

Interpretation of Frequency Shifts Due to Electron Exchange Collisions

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Experiments by Hobart and Franken in 1961 demonstrated a shift in the free-electron spin-resonance frequency due to collisions with sodium atoms whose electron spins were polarized. The results have been interpreted on the assumptions that the S -wave phase shifts were proportional to the wave number k and that higher partial waves were not important. The triplet and singlet electron-sodium scattering lengths of Salmona and Seaton were used, but no check on the calculation was made since the sodium polarization was not known. Recently Balling, Hanson, and Pipkin have measured the shift for collisions with highly polarized rubidium atoms. They have also derived complete formulas for the frequency shift and line broadening in terms of the phase shifts with all partial waves included. In the present paper, an alternate derivation of the frequency shift and line broadening formulas is given and the experimental results are discussed on the basis of the phase-shift information that is available for hydrogen, sodium, and cesium. The small size of the observed ratio of frequency shift to line broadening for rubidium appears somewhat surprising in view of the larger ratios calculated for other alkalis.

1. INTRODUCTION

A MEASUREMENT of the free-electron g factor has been reported by Dehmelt.¹ His method involves polarization of the electrons by exchange collisions with sodium atoms which in turn have been polarized by optical pumping.^{2,3} An exchange broadening cross section of $260\pi a_0^2$ or larger at 400°K was also measured. Salmona and Seaton⁴ discussed this result on the basis of their calculated S -wave scattering lengths and found that the zero-energy-exchange cross section is large because the triplet and singlet scattering lengths are of opposite sign and are both large.

Hobart and Franken have repeated the electron g -factor experiment using a more homogeneous magnetic field.^{5,6} During the experiment, they discovered a shift in the electron-spin-resonance frequency with the sodium polarization and density. The sample temperature was about 410°K and the magnetic field about 3.7 G. The pulsed discharge which produced the electrons was short and uncorrelated with the modulation frequency used to observe the electron resonance. An argon buffer gas at pressures of between a few Torr and about 50 Torr was present, so the electrons were presumably thermal. The frequency shift was interpreted as due to phase shifts in the off-diagonal elements of the electron-spin density matrix introduced by the electron-sodium exchange collisions. Maximum shifts of about 100 cps were observed under conditions where the electron resonance broadening by electron-sodium exchange collisions was about 2000 cps (half-width at half-maximum).⁷

The expected ratio of frequency shift to line broaden-

ing for the conditions of the Hobart and Franken experiment has been estimated⁸ using Salmona and Seaton's triplet and singlet S -wave scattering lengths. The formula obtained, including only the S -wave contribution to the shift and broadening, was

$$(d'/w') = -P_{Na} \langle (\sin 2\Delta_0) \rangle_{av} / \langle (1 - \cos 2\Delta_0) \rangle_{av}. \quad (1)$$

Here d' and w' are the frequency shift and half-width, P_{Na} is the sodium electron polarization, $\Delta_0 = \delta_0(1) - \delta_0(0)$ is the difference of the triplet and singlet S -wave phase shifts, and the average is over the thermal distribution of electron energies. If the scattering length approximation for the S -wave phase shifts is adequate and higher partial waves are not important, the observed ratio of shift to broadening requires a sodium polarization of about 10%. However, since the sodium polarization was not measured, the observations do not provide a check on the correctness of Eq. (1) or of the assumptions which were made.

Recently Balling, Hanson, and Pipkin⁹ have measured shifts in the free-electron spin-resonance frequency due to collisions with polarized rubidium atoms. In this work the rubidium polarization was 90% or higher and the electrons were believed to be well thermalized. They also derived complete theoretical formulas for the shift and broadening of the electron spin resonance due to electron-atom exchange collisions in terms of the differences between the triplet and singlet scattering phase shifts for all partial waves. Their interpretation of the observed ratio of shift to half-width of -0.05 ± 0.01 was that the S -wave phase-shift difference was near some multiple of $(\pi/2)$ for electrons of the average energy, with $(\pi/2)$ itself most likely, and that higher partial waves were probably not important.

In Sec. 2 of the present paper an alternate derivation of the frequency shift and line broadening formulas for electron-atom exchange collisions is given. This deri-

¹ H. G. Dehmelt, *Phys. Rev.* **109**, 381 (1958).

² A. Kastler, *J. Phys. Radium* **11**, 255 (1950).

³ H. G. Dehmelt, *Phys. Rev.* **105**, 1487 (1957).

⁴ A. Salmona and M. J. Seaton, *Proc. Phys. Soc. (London)* **77**, 617 (1961).

⁵ J. Hobart and P. Franken, International Conference on Optical Pumping, Heidelberg University, April, 1962 (unpublished abstract).

⁶ J. L. Hobart, thesis, University of Michigan, 1962 (unpublished).

⁷ P. Franken (private communication).

⁸ P. L. Bender, International Conference on Optical Pumping, Heidelberg University, April, 1962 (unpublished abstract).

