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Noble-Gas-Induced Rubidium Spin Disorientation*

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

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Cross sections for noble-gas-induced Rb spin disorientation are calculated, taking into account second-order cross terms in the spin-orbit and $\mathbf{K}\cdot\mathbf{L}$ couplings, as initially proposed by Bernheim. Contrary to Bernheim, it is argued that spin-orbit effects are negligible in first order. Using simple wave functions, it is shown that the spin-orbit coupling provided by the electric field of the Rb ionic core, when the valence electronic orbital is deformed in short-range encounters, is sufficient to yield the observed relaxation rates. For He, the calculated disorientation cross section shows agreement to within a factor of 6 with the experimentally determined cross section for depolarization of optically oriented Rb vapor. Moreover, if, for all Rb–rare-gas pairs, we assume the same proportionality between the short- and calculated long-range energies at the kinetic radius, agreement to within a factor of 6 for Ne, A, Kr and Xe is also obtained.

I. INTRODUCTION

THE depolarization of optically-pumped alkali vapors in various buffer gases is a phenomenon well known to experimentalists. For example, the disorientation of polarized Rb atoms in collisions with noble-gas atoms has been the subject of detailed investigations.[1,2] More recently, similar effects in rare-gas Na and rare-gas Cs mixtures[3–5] have been studied extensively.

The phenomenon of spin exchange in binary collisions where each atom has an unpaired electron is well understood in general.[6] For some time, however, the mechanism by which paramagnetic spherical atoms alter their spin direction in collisions with neutral, spinless, spherical atoms has remained somewhat as a mystery. The first explanation for this type of relaxation was proposed by Bernheim,[2] who suggested that spin-orbit couplings in the rare-gas nuclear Coulomb field during collisions cause electronic spin precession (spin-orbit relaxation). He then employed semiquantitative arguments to explain the orders of magnitude and rare-gas-dependence of the measured Rb disorientation cross sections. To date, no quantitative calculation of the cross sections has been published, however.

The present paper has two purposes. The first is to critically review Bernheim's treatment of the problem (Sec. II). Whereas, he obtained first- and second-order contributions to the spin-flip amplitude, both of which appeared to have the same order of magnitude, the present paper makes the point that first-order effects, while present, are much less important than Bernheim supposed. The second-order contributions obtained here have the same form as those obtained by Bernheim, but only half the magnitude. Secondly, using the results of Sec. II, we shall make quantitative estimates of the Rb spin disorientation cross sections (Secs. III, IV). Agreement with experiment to within a factor of 6 is achieved in all cases. One cannot reasonably expect better agreement, in view of the number and importance of the approximations made in the calculation, and the uncertainties in "known" parameters, such as the gas kinetic radii. The fact that such agreement is achieved lends weight to the belief that the mechanism by which optically pumped Rb vapor is disoriented by inert buffer gases is presently well understood.

II. THEORY OF SPIN ORBIT RELAXATION

In analyzing spin-orbit disorientation, Bernheim proposed two ways in which the relaxation might occur. The first of these amounts simply to a statement of the fact that as the foreign gas atom passes the alkali, the motion of the nuclear charge sets up a fluctuating magnetic field in which the alkali spin precesses. The interaction Hamiltonian governing this process is

$$\mathcal{H}'=(2\mu_0/\hbar c)(Z_Be/r_{1B}^3)\mathbf{r}_{1B}\times\mathbf{V}_{BA}\cdot\mathbf{S}_1\,, \tag{1}$$

where e, $\hbar$, and c have their usual meaning, μ_0 is the Bohr magneton, $\mathbf{r}_{1B}$ is the radius vector extending from the foreign gas (B) to the valence electron (1), $\mathbf{V}_{BA}$ is the collision velocity of the noble-gas atom relative to the alkali (A), and $\mathbf{S}_1$ is the spin operator for the alkali valence electrons ($S_1=\hbar/2$). According to Bernheim, this is the only operator which, in first order, causes appreciable spin reorientation.

One immediately senses an error in this viewpoint, however. Even at large separations (overlap and wave function deformations being negligible) Bernheim's result states that a neutral atom creates a magnetic field as it passes an external field point. To the contrary, electromagnetic theory states that spherical neutral charge distributions produce neither electric nor magnetic fields at external points. It is quite obvious, therefore, that the rare-gas electronic "drift current" must also be taken into account, and when this is

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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.

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[5] F. A. Franz and E. Lüscher, Phys. Rev. **135**, A582 (1964).

