PHYSICAL REVIEW VOLUME 137, NUMBER 4A 15 FEBRUARY 1965

Theory of Spin Exchange between Optically Pumped Rubidium and Foreign Gas Nuclei*

R. M. HERMAN†
TRW Space Technology Laboratories, Redondo Beach, California

(Received 9 September 1964)

Cross sections for spin exchange between alkali valence electrons and foreign nuclei in collisions of atomic Rb with atomic He, Ne, Kr, and molecular hydrogen are calculated. It is concluded that while classical dipolar hyperfine interactions are negligible, scalar interaction strengths are greatly magnified as a result of electron exchange. Specifically, it is shown that cross sections associated with the latter are as much as 10^5 times those calculated if exchange effects are neglected. For He^3, Ne^{21}, Kr^{83}, H_2, and D_2, the estimated cross sections for mutual spin flip are 1.1×10^{-24}, 1.0×10^{-23}, 1.0×10^{-22}, 3.6×10^{-25}, and 5.5×10^{-26} cm^2. For He^3 and Ne^{21}, these are comparable in magnitude to the corresponding experimental cross sections for the deplorization of optically oriented Rb. For the other gases considered, they are relatively much smaller, however. Cross sections for Rb electronic spin disorientation through spin-orbit interactions in collisions with molecular hydrogen are also calculated. They are considerably larger than those observed for the disorientation of optically pumped Rb vapor.

I. INTRODUCTION

IN a recent article,[1] the disorientation of atomic Rb electronic spins in collisions with rare-gas atoms was analyzed. There, it was concluded that spin-orbit effects give rise to the observed disorientation of optically oriented Rb vapor in rare-gas buffer atmospheres. In the present discussion, we shall analyze another process of importance in the spin dynamics of alkali vapor–rare-gas mixtures. This is the simultaneous flip of alkali valence electronic and rare-gas nuclear spins under the influence of magnetic hyperfine interactions, in cases where the rare-gas nuclei have nonzero spin. Such a phenomenon has been observed by Bouchiat, Carver, and Varnum,[2] who detected a polarization of He^3 nuclei in mixtures with optically oriented Rb vapor. Unfortunately, the cross section for spin exchange was not reported by those investigators, although in a calculation based on their data, Brewer[3] estimated its magnitude as approximately 4×10^{-26} cm^2, an order of magnitude smaller than the observed[4] cross section for disorientation of optically pumped Rb by natural He. To further test the relative importance of spin exchange in the depolarization of alkali vapors, Brewer[3] has also measured disorientation cross sections for Rb-H_2 and Rb-D_2 collisions. From his data, he concluded that hyperfine interactions play a relatively minor role in Rb spin disorientation.

In the present paper, cross sections for Rb valence electronic–rare-gas nuclear spin exchange are calculated. Because of exchange correlations, the calculated cross sections are unexpectedly large, in some cases comparable in magnitude to observed and predicted spin-orbit relaxation cross sections. This is surprising, in view of existing experimental evidence, as well as in view of the weakness of hyperfine—as compared to spin-orbit—interactions in general. Because of the availability of experimental data[3,5] on Rb spin relaxation associated with H_2 and D_2, calculations of the spin-orbit and spin-exchange depolarization cross sections are also made for these encounters. The results are tabulated, along with existing experimental data, in Tables I and II, Sec. IV.

II. GENERAL CONSIDERATIONS

In the present treatment, the alklai is regarded as a single-electron atom and, for simplicity, we shall neglect the alkali nuclear spin. The hyperfine interactions experienced by the rare-gas nucleus in binary collisions with alkalis are governed by the Hamiltonian[6]

$$\mathcal{H}' = -2g_n\beta_n\beta\sum_{i=1}^{n}\left\{\frac{\mathbf{I}\cdot\mathbf{S}_i}{r_{iB}^3} - 3\frac{(\mathbf{I}\cdot\mathbf{r}_{iB})(\mathbf{S}_i\cdot\mathbf{r}_{iB})}{r_{iB}^5} - \frac{8\pi}{3}\delta(\mathbf{r}_{iB})\mathbf{I}\cdot\mathbf{S}_i\right\}, \quad (1)$$

where $\mathbf{I}$ is the rare-gas nuclear spin, $\mathbf{S}_i$ the ith electronic spin (units of $\hbar$), β the Bohr magneton, β_n the nuclear magneton, and g_n the nuclear gyromagnetic ratio. The first two terms in the brace of Eq. (1) represent the polar interaction between two point magnetic dipoles, $\mathbf{r}_{iB}$ being the radius vector extending from the rare-gas nucleus (B) to the ith electron. The third term represents the Fermi contact potential, $\delta(\mathbf{r}_{iB})$ being the three-dimensional delta function in the coordinates of the ith electron relative to the rare-gas nucleus. The summation over i refers to the alkali valence (1) and rare-gas $(2\cdots n)$ electrons.