⁹ L. C. Balling, R. J. Hanson, and F. M. Pipkin, *Phys. Rev.* **133**, A607 (1964).

vation is based on the expressions one would obtain from Baranger's general impact theory¹⁰ if the triplet and singlet states were energy eigenstates during the time between collisions. The proof that the resulting formulas hold for arbitrary alkali nuclear spin is given in the Appendix.

In Sec. 3 the available theoretical information on phase shifts for electron-alkali scattering is reviewed. The modified effective range theory expansions of the *S*-wave phase shifts in terms of the wave number *k* appear useful for hydrogen and sodium but break down for cesium in the temperature range of interest. Phase-shift calculations as a function of energy for hydrogen and cesium and the scattering lengths for sodium are used in discussing the frequency-shift ratio for rubidium. The experimentally observed result is not easy to understand in this way, and thus more extensive phase-shift calculations as well as further frequency-shift experiments with cesium and sodium appear to be desirable.

2. ALTERNATE DERIVATION OF ELECTRON SPIN RESONANCE FREQUENCY SHIFT

For the experimental conditions of Hobart and Franken⁵ and of Balling, Hanson, and Pipkin,⁹ the alkali and buffer gas densities are low enough so that the impact approximation is very good. The number of electrons is much less than the number of alkali atoms, and we thus consider only electron-alkali collisions. Magnetic interaction energies are small enough to be neglected during collisions. We take the axis of quantization as along the magnetic-field direction. The components of the free-electron spin and the valence-electron spin along the axis are labeled as m_e and m_J , respectively, while the total electron spin and its component along the axis are S and m_S . We assume that the alkali nuclear spin is zero for simplicity and show in the Appendix that the result is independent of the nuclear spin. However, we do require that the off-diagonal elements of the alkali atom density matrix in the energy (i.e., F , M_F) representation between collisions be negligible.

If the triplet and singlet states of the coupled free electron and alkali-valence electron were nondegenerate energy eigenstates between collisions, we could use the general impact theory results of Baranger¹⁰ to obtain the shift and broadening of the transition between these levels in terms of the scattering phase shifts $\delta_l(1)$ and $\delta_l(0)$ for the triplet and singlet states, respectively. The subscript refers to the *l*th partial wave. Taking the triplet as the higher level, the half-width and the shift are given, respectively, in angular frequency by

$$W = \left\langle \frac{1}{2} \int d\Omega |f_1(\Omega) - f_0(\Omega)|^2 \right\rangle_{av}, \quad (2)$$

$$d = \left\langle - (2\pi n v / k) R [f_1(0) - f_0(0)] + \frac{1}{2} n v i \int d\Omega [f_0^*(\Omega) f_1(\Omega) - f_0(\Omega) f_1^*(\Omega)] \right\rangle_{av}. \quad (3)$$

Here $f_1(\Omega)$ and $f_0(\Omega)$ are the triplet and singlet elastic scattering amplitudes as a function of direction, R means the real part, n is the number of scatterers per a_0^3 , v is the electron velocity in a_0/sec , a_0 is the Bohr radius for hydrogen, and k^2 is the electron energy in units of 13.6 eV. The average is over the electron-velocity distribution, which is assumed to be Maxwellian. Since

$$f_S(\theta) = (2ik)^{-1} \sum_l (2l+1) (e^{2i\delta_l(S)} - 1) P_l(\cos\theta), \quad (4)$$

where $S=1$ and 0 correspond to the triplet and singlet amplitudes, we find

$$w = \langle (\pi n v / k^2) \sum_l (2l+1) [1 - \cos 2\Delta_l] \rangle_{av}, \quad (5)$$

$$d = \langle - (\pi n v / k^2) \sum_l (2l+1) [\sin 2\Delta_l] \rangle_{av}, \quad (6)$$

where $\Delta_l = \delta_l(1) - \delta_l(0)$. Converting n and v to cgs units and labeling the most probable electron velocity as v_m and the corresponding value of k as k_m , we have

$$w = \left(\frac{\pi a_0^3 n v_m}{k_m^2} \right) \sum_l (2l+1) \langle (1 - \cos 2\Delta_l) / (v/v_m) \rangle_{av}, \quad (7)$$

$$d = - \left(\frac{\pi a_0^3 n v_m}{k_m^2} \right) \sum_l (2l+1) \langle (\sin 2\Delta_l) / (v/v_m) \rangle_{av}. \quad (8)$$

This is equivalent to the following collisional rates of change of the density matrix elements ${}^o\sigma_{ij}$ in the electron-spin-coupled representation:

$$(d{}^o\sigma_{ij}/dt)_{\text{Col.}} = - (w - id) {}^o\sigma_{ij} \quad (9)$$

for i corresponding to a singlet state and j to a triplet state, and

$$(d{}^o\sigma_{ij}/dt)_{\text{Col.}} = 0 \quad (10)$$

for i and j both corresponding to singlet or both to triplet states.