[6] E. M. Purcell and G. B. Field, Astrophys. J. **124**, 542 (1956); J. P. Wittke and R. H. Dieke, Phys. Rev. **103**, 620 (1956).

properly done, Eq. (1) is replaced by

$$\mathcal{H}' = -(2\mu_0/\hbar c)\mathbf{E}_{B1}\times\mathbf{V}_{BA}\cdot\mathbf{S}_1\,, \tag{1a}$$

where now $\mathbf{E}_{B1}$ is the electric field associated with the noble-gas atom at the position of the alkali valence electron. Once again, $\mathcal{H}'$ yields nonzero diagonal matrix elements. However, they are now too small to be consequential, being finite only when the colliding atoms overlap.[7] For the remainder of the paper, therefore, we shall neglect all first-order spin-orbit effects.

Bernheim's second-order interaction is derived as follows: Consider only the strongest spin-orbit coupling, that between the alkali valence electronic spin and its orbital motion in the combined fields of the alkali positive ion and the noble-gas atom. During the collision, while the electronic wave functions are deformed and during which overlap takes place, the spin-orbit coupling introduces a further deformation into the ground-state eigenfunction, which is characterized by a net internal atomic orbital angular momentum **L**. Since the total angular momentum of the collision **J** is conserved, the angular momentum of rigid rotation $(\mathbf{J}-\mathbf{S}-\mathbf{L})$ suffers a change during the collision (**S** denotes the sum of the electronic spin operators). In writing the Schrödinger equation for atomic radial motion in binary collisions (Born-Oppenheimer approximation), the "centrifugal potential" is $(\mathbf{J}-\mathbf{S}-\mathbf{L})^2/2I$, where I is the moment of inertia operator for the collision pair. The spin-orbit-induced incremental **L** therefore leads to a corresponding perturbation in energy equal to $-\mathbf{K}\cdot\mathbf{L}/I$, with[8] $\mathbf{K}=\mathbf{J}-\mathbf{S}$.

The electronic Hamiltonian relevant to our problem is, therefore,

$$\mathcal{H}=\mathcal{H}_0-\mathbf{K}\cdot\mathbf{L}/I+(\mu_0/\hbar mc)\mathbf{E}_1\times\mathbf{p}_1\cdot\mathbf{S}_1\,, \tag{2}$$

where $\mathcal{H}_0$ represents the Coulomb and kinetic energies for all electrons in the colliding atoms (fixed nuclei), $\mathbf{E}_1$ is the electric field of all charges (except the valence electron) at the position of the valence electron, and $\mathbf{p}_1$ is the momentum operator for that electron. If, as in some instances, antisymmetrized many-electron eigenfunctions are to be used, the appropriate generalization of the spin-orbit operator is

$$(\mu_0/\hbar mc)\sum_i \mathbf{E}_i\times\mathbf{p}_i\cdot\mathbf{S}_i\,, \tag{2a}$$

where the indices i successively indicate all electrons included in the biatomic wavefunction.

For the moment, let us assume that we have solved the Schrödinger equation for the eigenstates and -energies of $\mathcal{H}_0$, the ground state being denoted by $|0\rangle$, excited states by $|\lambda\rangle$. In this representation, the last two terms on the right-hand side of Eqs. (2), (2a) have no nonzero first-order matrix elements with the ground state; however, the second-order energy is nonzero, and can be written as an effective KS coupling as follows:

$$\mathcal{H}_{\mathrm{eff}}'=\sum_i \mathbf{K}\cdot\boldsymbol{\gamma}^i\cdot\mathbf{S}_i/I\,, \tag{3}$$

with $\boldsymbol{\gamma}^i$, a second-order tensor, having elements

$$\gamma_{jk}{}^i=2\sum_\lambda{}' \frac{\langle 0|L_j|\lambda\rangle\langle\lambda|(\mu_0/\hbar mc)(\mathbf{E}_i\times\mathbf{p}_i)_k|0\rangle}{E_{\lambda 0}}\,, \tag{4}$$

with $j, k=x, y$, or z. Because of cylindrical symmetry in the biatomic groundstate, $\boldsymbol{\gamma}^i$ is diagonal in any system of coordinates in which one axis coincides with the instantaneous interatomic axis. Specifically, if we let the z axis coincide with the diatomic figure axis, the relations

$$\begin{gathered}\gamma_{xx}{}^i(\theta)=\gamma_{yy}{}^i(\theta)\equiv\gamma^i(R)\,,\\ \gamma_{zz}{}^i=\gamma_{xy}{}^i=\gamma_{xz}{}^i=\gamma_{yz}{}^i=0\,,\end{gathered} \tag{5}$$

hold, R being the interatomic separation, so that Eq. (3) may be written

$$\mathcal{H}_{\mathrm{eff}}'=\sum_i \gamma^i(R)(\mathbf{K}\cdot\mathbf{S}_i-K_zS_{zi})/I\,.$$

