeter, *Quantum Mechanics of One- and Two-Electron Atoms* (Academic, New York, 1957).
[10]H. Kopferman, *Nuclear Moments*, translated by E. E. Schneider (Academic, New York, 1958).
[11]H. Collard *et al.*, Phys. Rev. Letters 11, 132 (1963). M. M. Block *et al.*, Phys. Rev. Letters 26B, 464 (1968).
[12]J. M. Burger and A. Lurio, preceding paper, Phys. Rev. A 3, 64 (1971).
[13]J. C. Pearl, D. P. Donnelly, and J. C. Zorn, Phys. Letters 30A, 145 (1969); R. T. Robiscoe and T. W. Shyn, Phys. Rev. Letters 24, 559 (1970).
[14]G. Araki, K. Mano, and M. Ohta, Phys. Rev. 115, 1222 (1959).
[15]M. Machacek, F. Sanders, and C. W. Scherr, Phys. Rev. 136, A680 (1964).
[16]A. P. Stone, Proc. Phys. Soc. (London) 68, 1152 (1955).

PHYSICAL REVIEW A VOLUME 3, NUMBER 1 JANUARY 1971

Hartree-Fock Theory with Exchange Cutoff*†

Thomas A. Weber‡ and Robert G. Parr
Department of Chemistry, The Johns Hopkins University, Baltimore, Maryland 21218
(Received 19 June 1970)

A new Fock-type operator is defined which varies between the Hartree and the Hartree-Fock operator depending on a cutoff parameter in the exchange potential. The corresponding pseudo—Hartree-Fock equations require each orbital ϕ_i to behave asymptotically as $\exp[-(-2\epsilon_i)^{1/2}r]$. Calculations are reported for the Ne atom.

I. INTRODUCTION

Handy, Marron, and Silverstone[1] (hereafter HMS) have shown that the long-range behavior of Hartree-Fock orbitals for atoms is

$$\phi_i \to \exp[-(-2\epsilon_{smallest})^{1/2}r] \text{ as } r\to\infty, \quad (1)$$

except for the case of an atom consisting entirely