In reality, the states between which transitions are observed are the free-electron spin states. We will let ρ be the free-electron spin density matrix in the usual representation. Ignoring the off-diagonal elements for the alkali spin density matrix u and also ignoring correlations between the free-electron and alkali-electron density matrices, we can write the total spin

¹⁰ M. Baranger, Phys. Rev. 111, 481 (1958).

density matrix $\sigma = \rho \times u$ as

$$\sigma = \begin{array}{c|cccc} & M_e, M_J & & & \\ & \frac{1}{2}, \frac{1}{2} & -\frac{1}{2}, \frac{1}{2} & \frac{1}{2}, -\frac{1}{2} & -\frac{1}{2}, -\frac{1}{2} \\ \hline M_e, M_J & & & & \\ \frac{1}{2}, \frac{1}{2} & A\rho_{11} & A\rho_{12} & 0 & 0 \\ -\frac{1}{2}, \frac{1}{2} & A\rho_{21} & A\rho_{22} & 0 & 0 \\ \frac{1}{2}, -\frac{1}{2} & 0 & 0 & B\rho_{11} & B\rho_{12} \\ -\frac{1}{2}, -\frac{1}{2} & 0 & 0 & B\rho_{21} & B\rho_{22} \end{array} \quad (11)$$

Transforming to the electron-spin-coupled representation by the transformation

$${}^e\sigma = \Gamma \sigma \Gamma', \quad (12)$$

where

$$\Gamma = \begin{array}{c|cccc} & M_e, M_J & & & \\ & \frac{1}{2}, \frac{1}{2} & -\frac{1}{2}, \frac{1}{2} & \frac{1}{2}, -\frac{1}{2} & -\frac{1}{2}, -\frac{1}{2} \\ \hline S, M_S & & & & \\ 1, 1 & 1 & & & \\ 1, 0 & & 1/\sqrt{2} & 1/\sqrt{2} & \\ 1, -1 & & & & 1 \\ 0, 0 & & -1/\sqrt{2} & 1/\sqrt{2} & \end{array} \quad (13)$$

gives

$${}^e\sigma = \begin{array}{c|cccc} & S, M_S & & & \\ & 1, 1 & 1, 0 & 1, -1 & 0, 0 \\ \hline S, M_S & & & & \\ 1, 1 & \dots & \dots & \dots & -(A\rho_{12})/\sqrt{2} \\ 1, 0 & \dots & \dots & \dots & (\rho_{11}-A)/2 \\ 1, -1 & \dots & \dots & \dots & (B\rho_{21})/\sqrt{2} \\ 0, 0 & -(A\rho_{21})/\sqrt{2} & (\rho_{11}-A)/2 & (B\rho_{12})/\sqrt{2} & \dots \end{array} \quad (14)$$

The other elements are not necessarily zero but are not needed. From Eq. (9), setting $p = \frac{1}{2}(w - id)$,

$$({}^e d\sigma/dt)_{\text{Col.}} = \begin{array}{c|cccc} & S, M_S & & & \\ & 1, 1 & 1, 0 & 1, -1 & 0, 0 \\ \hline S, M_S & & & & \\ 1, 1 & 0 & 0 & 0 & \sqrt{2}p^*A\rho_{12} \\ 1, 0 & 0 & 0 & 0 & -p^*(\rho_{11}-A) \\ 1, -1 & 0 & 0 & 0 & -\sqrt{2}p^*B\rho_{21} \\ 0, 0 & \sqrt{2}pA\rho_{21} & -p(\rho_{11}-A) & -\sqrt{2}pB\rho_{12} & 0 \end{array} \quad (15)$$

Returning to the uncoupled representation by the transformation

$$({}^e d\sigma/dt)_{\text{Col.}} = \Gamma' (d^e\sigma/dt)_{\text{Col.}} \Gamma \quad (16)$$

gives

$$({}^e d\sigma/dt)_{\text{Col.}} = \begin{array}{c|cccc} & M_e, M_J & & & \\ & \frac{1}{2}, \frac{1}{2} & -\frac{1}{2}, \frac{1}{2} & \frac{1}{2}, -\frac{1}{2} & -\frac{1}{2}, -\frac{1}{2} \\ \hline M_e, M_J & & & & \\ \frac{1}{2}, \frac{1}{2} & 0 & -p^*A\rho_{12} & p^*A\rho_{12} & 0 \\ -\frac{1}{2}, \frac{1}{2} & -pA\rho_{21} & (w/2)(\rho_{11}-A) & -i(d/2)(\rho_{11}-A) & pB\rho_{12} \\ \frac{1}{2}, -\frac{1}{2} & pA\rho_{21} & i(d/2)(\rho_{11}-A) & -(w/2)(\rho_{11}-A) & -pB\rho_{12} \\ -\frac{1}{2}, -\frac{1}{2} & 0 & p^*B\rho_{21} & -p^*B\rho_{21} & 0 \end{array} \quad (17)$$