However, because the component along the figure axis of the angular momentum of rigid rotation is always zero, we write

$$\mathcal{H}_{\mathrm{eff}}'=\sum_i\gamma^i(R)\mathbf{K}\cdot\mathbf{S}_i/I\,, \tag{6}$$

where now

$$\gamma^i(R)=\sum_\lambda{}' \frac{\langle 0|\mathbf{L}|\lambda\rangle\cdot\langle\lambda|(\mu_0/\hbar mc)(\mathbf{E}_i\times\mathbf{p}_i)|0\rangle}{E_{\lambda 0}}\,, \tag{7}$$

which is less than Bernheim's result by a factor 2. [Notice also that we have included the $1/I$ dependence explicitly in Eq. (3), *et seq.*, thereby making γ^i dimensionless.] Formally, of course, $\mathcal{H}_{\mathrm{eff}}'$ can be written

$$\mathcal{H}_{\mathrm{eff}}'=\gamma(R)\mathbf{K}\cdot\mathbf{S}/I\,. \tag{6a}$$

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[7] An estimate of the cross section derived on the basis of Eq. (1a) has been carried out for Rb–He collisions. In the calculation, exchange is of no importance, since the rare-gas orbitals follow their nucleus, and all matrix elements on $\mathcal{H}'$ involving these orbitals consequently vanish. By choosing hydrogenlike orbitals for He (see footnote 13) and approximating the Rb valence orbital by a constant term plus one linear in the displacement from the He nucleus along the interatomic axis, the effective coupling $\mathcal{H}_{\mathrm{eff}}'=\gamma(R)\mathbf{K}\cdot\mathbf{S}/I$ is obtained, with $\gamma(R)=8\pi(1/137)^2(16/27)^2\times a_0{}^3Ru_1(R)(du_1(R)/dR)$. The notation here is the same as in Eq. (3), *et seq.* Numerically, for He–Rb collisions, $\gamma(b_0)\approx 2.3\times 10^{-7}$, leading to a cross section $\sigma\approx 10^{-29}$ cm^2. Similar arguments can be used to show that for Xe–Rb collisions, $\sigma\approx 10^{-26}$ cm^2 results. Comparison with the cross sections listed in Table II therefore reveals that first-order effects are negligible.

[8] The above derivation follows J. H. van Vleck, Rev. Mod. Phys. **23**, 213 (1951). The operator $\mathbf{K}/I$ is simply $\boldsymbol{\omega}$, the instantaneous angular velocity with which the interatomic axis rotates during collisions, the $-\boldsymbol{\omega}\cdot\mathbf{L}$ interaction governing an effect whereby the diatomic rotation generates an internal electronic angular momentum. The ρ-type doubling phenomenon in $^2\Sigma$-state molecules is closely related to spin-orbit relaxation, inasmuch as the Hamiltonians governing both phenomena are identical (R. G. Brewer, private communication). The energies associated with ρ-type doubling bear simple relationships to phase shifts appearing in the calculation of spin-orbit relaxation cross sections.

Equations (6) and (7) will be used as the starting point in the calculation of $\gamma(R)$ to follow.

III. EVALUATION OF THE KS COUPLING STRENGTH

In determining the relative magnitudes of the various contributions to $\gamma(R)$, we shall perform calculations at typical interatomic separations—those corresponding to the kinetic radii b_0 for the collision pairs. Sample calculations will be carried out for Rb–He, Ne collisions. It is apparent that eigenstate deformations and/or overlap effects during collisions must be taken into account, inasmuch as

$$\sum_i \mathbf{E}_i \times \mathbf{p}_i \cdot \mathbf{S}_i |0\rangle = 0$$

holds when the colliding atoms are isolated.

1. Eigenstate Deformations

One possibility for spin-orbit relaxation arises from the fact that Coulomb and exchange forces deform the biatomic ground state, in which case $\gamma(R)$ may be finite. In the present calculation, overlap effects are neglected so that simple product eigenfunctions may be employed without antisymmetrization.