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*Research supported by the TRW Space Technology Laboratories Independent Research Program.

† Present address: Physics Department, The Pennsylvania State University, University Park, Pennsylvania.

[1] R. M. Herman, Phys, Rev. **136**, A1576 (1964), henceforth re-referred to as I.

[2] M. A. Bouchiat, T. R. Carver, and C. N. Varnum, Phys. Rev. Letters **5**, 373 (1960).

[3] R. G. Brewer, J. Chem. Phys. **37**, 2504 (1962).

[4] R. A. Bernheim, J. Chem. Phys. **36**, 135 (1962).

[5] R. J. McNeal, J. Chem. Phys. **37**, 2726 (1962).

[6] A. Abragam, *The Principles of Nuclear Magnetism* (Oxford University Press, London, 1961).

The conventional technique for estimating spin reorientation cross sections associated with hyperfine interactions appears to be that of (1) estimating the strength of the magnetic interaction between the rare-gas nucleus and the alkali valence electron, thought to be localized at the alkali nuclear site, and (2) then employing standard arguments to estimate the cross sections. In the present treatment, however, we consider primarily the contact interactions. (An estimate of the polar interaction strength in Rb-Ne collisions is made and it is concluded that in general, these interactions are unimportant.) It is shown that electron-exchange effects lead to a marked enhancement of the scalar coupling, thereby causing the associated cross sections to greatly exceed those calculated if one fails to antisymmetrize the electronic eigenfunction for the collision pair. The importance of the exchange-enhanced scalar interaction is dramatized in Table I, where for He^3, Ne^{21}, and Kr^{83}, the depolarization cross sections, as calculated from the contact interaction with exchange effects included, are compared with those calculated on the point-dipole approximation. The former are a few orders of magnitude larger in all cases.

The present treatment of the hyperfine interactions between paramagnetic electrons and neighboring nuclei is not original with the author, having previously been employed by Adrian[7] in his study of magnetic interactions between paramagnetic impurity atoms and lattice nuclei in van der Waals' crystals. The present example of exchange enhancement is possibly more dramatic, however, inasmuch as in the calculation of cross sections it is the *square* of the energy which is of importance.

III. THEORY

Scalar Interactions in Rb–Rare-Gas Collisions

The problem of calculating the scalar interaction strength is, of course, one of first calculating the unpaired spin density at the rare-gas nucleus during collisions. If one were to accept the simple product wave function as a reasonable approximation to the actual many-electron eigenfunction, the effective hyperfine coupling would simply be

$$\mathcal{H}_{\mathrm{eff}}'=(16\pi/3)g_n\beta_n\beta u_1(B)^2\mathbf{I}\cdot\mathbf{S}\,, \tag{2}$$

where $u_1(B)^2$ is the probability density for locating the alkali valence electron at a distance equal to the internuclear separation from the alkali nucleus. The Pauli principle requires the use of antisymmetric many-electron wave functions, however. Accordingly, a more suitable approximation is the Slater function

$$\psi=(1/n!)^{1/2}\det|\varphi_1\varphi_2\cdots\varphi_n|\,, \tag{3}$$

where the φ_i are spin-orbitals of the rare-gas–alkali valence electronic system, each taken to be functionally unchanged from its form in isolated atoms. By using the wave function given above, the effective hyperfine coupling

$$\mathcal{H}_{\mathrm{eff}}'=(16\pi/3)g_n\beta_n\beta u_1(B)^2\eta^2\mathbf{I}\cdot\mathbf{S} \tag{4}$$

is readily obtained. Here, the *exchange enhancement factor* η is given by

$$\eta(R)=\left(1-\sum_{i=2}^{n}\frac{\langle i|1\rangle u_i(B)}{u_1(B)}\right), \tag{5}$$

R being the internuclear separation, the factors $\langle i|1\rangle$ being overlap integrals (which are nonzero only if the spin parts of the spin-orbitals are identical), and $u_i(B)$ the amplitude of the ith orbital at the rare-gas nucleus.