Finally, by contracting we obtain

$$\begin{array}{c}
 M_e \\
 \swarrow \\
 M_e \\
 \downarrow \\
 (d\rho/dt)_{\text{Col.}} = \begin{array}{c} \frac{1}{2} \\ -\frac{1}{2} \end{array}
 \end{array}
 \begin{array}{c}
 \frac{1}{2} \qquad \qquad \qquad -\frac{1}{2} \\
 \hline
 \begin{array}{cc}
 -\frac{1}{2}w(\rho_{11}-A) & -[\frac{1}{2}w+\frac{1}{2}id(A-B)]\rho_{12} \\
 -[\frac{1}{2}w-\frac{1}{2}id(A-B)]\rho_{21} & \frac{1}{2}w(\rho_{11}-A)
 \end{array}
 \end{array}
 \quad (18)$$

The above collisional rates of change for the off-diagonal elements of ρ correspond to the following half-width and frequency shift for the free-electron spin resonance:

$$w' = \frac{1}{2}w, \quad (19)$$

$$d' = \frac{1}{2}P_A d, \quad (20)$$

where $P_A = A - B$ is the alkali electron spin polarization. These formulas are the same as those obtained by Balling, Hanson, and Pipkin⁹ by essentially repeating Baranger's calculation for the case of electron exchange collisions. They have been rederived here mainly for pedagogic reasons. The ratio of shift to broadening for the case where only S -wave collisions are important agrees with our earlier estimated value except that the velocity averaging procedure is now specified.

3. LOW-ENERGY ELECTRON-ALKALI ELASTIC SCATTERING

We are now ready to review the available information on low-energy electron-alkali elastic scattering phase shifts. The only calculations available which extend over the necessary energy range are for hydrogen and cesium. For sodium, only the S -wave scattering lengths are available.

We define

$${}^s I_l \equiv \langle (\sin 2\Delta_l) / (v/v_m) \rangle_{\text{av}}, \quad (21)$$

$${}^c I_l \equiv \langle (1 - \cos 2\Delta_l) / (v/v_m) \rangle_{\text{av}}, \quad (22)$$

$$R \equiv (-d'/P_A w'), \quad (23)$$

$$x \equiv (v/v_m) = (k/k_m). \quad (24)$$

Then,

$$R = \left[\sum_l (2l+1) {}^s I_l \right] / \left[\sum_l (2l+1) {}^c I_l \right], \quad (25)$$

where

$${}^s I_l = (4/\sqrt{\pi}) \int_0^\infty x [\sin 2\Delta_l(k)] e^{-x^2} dx, \quad (26)$$

$${}^c I_l = (4/\sqrt{\pi}) \int_0^\infty x [1 - \cos 2\Delta_l(k)] e^{-x^2} dx. \quad (27)$$

For hydrogen and cesium, we will use $T = 290^\circ\text{K}$, corresponding to the rubidium experiments of Balling, Hanson, and Pipkin,⁹ while for sodium we will also use $T = 410^\circ\text{K}$, corresponding roughly to the sodium experiments of Hobart and Franken^{5,6} and of Dehmelt.¹

We have $k_m(290^\circ\text{K}) = 0.0429$ and $k_m(410^\circ\text{K}) = 0.0510$.

For the hydrogen S wave, we take the results of Schwartz.¹¹ However, his lowest points are for $k^2 = 0.01$ and 0.02 . We must therefore use an interpolation formula. O'Malley, Spruch, and Rosenberg^{12,13} have shown that the normal effective range theory expansion is not valid in the presence of a long-range potential such as the polarization potential $V(r) = -\alpha/r^4$. However, a modified effective range theory expansion which is valid for atoms which have spherically symmetric ground states has been given by these authors. From Eq. (2.3) of O'Malley,¹⁴ we obtain

$$\Delta_0 = [\Lambda(1) - \Lambda(0)]k + \frac{4}{3}[\Lambda(1) - \Lambda(0)](\alpha/a_0^3)k^3/mk + 0(k^3), \quad (28)$$

$$\Delta_1 = 0(k^3). \quad (29)$$

Here $\Lambda(1)$ and $\Lambda(0)$ are the triplet and singlet S -wave scattering lengths and α is the atomic polarizability. From Schwartz's paper $[\Lambda(1) - \Lambda(0)] = 4.196$. Using the hydrogen polarizability¹⁵ of $4.5a_0^3$ to calculate the coefficient of k^3/mk and including a k^3 term, we obtain

$$\Delta_0 = 4.196k + 25.2k^3/mk + 24k^3, \quad (30)$$

where the coefficient of k^3 has been fit to Schwartz's value at $k = 0.1$. With this interpolation formula, ${}^s I_0 = 0.339$ and ${}^c I_0 = 0.066$.

For the P wave we use the results of Burke and Schey.¹⁶ Including only a k^3 term and fitting to their lowest point, we find $\Delta_1 = 3.8k^3$, ${}^s I_1 = 0.001$, ${}^c I_1 = 0.000$. Also from Burke and Schey, higher partial waves are negligible. Thus, $R_H(290^\circ\text{K}) = 5.2$.