We shall consider two types of interatomic interactions which lead to eigenstate deformations. The first of these are the long-range Coulomb interactions, responsible for dispersion forces and also for correlations between the positions of electrons within different atoms. The other type consists of short-range interactions which yield first-order (repulsive) interaction energies and cause atomic deformations without necessarily leading to correlations in the instantaneous positions of electrons within different atoms.

Consider, first, deformations caused by long-range forces. The interatomic potential energy operator, in dipole-dipole approximation, is[9]

$$V' = -\frac{e^2}{R^3} \sum_{i=2}^{n} (2z_i z_1 - y_i y_1 - x_i x_1)\,, \tag{8}$$

where the summation includes all noble-gas electrons. The coordinates $(x_1 y_1 z_1)$ and $(x_i y_i z_i)$ are measured from the nuclei of the alkali and noble gas, the z axis being coincident with the intermolecular axis. According to perturbation theory the ground-state eigenfunction, corrected to include terms first-order in V', is

$$|0\rangle = u_0(1) u_0(2,3 \cdots n) - {\sum_{\kappa k}}' \frac{\langle \kappa k | V' | 00 \rangle}{E_{\kappa k}} u_k(1) u_\kappa(2,3,\cdots n)\,, \tag{9}$$

where κ and k refer to excited noble-gas and alkali states, the prime on the summation indicating that the ground state $(\kappa k) = (00)$ is omitted from the sum. The only alkali states of importance in Eq. (9) are the first excited (resonant) P states. For this reason, those states to be strongly connected to $|0\rangle$ by the spin-orbit and $\mathbf{K} \cdot \mathbf{L}$ operators are, likewise, product alkali resonant P-excited rare-gas states. That is,

$$\gamma \approx \sum_{\kappa\kappa' 1 1' 1''} \frac{\langle 00 | V' | \kappa 1 \rangle \langle \kappa 1 | \mathbf{L} | \kappa' 1' \rangle \cdot \langle \kappa' 1' | (\mu_0 / \hbar mc)(E_{a1}/r) \mathbf{L}_1 | \kappa' 1'' \rangle \langle \kappa' 1'' | V' | 00 \rangle}{(E_\kappa + \bar{E})^3}\,, \tag{10}$$

where 1, 1′, and 1″ stand for alkali resonant P states, κ and κ' for noble-gas excited states having energy E_κ, $\bar{E}$ is the alkali resonance energy and E_{a1} is electric field produced by the alkali positive ion acting on the valence electron. Denoting the alkali resonant P states by $(1_x, 1_y, 1_z)$ and the relevant noble-gas states by $(\kappa_x, \kappa_y, \kappa_z)$, the summation in Eq. (10) can readily be reduced to

$$\gamma = \sum_{\kappa_z} \frac{\langle 00 | V' | \kappa_z 1_z \rangle \langle 1_z | (\mu_0 \hbar / 2mc)(E_{a1}/r) | 1_z \rangle \langle \kappa_z 1_z | V' | 00 \rangle}{(E_\kappa + \bar{E})^3}\,. \tag{10a}$$

Inasmuch as the fine structure splitting of the alkali resonant ${}^2P$ states is

$$E_{so}(\text{res } {}^2P) = (3\mu_0 \hbar / 2mc) \langle 1_z | (E_{a1}/r) | 1_z \rangle \tag{11}$$

and the London dispersion energy for alkali–rare-gas systems is[9]

$$\Delta E_{\text{disp}}(R) \approx -\sum_{\kappa 1} \frac{\langle 00 | V' | \kappa 1 \rangle^2}{E_\kappa + \bar{E}} = -\tfrac{3}{2} \sum_{\kappa_z} \frac{\langle 00 | V' | \kappa_z 1_z \rangle^2}{E_\kappa + \bar{E}}\,, \tag{12}$$

we obtain, assuming that all E_κ of importance can be replaced by the noble-gas ionization energy I_2,

$$\gamma(R) \approx -\frac{2}{9} \left(\frac{\Delta E_{\text{disp}}(R)}{\bar{E} + I_2} \right) \left(\frac{E_{so}(\text{res } {}^2P)}{\bar{E} + I_2} \right). \tag{13}$$

Substituting into Eq. (13) the appropriate values of the dipole-dipole dispersion energy, $-C_6/b_0^6$ (see Table I), along with $E_{so}(5\,{}^2P)(=0.03\text{ eV})$, $\bar{E}$, and I_2,

$$(\gamma(b_0))_{\text{long range}} = 8.8 \times 10^{-8} \tag{14}$$

is obtained for the Rb–He system.