The presence of the exchange terms in Eq. (5) is expected, of course. Somewhat surprising, however, is their magnitude, for the exchange terms involving rare-gas s orbitals are considerably larger than unity, because these orbitals are sharply peaked at their nucleus. By way of example, let us suppose u_1 to be uniform $[=u_1(B)]$ over the volume of a colliding He^3 atom. (This is a good approximation, inasmuch as the alkali orbital can be represented, to good approximation, by

$$u_1\cong u_1(B)+(du_1/dz)_B(z-z_B) \tag{6}$$

in the vicinity of the rare-gas, the z axis being coincident with the interatomic axis. While the linear term is important in the enhancement of polar interactions in the heavier rare gases, it does not influence the scalar coupling.) Assuming the He $1s$ orbitals to be hydrogen-like, with effective nuclear charge parameter Z, it is then readily verified that

$$\eta_{\mathrm{He}}=(1-8)=-7\,, \tag{7a}$$

independent of the value of Z. Because cross sections for spin exchange vary as η^4, application of the Pauli principle is seen to lead directly to a 2400-fold increase in the importance of scalar interactions in causing spin exchange. In heavier rare gases, electrons exist also in higher s orbitals. If we assume each of these to be hydrogen-like ($n=2,3,\cdots$) as well, each with individual effective nuclear charge parameter (or, alternately, screening constant[8]) we find, similarly,

$$\eta_{\mathrm{Ne}}=(1-8+16)=9\,, \tag{7b}$$

$$\eta_{\mathrm{A}}=(1-8+16-24)=-15\,, \tag{7c}$$

$$\eta_{\mathrm{Kr}}=17\,, \tag{7d}$$

$$\eta_{\mathrm{Xe}}=-23\,. \tag{7e}$$

For heavier rare gases, under the above assumptions, exchange correlations thus lead to an increase by some 10^5 in the magnitudes of spin flip cross sections governed by the contact potential.

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[7] F. J. Adrian, J. Chem. Phys. 32, 972 (1960).

[8] See, for instance, L. Pauling and E. B. Wilson, *Introduction to Quantum Mechanics* (McGraw-Hill Book Company, Inc., New York, 1935).

Now the above estimates for η are too small for the following reasons: (1) When the exact form for u_1 is used in place of Eq. (6), the overlap with rare-gas s orbitals is always found to be larger than is obtained with the approximate form for u_1. These changes are relatively negligable in the numerical calculations which have been performed, however. (2) The actual rare-gas s orbitals are more peaked at their nucleus than are the corresponding hydrogen-like functions. This results from the fact that attractive Coulomb forces are relatively stronger (than those corresponding to the $1/r$ potential) near the nuclei, thus tending to "pull in" the orbitals. In all cases, therefore, the values of η as calculated with accurate rare-gas orbitals exceed those calculated on the assumption of hydrogen-like s orbitals. Using as the Rb valence electronic wave function the single-electronic orbital of Callaway and Morgan,[9] simple hydrogen-like orbitals (effective nuclear charge $Z=27/16$) for He,[10] Brown's[11] analytic wave functions for Ne, and the self-consistent-field orbitals of Worsley[12] for Kr, refined values of η have been calculated. The results are

$$\eta_{\mathrm{He}}(b_0)=(1-8.0)=-7.0\,, \tag{8a}$$

$$\eta_{\mathrm{He}}(b_0)=(1-8.0+24.0)=17.0\,, \tag{8b}$$

$$\eta_{\mathrm{Kr}}(b_0)=(1-8.0+17.5-30.6+45.7)=25.6\,, \tag{8c}$$

to be compared with Eqs. (7a), (7b), and (7d), where b_0 is the kinetic radius for the collision pair.