For cesium, the only calculated phase shifts which appear to be useful for the present problem are the very recent ones of Stone and Reitz.¹⁷ Values of Δ_0 , Δ_1 , and Δ_2 obtained from their results are given in Table I. It appears that the first three or four terms of the modified effective range theory expansion are not adequate to represent the results even at moderate values of k . This is not surprising in view of the high

¹¹ C. Schwartz, Phys. Rev. **124**, 1468 (1961).

¹² T. F. O'Malley, L. Spruch, and L. Rosenberg, J. Math. Phys. **2**, 491 (1961).

¹³ T. F. O'Malley, L. Rosenberg, and L. Spruch, Phys. Rev. **125**, 1300 (1962).

¹⁴ T. F. O'Malley, Phys. Rev. **130**, 1020 (1963).

¹⁵ N. F. Mott and I. N. Sneddon, *Wave Mechanics and its Applications* (Clarendon Press, Oxford, 1948).

¹⁶ P. G. Burke and H. M. Schey, Phys. Rev. **126**, 147 (1962).

¹⁷ P. M. Stone and J. R. Reitz, Phys. Rev. **131**, 2101 (1963).

TABLE I. Triplet-singlet phase-shift differences Δ_l for the S , P , and D partial-wave scattering of electrons from cesium.^a The functions $f_0=(0.78)[1-\exp(-36k)]$ and $f_1=-0.66k \times [1-\exp(-300k^2)]$ are chosen to approximate Δ_0 and Δ_1 in the energy range of interest.

k^2	Δ_0	Δ_1	Δ_2	f_0	f_1
0.001	0.55	-0.05	0.00	0.53	-0.05
0.003	0.65	-0.21	0.01	0.67	-0.21
0.005	0.70	-0.37	0.01	0.72	-0.36
0.007	0.74	-0.49	0.00	0.74	-0.48
0.010	0.77	-0.64	0.03	0.76	-0.63
0.013	0.79	-0.75	0.04	0.77	-0.74
0.020	0.83	-0.93	0.15	0.77	-0.93

^a See Ref. 17.

polarizability of cesium.¹⁸ Instead, we represent Δ_0 and Δ_1 by functions $f_0=(0.78)[1-\exp(-36k)]$ and $f_1=-0.66k[1-\exp(-300k^2)]$ which give adequate agreement with Δ_0 and Δ_1 over the range of interest and which have leading terms proportional to k and k^3 , respectively, near zero energy. These leading terms agree with the modified effective range theory. If one interprets the coefficient of the leading term in f_0 as a rough approximation to the triplet-singlet scattering-length difference, this gives $\Lambda(1)-\Lambda(0)=28$. Using f_0 and f_1 , we find for cesium ${}^sI_0=0.94$, ${}^eI_0=0.61$, ${}^sI_1=-0.03$, and all other contributions are 0.01 or less. Thus, we obtain $R_{Cs}(290^\circ\text{K})\simeq 1.4$. Since the contributions from P and higher partial waves are small for cesium as well as hydrogen, the S -wave approximation is presumably good for the other alkalis also.

A possible difficulty with the interpretation given above appears when one looks at the calculated triplet S -wave phase shifts rather than just the phase-shift differences. The triplet phase shifts decrease fairly slowly, but the first one is 0.37 rad above 3π . Since the zero-energy limit must be a multiple of π , this raises the possibility that the zero-energy value consistent with the finite energy values is 4π . If so, all the values of Δ_0 in Table I should be increased by π . This would change only the way in which one extrapolates from the lowest calculated point to zero energy and would probably not change the value of R by more than 20%.

Actually, a scattering length difference large enough to give such a steep initial slope for Δ_0 as a function of k seems questionable. Some support for this view comes from the fact that the P -wave triplet phase shifts are also slowly decreasing and the lowest energy one is 0.05 rad above 2π . Since a zero-energy limit of anything but 2π seems inconceivable, it appears that the low-energy values for the S -wave phase shifts may also be somewhat offset by the computational procedure used by Stone and Reitz. This makes the uncertainty in Δ_0 appear to be of the order of 0.4 rad or larger and raises the possibility that Δ_0 could approach or go through $(\pi/2)$ at thermal energies and give a very small value for R_{Cs} .

¹⁸ G. E. Chamberlain and J. C. Zorn, Phys. Rev. **129**, 677 (1963).