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[9] H. Margenau, Rev. Mod. Phys. **11**, 1 (1939).

We now consider eigenstate deformations arising from short-range interactions. Here, alkali excited states other than the resonant P states are important. As a matter of fact, were all alkali excited (bound) states equal in energy, the short-range Coulomb and exchange interactions would lead to alkali deformations local to the rare-gas atom, but vanishingly small elsewhere. Hence, spin-orbit coupling in the field of the Rb nucleus would be virtually nonexistent, for in the vicinity of the Rb nucleus, the valence electronic state would be almost entirely S like in character. A more realistic approach consists of saying that the resonant P states have energy $\bar{E}$, while all other excited bound states have energy E_{av}, taken to be the mean value of the alkali ionization potential and $\bar{E}$ (for Rb, $\bar{E}=1.58$ eV; $E_{\mathrm{av}}=3.38$ eV). Then, if we denote the resonant P-wave amplitude in the collision-deformed alkali ground state by Λ, the matrix elements $\langle 0|\mathbf{L}|\lambda\rangle$ of Eq. (7) are proportional to Λ, whereas the elements $\langle\lambda|(\mu_0/\hbar mc)(\mathbf{E}_i\times\mathbf{p}_i)|0\rangle$ are proportional to $\Lambda(1-\bar{E}/E_{\mathrm{av}})$, the "uncompensated" P-wave amplitude near the Rb nucleus. The coupling, $\gamma(R)$, found through straightforward application of Eq. (7) is

$$(\gamma(R))_{\text{short range}}\approx\tfrac{4}{3}\Lambda(R)^2(1-\bar{E}/E_{\mathrm{av}})E_{\mathrm{so}}(\mathrm{res}\ {}^2P)/\bar{E}\,,\qquad(15)$$

therefore.

To find the proportion of resonant P state mixed into the ground-state eigenfunction of the alkali through short-range interactions, a variational calculation is employed. The alkali ground state is thought to consist of Λ parts resonant P_z state to 1 part undeformed ground state (that is, $|0\rangle\propto u_0+\Lambda u_{1_z}$). The parameter Λ is adjustable, to be chosen so as to minimize the total energy of the biatomic system. In the Appendix, it is shown that, for $R=b_0$, the total energy is minimized when Λ is given by

$$\Lambda(b_0)\approx-\frac{\Delta E_{\mathrm{s.r.}}(b_0)}{(E_H\bar{E})^{1/2}}(b_0/a_0)\,,\qquad(16)$$

where $\Delta E_{\mathrm{s.r.}}(R)$ represents the short-range interaction energy, E_H is the ionization potential of hydrogen, and a_0 the first Bohr radius. The short-range interaction energy has been calculated (approximately) for the Rb–He collision (see Table I). Thus, the numerical value of $\gamma(b_0)$, found through straightforward application of Eqs. (15) and (16), is:

$$(\gamma(b_0))_{\text{short range}}\approx1.1\times10^{-4}\,,\qquad(17)$$

to be compared with Eq. (14).

2. Overlap Effects

We now examine the influence of overlap in spin-orbit relaxation. To correctly account for these effects, we must first write the electronic ground state (of $\mathcal{H}_0$) as a Slater determinant, as follows:

$$|0\rangle=\left(\frac{1}{n!}\right)^{1/2}\begin{vmatrix}\phi_1(1) & \phi_2(1) & \cdots & \phi_n(1)\\ \phi_1(2) & \phi_2(2) & \cdots & \phi_n(2)\\ \cdots & \cdots & \cdots & \cdots\\ \phi_1(n) & \phi_2(n) & \cdots & \phi_n(n)\end{vmatrix}\,.\qquad(18)$$

For simplicity, we shall neglect writing the spin-orbitals of the Rb core electrons, letting ϕ_1 represent the Rb valence electronic orbital while $\phi_2\cdots\phi_n$ are those of the rare gas, which we consider to remain undeformed during collisions. Consider, for the moment, that part of $|0\rangle$ involving the undeformed S-wave contribution to ϕ_1. Then $\mathbf{L}$, operating individually on each term in the expansion of the resulting determinant, yields zero. Hence, as before, it is necessary to take into account the deformations in ϕ_1 caused by the interatomic interactions.[10]