By making the same kinematical approximations, where pertinent, as in I, the spin-flip cross section

$$\sigma \cong 2\varphi_+(b_0)^2\sigma_{\mathrm{kin}} \tag{9}$$

is obtained for nuclear spin $\frac{1}{2}$, after averaging over initial nuclear spin states (assuming equal populations of magnetic substates) and integration over impact parameter. Here, σ_{kin} is the gas kinetic cross section ($=\pi b_0^2$) and $\varphi_+(b_0)$ is the phase shift experienced in a single encounter in which the impact parameter is equal to b_0, and the nuclear and electronic spins are parallel. It is given approximately by

$$\varphi_+(b_0)\cong(4\pi/3)(g_n\beta_n\beta b_0/\hbar\bar{V})u_1(b_0)^2\eta(b_0)^2\,, \tag{10}$$

assuming all collisions to take place with mean relative thermal velocity $\bar{V}$. For arbitrary nuclear spin, the more general result

$$\sigma=\tfrac{2}{3}(8\pi g_n\beta_n\beta u_1(b_0)^2\eta(b_0)^2b_0/3\hbar\bar{V})^2I(I+1)\sigma_{\mathrm{kin}} \tag{11}$$

is readily obtained.

Polar Interactions in Rb–Rare-Gas Collisions

In examining the polar interactions, we also find them to be exchange-enhanced when the atoms overlap. Here, the enhancement is dependent on the overlap between rare-gas p orbitals and u_1 [particularly the linear term in Eq. (6)]. Explicit calculation of the polar interaction strength in heavy rare gases is quite involved, owing to the complicated nature of the spin-density function in the interacting biatomic system and of the integrals which must be evaluated. For He and Ne, however, the situation is simpler. Specifically, in He, polar interaction enhancement is absent because He does not contain electrons in p orbitals. In Ne, only one p orbital must be considered. Using the Rb and Ne wave functions already cited[9,11], exchange effects are found to produce a 50-fold increase in the cross section associated with polar interactions, as compared to a 35 000-fold exchange-dependent increase in the cross section associated with the scalar coupling. This makes the latter more than 100 times the polar-interaction cross section. The relative weakness of the exchange enhancement in polar interactions appears to result from the facts that (1) hyperfine interactions generally tend to be weak for electrons in p orbitals and, to a lesser extent, (2) for Rb, $(du_1/dz)_B$ is small, causing the pertinent overlap integrals to be small. Based on the results for Ne-Rb collisions, we shall assume polar interactions to play a negligible role in all Rb–rare-gas encounters.

Scalar Interactions in Rb–Molecular Hydrogen Collisions

In calculating the spin-flip cross sections for H_2 and D_2, the Wang function,[13] of form

$$\psi(2,3)=(1/2(1-\Delta^2))(u_{\mathrm{A}}(2)u_B(3) +u_A(3)u_B(2))(\alpha_2\beta_3-\beta_2\alpha_3) \tag{12}$$

is employed. Here u_{A} and u_B are hydrogen-like $1s$ functions centered on nuclei A and B of the hydrogen molecule, separated by the equilibrium distance in H_2. The effective charge parameter for the $1s$ functions is 1.166, chosen so as to minimize the electronic ground-state energy. The overlap between the functions u_A and u_B is represented by Δ. The Wang function can be expressed as a linear combination of two Slater-type functions. Accordingly, when the valence electron of Rb is considered, the three-electron wave function can also be represented as a linear combination, thus

$$\psi(1,2,3)=(1/2\sqrt{3}(1-\Delta^2)) \times\{\det|\varphi_1u_A\alpha u_B\beta|-\det|\varphi_1u_A\beta u_B\alpha|\}\,. \tag{13}$$

A straightforward calculation of the spin density at either nucleus, under the approximation $u_1=$ constant over the hydrogen molecular volume, then yields for the enhancement factor

$$\eta^2{}_{\mathrm{H}_2,\mathrm{D}_2}=\{1-8/(1-\Delta)\{1+u_B(A)/u_{\mathrm{A}}(A)\} +32/(1-\Delta^2)\{1-u_B(A)/u_A(A)\}\}=21.4. \tag{14}$$

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[9] J. Callaway and D. F. Morgan, Jr., Phys. Rev. 112, 334 (1958).
[10] See L. Pauling and E. B. Wilson, Ref. 8, pp. 184–5.
[11] F. W. Brown, Phys. Rev. 44, 214 (1933).
[12] B. H. Worsley, Proc. Roy. Soc. (London) A247, 390 (1958).
[13] See Ref. 8.