In the case of sodium the main pieces of information available are the triplet and singlet S -wave scattering lengths $\Lambda(1)=9$ and $\Lambda(0)=-12$ calculated by Salmona and Seaton. If the scattering length approximation under which $\delta_0(1)=k\Lambda(1)$, $\delta_0(0)=k\Lambda(0)$ were valid, we would have $\Delta_0=21k$. Including only the S -wave contribution, this gives ${}^sI_0=0.68$, ${}^eI_0=1.28$, $R_{Na}=0.53$, at 410°K while at 290°K ${}^sI_0=0.80$, ${}^eI_0=1.10$, $R_{Na}=0.73$. In the same approximation, defining

$$\bar{Q}_{\text{ex}}=\langle(vQ_{\text{ex}}(v))\rangle_{\text{av}}/(\bar{v}), \quad (31)$$

we find,

$$\bar{Q}_{\text{ex}}=\pi a_0^2(\sqrt{\pi}{}^eI_0/4k_m^2). \quad (32)$$

At 410°K this gives $\bar{Q}_{\text{ex}}=220\pi a_0^2$. Dehmelt's experimental result,¹ adjusted to correspond to \bar{v} instead of v_{rms} , is $Q_{\text{ex}}\geq 280\pi a_0^2$. Salmona and Seaton's zero energy cross section is $Q_{\text{ex}}=440\pi a_0^2$.

We will next calculate the modified effective range theory expansion for sodium. From Eq. (4.9) of O'Malley, Rosenberg, and Spruch¹³ we find

$$\Delta_0=[\Lambda(1)-\Lambda(0)]k+Ak^3lnk+Bk^3+Ck^4+\dots \quad (33)$$

Here,

$$A=\frac{4}{3}(\alpha/a_0^3)[\Lambda(1)-\Lambda(0)], \quad (34)$$

$$B=\{A \cdot \ln[1.23(\alpha/a_0^3)^{1/2}] + \frac{1}{3}\pi(\alpha/a_0^3)^{1/2}[\Lambda^2(0)-\Lambda^2(1)] - \frac{1}{3}[\Lambda^3(1)-\Lambda^3(0)] + \frac{1}{2}[\Lambda^2(0)r_{\text{poS}}-\Lambda^2(1)r_{\text{poT}}]/a_0\}, \quad (35)$$

$$C=\frac{2}{3}\pi(\alpha/a_0^3)[\Lambda^2(1)-\Lambda^2(0)], \quad (36)$$

where r_{poT} and r_{poS} are the triplet and singlet modified effective ranges and α is the polarizability. Using¹⁸ $\alpha=21 \times 10^{-24}$ cm³, we calculate $A=3970$, $C=-18700$, and $B=10600+72(r_{\text{poS}}/a_0)-40.5(r_{\text{poT}}/a_0)$. Transforming to the variable $x=(k/k_m)$

$$\Delta_0(410^\circ\text{K})=1.07x-0.16x^3 + [0.0095(r_{\text{poS}}/a_0)-0.0054(r_{\text{poT}}/a_0)]x^3 + 0.52x^3lnx-0.127x^4+\dots \quad (37)$$

We do not know the modified effective ranges, but at least one of them must be very large in order to make the coefficient of x^3 approach one. Since the other coefficients of x^3 and higher terms are fairly small, it appears that the modified range theory expansion may be useful for sodium at 410°K . The exchange cross section and the ratio of electron frequency shift to line broadening calculated in the scattering length approximation thus may be fairly accurate.

Another procedure is to approximate the sodium phase-shift differences by the same function of (k/k_{ex}) as was used to fit the cesium results of Stone and Reitz. Here k_{ex} is the excitation energy for the atom in question. The reason for trying this is that the values of Δ_0 for cesium derived from Stone and Reitz are rather similar to those for hydrogen if both are plotted as a function of (k/k_{ex}) . At 410°K we obtain ${}^eI_0\simeq 0.94$, ${}^sI_0\simeq 0.60$, $R_{Na}\simeq 1.6$, and $\bar{Q}_{\text{ex}}\simeq 100\pi a_0^2$. This procedure

gives poor agreement with Dehmelt's quoted lower limit for the experimental exchange cross section. While Dehmelt's number is not actually a lower limit, since no uncertainties are included, it would indicate a definite error in the experiment if the cross section were as low as $100\pi a_0^2$. Thus, the somewhat similar behavior of the presently available phase-shift differences for cesium and hydrogen does not appear to be characteristic of sodium.

One other possible source of information concerning the phase-shift difference for sodium comes from a rough estimate of the sodium polarization in Hobart's experiment based on a trace he gives⁶ of the sodium Zeeman resonances at 3.68 G. This trace (Fig. 3.10 of Ref. 6) indicates a ratio of roughly 2.8:1 for the strongest and weakest $F=2$ Zeeman components. Assuming that the sublevel populations are independent of F and that sublevels differing in M_F by 1 have a constant ratio of populations leads to an approximate sodium-electron polarization $P_A = -0.17$. These assumptions correspond to spin-exchange equilibrium between the sodium atoms. Actually, the small amplitude of the $F=1$ resonances indicates that the magnitude of the polarization was probably higher. However, since we do not know precisely what correction to make, we will use the above number. Combining this with the value $R_{\text{Na}} = 0.53$ calculated on the scattering length approximation using the scattering lengths of Salmona and Seaton gives a ratio of shift to half-width of 0.09. While the maximum ratio of shift to half-width observed was only 0.05, it is not clear that the trace given by Hobart applies to the same experimental conditions. Thus, little can be said about the agreement of theory and experiment for sodium. However, it would not be surprising if the sodium phase-shift difference curve actually rose somewhat more rapidly than the scattering length approximation curve which we have used.