The contributions to $\gamma(R)$ arising from spin-orbit interactions in the field of the alkali ion have already been calculated above; only minor changes are now introduced by taking into account atomic overlap. However, in accounting for overlap, we must also consider spin-orbit interactions in the field of the noble-gas atom. The calculation is straightforward; only a brief outline of the procedure is given here. We assume, as before, that ϕ_1 is well represented by $u_0+\Lambda u_{1_z}$. We then compute the deformations in ϕ_1 caused by the $\mathbf{K}\cdot\mathbf{L}$ perturbation. (The latter are finite, of course, since $\mathbf{L}u_{1_z}\neq0$.) At this point ϕ_1, modified so as to include the $\mathbf{K}\cdot\mathbf{L}$-induced deformation, is orthogonalized to the rare-gas orbitals through the Schmidt orthogonalization procedure. The spin-orbit energy is then simply the expectation value of the spin-orbit operator summed over all (orthogonalized) orbitals. Since the rare-gas orbitals are paired and therefore yield no net contribution, the spin-orbit energy reduces to the expectation value on ϕ_1 (after having been modified to account for the $\mathbf{K}\cdot\mathbf{L}$ perturbation and orthogonalized to the rare-gas orbitals). Upon identification of this energy with the expectation value of $\mathcal{H}_{\mathrm{eff}}'$, the following expression for $\gamma(R)$ in collisions between the alkali and He, Ne or A atoms is obtained:

$$(\gamma(R))_{\text{overlap}}\approx\tfrac{4}{3}\Lambda\sum_{\kappa}S_{0\kappa_z}S_{1_x\kappa_x}E_{\mathrm{so}}(\kappa)/\bar{E}\,,\qquad(19)$$

where the summation is over all P-state subshells of the rare-gas atom. The quantities $S_{0\kappa_z}$ and $S_{1_x\kappa_x}$ are overlap integrals involving the undeformed alkali ground- and resonant P_x-state orbitals, and $E_{\mathrm{so}}(\kappa)$ is the calculated[11] spin-orbit splitting factor for the κth rare-

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[10] This conclusion is independent of whether or not we orthogonalize ϕ_1 to the rare-gas orbitals (through the Schmidt orthogonalization procedure) before operating with $\mathbf{L}$, as can easily be seen if one works with the complete determinantal wave function at all times.

[11] D. Y. Smith, Phys. Rev. **133**, A1087 (1964).

gas subshell. Thus, in Rb–He collisions,

$$(\gamma(b_0))_{\text{overlap}}\approx 0\,, \tag{20}$$

since He has no P-state orbitals. For Ne, however, Eq. (19) yields a nonzero result. Through arguments similar to those employed in the Appendix, it can be shown that

$$S_{1_x\kappa_x}\approx\frac{1}{\alpha a_0}(\bar{E}/E_H)^{1/2}S_{0\kappa_z}\,, \tag{21}$$

where α is the logarithmic derivative, with respect to r, of the Rb 5S orbital at interatomic separation R ($\alpha a_0\approx 0.38$ for all R values of interest).[12] Substituting Eq. (21) and Λ as given by Eq. (16) [using the appropriate value of $\Delta E_{\text{s.r.}}(b_0)$ from Table I] into Eq. (19),

$$(\gamma(b_0))_{\text{overlap}}\approx 1.7\times 10^{-5} \tag{22}$$

is obtained[12] for Rb–Ne, which compares with the short-range contribution for this case,

$$(\gamma(b_0))_{\text{short range}}\approx 3.3\times 10^{-4}. \tag{23}$$

From Eqs. (14), (17), (20), (22), and (23), we conclude (a) that deformations caused by long-range Coulomb interactions lead to negligible spin-orbit couplings and (b) for Rb inert-gas collisions in general the most important spin-orbit coupling appears to take place in the alkali-ionic field, making overlap effects secondary in importance. Similarly, for rare-gas-Cs collisions, the same conclusions are probably true. For the lighter alkalis (Li and possibly Na), however, the situation presumably would be reversed, in that spin-orbit splittings are very much less for those atoms than for Rb or the P-states of the heavier noble gases. Finally, it should be noted that spin-orbit depolarization cross sections in Li–He and Na–He collisions are probably very small indeed, in view of the fact that p orbitals are absent in He, and the electric fields involved are themselves very small. The observations of Anderson and Ramsay[3] tend to support this conclusion.