The effective contact interaction Hamiltonian now becomes

$$\mathcal{H}_{\mathrm{eff}}' = (16\pi/3) g_n \beta_n \beta u_1(H_2)^2 \eta_{\mathrm{H}_2}{}^2 \mathbf{I}\cdot\mathbf{S}\,, \tag{15}$$

where $\mathbf{I}=\mathbf{I}_A+\mathbf{I}_B$. In H_2, the possible resultant spins are 0 and 1, with statistical weights 1:3. For D_2 the possible spins are 0, 1, and 2 with statistical weights 1:3:5. Accordingly, the statistically weighted average value of the factor $I(I+1)$ appearing in Eq. (11) is $\frac{3}{2}$ for H_2 and 4 for D_2.

IV. RESULTS AND DISCUSSION

The depolarization cross sections, calculated according to Eq. (11) for He^3, Ne^{21}, and Kr^{83} are listed in Table I along with the nuclear spins and gyromagnetic ratios for these isotopes. Also included are the cross sections calculated on the point dipole model as explained previously, and the experimentally observed[4,14] cross sections for the depolarization of optically pumped Rb by natural He, Ne, and Kr. Comparison with Table II of I reveals that for He^3 and Ne^{21} cross sections associated with hyperfine interactions, as computed in the present work, are comparable in magnitude to those which have been observed and calculated for spin-orbit relaxation. The calculated cross section for nuclear spin polarization of He^3 is considerably larger than that estimated by Brewer[3] from the data of Bouchiat *et al.*[2] The present estimates indicate that it is also reasonable to expect that rare-gas nuclei other than He^3 might be detectably polarized in collisions with optically pumped alkalis.

TABLE I. Cross sections for the disorientation of Rb electronic spins in inert atmospheres.

Isotope	I	g_n	σ(calculated) Exchange-enhanced	σ(calculated) Point dipoles	σ(observed)[a] Total
He^3	$\frac{1}{2}$	-4.25	1.1×10^{-24} cm^2	1.9×10^{-27}	6.2×10^{-25}[b]
Ne^{21}	$\frac{3}{2}$	-0.44	1.0×10^{-23}	5.5×10^{-28}	5.2×10^{-23}[c]
Kr^{83}	$\frac{9}{2}$	-0.22	1.0×10^{-22}	1.8×10^{-27}	5.9×10^{-21}[c]

[a] Natural isotopic abundance.
[b] Reference 4.
[c] Reference 14.

The situation is somewhat different for H_2 and D_2. Here again, Eq. (11) is used to calculate the cross sections, with the enhancement factor given by Eq. (14), and the statistically averaged values of $I(I+1)$ replacing that factor in Eq. (11). The results are shown in Table II, where we have also tabulated the theoretical spin-orbit cross sections (calculated after the method of I) and the experimentally determined[3,5] cross sections for disorientation of optically pumped Rb vapor. Here, we see that the hyperfine interactions are less important than they are for He^3, primarily because the exchange enhancement is weaker. At the same time, spin-orbit disorientation cross sections are larger, in view of the stronger intermolecular forces experienced by Rb with H_2 and D_2. Somewhat disturbing is the discrepancy between the predicted and observed spin-orbit relaxation rates. Significant improvement is achieved if, instead of using the calculated long-range force constants to obtain the relative strengths of short-range interactions (see I), empirically determined Lennard-Jones parameters[15] are used to give us this comparison. When this is done, the calculated spin-orbit relaxation cross sections become 4.9×10^{-23} and 6.3×10^{-23} cm^2 for H_2 and D_2, while the calculated cross sections for the rare gases are not significantly changed. The hyperfine cross sections are, of course, unaffected by the change, inasmuch as the kinetic radii involved are the Lennard-Jones in all cases.

TABLE II. Cross sections for the disorientation of Rb electronic spins by molecular hydrogen.

Molecule	g_n	σ(calculated) Exchange-enhanced	σ(calculated) Spin-orbit	σ(observed) Total
H_2	5.59	3.6×10^{-25} cm^2	1.5×10^{-22}	2.2×10^{-24}[a] $3\ \ \times10^{-24}$[b]
D_2	0.96	5.5×10^{-26}	1.5×10^{-22}	4.3×10^{-24}[a]

[a] Reference 3.
[b] Reference 5.

ACKNOWLEDGMENT

The author takes pleasure in acknowledging helpful discussions with Dr. Robert Neusel.

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[14] W. Franzen, Phys. Rev. **115**, 850 (1959).

[15] *American Institute of Physics Handbook*, edited by D. E. Gray (McGraw-Hill Book Company, Inc., New York, 1957).