4. DISCUSSION

We are now ready to discuss the results of Balling, Hanson, and Pipkin.⁹ Their experimental value of $R = 0.05 \pm 0.01$ for rubidium at about 290°K is more than an order of magnitude less than the corresponding value for cesium calculated from the phase shifts of Stone and Reitz.¹⁷ If the phase-shift difference curve for rubidium had the same shape as that calculated for cesium, it would have to have more than twice as high a maximum in order to agree with experiment. However, it seems uncertain whether a calculation for rubidium done by a method similar to that of Stone and Reitz for cesium would give this much different a result. Also, it appears doubtful whether the rather high value for the cesium polarizability used by Stone and Reitz can account for the possible discrepancy.

The argument given by Balling, Hanson, and Pipkin that the Rb^- ion is just barely bound and that therefore $\delta_0(0)$ should be about $\pi/2$ appears to be open to question. This argument, which was also used by Dehmelt¹ for Na, is based on the result for a deep square-well

potential¹⁹ and is only valid if the binding energy is small compared with the incident electron energy. The modified effective range theory expansion^{12,13} shows that the square well is not a good approximation at extremely low energies. Also, the binding energies of alkali negative ions are believed to be much higher than thermal energies.²⁰ In particular, a calculation by Szasz²¹ gives binding energies of 0.43, 0.53, 0.49, 0.43, and 0.42 eV for Li, Na, K, Rb, and Cs. These results are not expected to be very accurate, as indicated by the value for Li of 0.62 eV obtained by Weiss in a much more thorough calculation.²⁰ However, the relative values may be good and fairly strong binding for Rb^- seems likely.

In view of the possible discrepancy mentioned above, the assumptions made in the frequency-shift calculation were reviewed. The least certain ones appeared to be that the alkali matrix in the F, M_F representation can be taken as diagonal and that direct interactions between the free electrons can be neglected. The first assumption is discussed briefly at the end of the Appendix and appears to hold for the rubidium experiments. The second assumption is more difficult to investigate because of the very long range of the electron-electron interaction. However, if such interactions were important one might expect that normal variations of the experimental conditions would have given erratic results.

Assuming that the experimental results and their interpretation in terms of the scattering phase shifts are correct, we are left with two possible hypotheses. One is that the rubidium S -wave phase-shift difference Δ_0 increases rapidly at very low energies and fortuitously passes through or approaches $(\pi/2)$ at the proper energy to make R small. This seems somewhat unlikely but cannot be ruled out. The other possibility is that Δ_0 for the higher alkalis rises rapidly initially but for some reason flattens out near $(\pi/2)$ at roughly thermal energies. This would require that the low-energy phase-shift differences for cesium taken from Stone and Reitz be off by approximately 1 rad.

5. CONCLUSIONS

In view of the large difference between the experimental ratio of shift to broadening for rubidium and the ratio calculated for cesium using the phase shifts of Stone and Reitz, the present situation appears to be somewhat unsatisfactory. The quickest approach to seeing if there is a real discrepancy between experiment and theory would be an experimental measurement on cesium.²² However, in view of the difficulty of calcu-

¹⁹ N. F. Mott and H. S. W. Massey, *The Theory of Atomic Collisions* (Clarendon Press, Oxford, 1949), 2nd ed.

²⁰ L. M. Branscomb, in *Atomic and Molecular Processes*, edited by D. R. Bates (Academic Press Inc., New York, 1962).

²¹ L. Szasz, *Acta Phys. Acad. Sci. Hung.* **6**, 307 (1956).

²² *Note added in proof.* Recent results for the ratio of frequency shift to line broadening in cesium appear to be similar to those for rubidium: L. C. Balling and F. M. Pipkin, *Bull. Am. Phys. Soc.* **9**, 91 (1964). There is thus a definite discrepancy with the cesium phase-shift calculation of Stone and Reitz.

lations on cesium, it also appears to be desirable to repeat the experiments for sodium or for hydrogen.

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APPENDIX: DERIVATION OF ELECTRON SPIN RESONANCE FREQUENCY SHIFT FOR ARBITRARY NUCLEAR SPIN