IV. CROSS SECTIONS FOR SPIN-ORBIT RELAXATION

In obtaining estimates for the spin-orbit relaxation cross sections, the classical path approximation will be used. Although the corresponding quantum mechanical calculation is straightforward, this step is not justified at the present time. For classical paths, assuming all collisions to occur with mean relative impact velocity $\bar{V}$ the cross section for relaxation is simply

$$\sigma=(4\pi/3)\int_0^\infty bdb\phi_+(b)^2\,, \tag{24}$$

a factor 2/3 appearing in the above expression as a result of spherical averaging. In Eq. (24), $\phi_+(b)$ is a phase shift governed by $\mathcal{H}_{\text{eff}}'$, associated with collisions characterized by impact parameter b, in which $K_zS_z=+(\hbar K/2)$. It is given by

$$\phi_+(b)=(K/2)\int_{\text{collision}}dt(\gamma(t)/I(t))\,, \tag{25}$$

with the integral over time taken for classical orbits. For order of magnitude estimates, we approximate the integral in Eq. (25) by

$$\int_{\text{collision}}dt\,\gamma(t)/I(t)\begin{array}{ll}=0\,, & b_0<b\\ =\gamma(b_0)/\bar{m}\bar{V}b_0\,, & b_0\geqslant b\end{array}, \tag{26}$$

$\bar{m}$ being the reduced mass of the collision pair. This approximation is reasonable, since short-range interactions fall off rapidly with intermolecular separation, the integral being relatively negligible for collisions which are not hard ($b>b_0$). Moreover, the classical equations of radial motion are somewhat identical for all $b<b_0$ at room temperature (centrifugal terms being unimportant) and at $b\approx b_0$ we know $\gamma(b_0)/\bar{m}\bar{V}b_0$ to be a good approximation to the integral. Substituting Eqs. (26) and (25) into Eq. (24), taking account of the fact $K=\bar{m}\bar{V}b$,

$$\sigma\approx(\gamma(b_0)^2/12)\sigma_{\text{kin}} \tag{27}$$

is obtained, σ_{kin} being the gas kinetic cross section, equal to πb_0^2. Because of the disappearance of $\bar{V}$ from Eq. (27), the cross sections are, in this approximation, independent of the collision velocity. Hence, the result Eq. (27) can be derived without the assumption of mean thermal velocities.

The short-range interaction energy at the kinetic radius has been calculated explicitly for the Rb–He collision,[13] with the approximation $\phi_1=$const over the volume occupied by the He atom [cf. Eq. (A1), Appendix]. The calculation of $\Delta E_{\text{s.r.}}(b_0)$ for the heavier rare gases is difficult, and will not be attempted at the present time. Instead, to estimate $\Delta E_{\text{s.r.}}(b_0)$ for these cases, we shall apply the following rule of thumb: For each rare gas–Rb binary pair, the short- and long (R^{-6} and R^{-8} terms, say) -range energies bear a constant ratio to one another at the kinetic radius. Hence, by knowing this ratio for He–Rb, $\Delta E_{\text{s.r.}}(b_0)$ can be estimated for other binary pairs, provided that the long-range force constants are known. Certainly, this procedure for arriving at $\Delta E_{\text{s.r.}}(b_0)$ cannot claim any real accuracy. It should provide a somewhat realistic variation in $\Delta E_{\text{s.r.}}(b_0)$ with rare-gas species, however. By knowing $\Delta E_{\text{s.r.}}(b_0)$, we now calculate $\Lambda(b_0)$, $\gamma(b_0)$ and finally σ from Eqs. (16), (15), and (27).

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[12] The Rb valence electronic wave function used is that given by Callaway and Morgan [J. Callaway and D. F. Morgan, Jr., Phys. Rev. 112, 334 (1958)] and Brown's [F. W. Brown, Phys. Rev. 44, 214 (1933)] analytic wave functions for Ne have been used.

[13] For He, hydrogen-like orbitals with effective nuclear charge $Z=27/16$ are used. See. L. Pauling and E. B. Wilson, *Introduction to Quantum Mechanics* (McGraw-Hill Book Company, Inc., New York, 1935), pp. 184–185.

TABLE I. Parameters used in the calculation of the Rb spin-orbit relaxation cross sections.