We will treat the case of electrons with an arbitrary 2×2 spin-density matrix ρ colliding with alkali atoms having an electron spin of $\frac{1}{2}$ and a nuclear spin I . ρ is taken to be in the M_e representation, where M_e is the free-electron spin component along the axis and the two states are ordered according to decreasing M_e . The alkali spin density matrix u_{F, M_F} in the F, M_F representation is assumed to be diagonal. The alkali sublevels are taken to be listed in order of decreasing M_F and subordered according to decreasing F ; i.e., the F, M_F order of listing is $[(I+\frac{1}{2}, I+\frac{1}{2}), (I+\frac{1}{2}, I-\frac{1}{2}), (I-\frac{1}{2}, I-\frac{1}{2}), (I+\frac{1}{2}, I-\frac{3}{2}), \dots]$. When u_F is transformed to the M_I, M_J representation in which the states are ordered according to decreasing M_I and subordered according to decreasing M_J , the resulting matrix u will have off-diagonal elements connecting only the second and third, the fourth and fifth, etc., states. This is because there can be no off-diagonal elements connecting states with different values of $(M_J + M_I)$. The diagonal elements can be labeled $(A_I, B_I, A_{I-1}, B_{I-1}, \dots)$, where A corresponds to $M_J = \frac{1}{2}$, B to $M_J = -\frac{1}{2}$, and the subscript to M_I . Note that the expectation value of the electron polarization for the atom is given by

$$P_A = \sum_{M_I=-I}^I (A_{M_I} - B_{M_I}). \quad (38)$$

We now form the density matrix σ for the electron-plus-atom system in the (M_e, M_J, M_I) representation by taking the direct product of ρ and of u in the (M_J, M_I) representation. The states of σ are ordered according to decreasing M_I , first subordered according to decreasing M_J , and second subordered according to decreasing M_e . σ can be thought of as made up of $(2I+1)^2 4 \times 4$ submatrices. The 4×4 submatrices σ_{M_I} along the diagonal of σ which correspond to different M_I are of the form given in Eq. (11) except that A and B are replaced by A_{M_I} and B_{M_I} .

The transformation of σ to the representation with the electron spins coupled and the states ordered by decreasing M_I , first subordered by decreasing values of the total electron spin S , and second subordered by decreasing values of M_J is given by the following

transformation:

$${}^c\sigma = \Gamma_I \sigma \Gamma_I'. \quad (39)$$

Γ_I is made up of $2I+1$ identical 4×4 submatrices Γ along its diagonal, with Γ given by Eq. (13). We find then that the $2I+1$ 4×4 submatrices along the diagonal of ${}^c\sigma$ are given by

$${}^c\sigma_{M_I} = \Gamma \sigma_{M_I} \Gamma'. \quad (40)$$

We can now make use of the results for the case of zero nuclear spin. When we find $(d\sigma/dt)_{\text{Col}}$, we will contract it to obtain $(d\rho/dt)_{\text{Col}}$, as was done in Sec. 2. The only parts of $(d\sigma/dt)_{\text{Col}}$, which we will need are the 4×4 submatrices $(d\sigma_{M_I}/dt)_{\text{Col}}$. However, since

$$(d\sigma_{M_I}/dt)_{\text{Col}} = \Gamma' (d{}^c\sigma_{M_I}/dt)_{\text{Col}} \Gamma \quad (41)$$

and since $(d{}^c\sigma_{M_I}/dt)_{\text{Col}}$ is obtained from ${}^c\sigma_{M_I}$ in the same way that $(d{}^c\sigma/dt)_{\text{Col}}$ was obtained from ${}^c\sigma$ in Sec. 2, the contribution to $(d\rho/dt)_{\text{Col}}$ from each σ_{M_I} is identical to that given in Eq. (18) except with A and B replaced by A_{M_I} and B_{M_I} . Thus, $(d\rho/dt)_{\text{Col}}$ is the same as for the case of zero nuclear spin except that $A \rightarrow \sum_{M_I} A_{M_I}$ and $B \rightarrow \sum_{M_I} B_{M_I}$. In particular, $w' = \frac{1}{2}w$ and $d' = \frac{1}{2}dP_A$, which are identical to Eqs. (19) and (20) for the case of zero nuclear spin.

In this calculation it was assumed that u_{F, M_F} was diagonal. However, u_{F, M_F} does have two off-diagonal elements which have approximately the same time dependence as the off-diagonal elements of ρ . While the rf field at the electron spin resonance frequency cannot directly produce finite values for these elements because the corresponding transition would require $\Delta M_I = 2I+1$, these elements can still be produced by the electron-alkali collisions. Thus, in order to be sure that off-diagonal elements of u_{F, M_F} do not change the electron frequency shift and line broadening, we must show that these elements are much smaller than the off-diagonal elements of ρ .

A direct calculation for arbitrary nuclear spin appears to be difficult. However, the calculation can be carried through for zero nuclear spin with the special condition that the rf field does not affect the alkali atom directly. In this case, it is found that the condition for the off-diagonal elements of u to be much smaller than those of ρ is as follows: The ratio of alkali density to electron density must be large compared with the ratio of the width of the electron spin resonance due to alkali collisions compared with the reciprocal of the decay time for the alkali off-diagonal elements. If the decay times for the off-diagonal elements of both ρ and u were determined by electron-alkali exchange collisions, this condition would not hold. However, as long as the decay time for the alkali off-diagonal elements is determined mainly by some other cause such as light absorption rather than by electron-alkali exchange collisions, then the assumption that u is diagonal should be quite good. This condition was apparently satisfied in the experiments of Balling, Hanson, and Pipkin, and of Hobart and Franken.