Gas	b_0(Å)[a]	C_6(erg cm^6)[b]	C_8(erg cm^8)[b]	$\Delta E_{\text{s.r.}}(b_0)$ (eV)[c]
He	3.55	30.9×10^{-60}	5.8×10^{-74}	0.062
Ne	3.66	59.4	13.0	0.105
A	3.98	242	57.0	0.245
Kr	4.06	349	80.1	0.301
Xe	4.30	557	137	0.333

[a] Based on an assumed Lennard-Jones radius of 4.53 Å for Rb (see text), and tabulated Lennard-Jones radii (Ref. 14) for rare gases.
[b] Reference 15.
[c] See text.

Parameters pertinent to the numerical calculation of σ for various noble gases are given in Table I. Here, the listed values of b_0 represent mean values of the Rb atomic diameter (taken to be 4.53 Å, the interatomic spacing in solid Rb) and the Lennard-Jones radii for the rare gases.[14] C_6 and C_8 are coefficients for the R^{-6}- and R^{-8}-dependent long-range interaction energies, after the work of Robinson,[15] while $\Delta E_{\text{s.r.}}(b_0)$ is the short-range interaction energy at the kinetic radius, obtained as described in the preceding paragraph. In Table II, we have listed the cross sections computed from Eq. (27). Also included in this table are the observed cross sections for the depolarization of optically pumped Rb vapor.

From Table II, it is apparent that good agreement with experiment has been achieved, considering the crudeness of the estimates. Inasmuch as the cross sections involve the squares of fourth-order perturbational energies (two powers in Λ and one each in the $\mathbf{K}\cdot\mathbf{L}$ and spin-orbit couplings), it is actually quite remarkable that the present agreement with experiment is as good as it is. Based on the current results, it is probably safe to say that the mechanism for spin disorientation in Rb–rare-gas collisions is presently reasonably well understood.

TABLE II. Calculated and observed Rb–noble-gas spin-orbit relaxation cross sections.

Gas	σ_{calc}(cm^2)	σ_{obs}(cm^2)
He	3.8×10^{-24}	6.2×10^{-25} [a]
Ne	3.8×10^{-23}	5.2×10^{-23} [b]
A	1.9×10^{-21}	3.7×10^{-22} [b]
Kr	4.8×10^{-21}	5.9×10^{-21} [b]
Xe	1.0×10^{-20}	1.3×10^{-20} [b]

[a] Reference 2.
[b] Reference 1.

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APPENDIX : THE SHORT RANGE *P*-STATE DEFORMATION PARAMETER

The problem is to find the fraction Λ of resonant P-state mixed into the undeformed alkali groundstate eigenfunction through short-range interactions. The variational procedure is employed here, Λ being chosen so as to minimize the total diatomic energy. The rare gases are considered to be "hard," in that the energies which separate their ground and excited states are so large as to prohibit extensive deformations. We therefore neglect the rare-gas deformations against those of the alkali.

For Rb-rare gas binary pairs separated by a distance R, the first-order interaction energy may be written, for practical purposes,

$$\Delta E_{\text{s.r.}}(R)\approx(1+c(R)\Lambda)^2E'(R)+\Lambda^2\bar{E}-c(R)\Lambda(1+c(R)\Lambda)A(R)\bar{E}. \quad \text{(A1)}$$

Here $E'(R)$ is the calculated short-range interaction between an undeformed ($\Lambda=0$) Rb and rare-gas atom, $A(R)$ is the sum of the squared overlap integrals, similarly associated with only the S-wave amplitude of the alkali groundstate, and $c(R)$ is the ratio of the resonant P-state amplitude u_{1_z}, to the S-wave amplitude u_0 at the rare-gas nucleus. We assume that the local variation in u_0 and u_{1_z} is negligible over the noble-gas volume. For Rb-rare-gas pairs, $A(R)\bar{E}$ is sufficiently less than $E'(R)$ and $\bar{E}/c^2$ that it is permissable to neglect the last term in Eq. (A1) as follows:

$$\Delta E_{\text{s.r.}}(R)\approx(1+c(R)\Lambda)^2E'(R)+\Lambda^2\bar{E}. \quad \text{(A2)}$$

At any given interatomic separation, all parameters (except Λ) in Eq. (A2) are independent of Λ. To minimize $E(R)$, therefore, we simply set its derivative with respect to Λ equal to zero, with the result

$$c(1+c\Lambda)E'(R)+\Lambda\bar{E}=0. \quad \text{(A3)}$$

Upon multiplying Eq. (A3) by $(1+c\Lambda)$, we obtain

$$c\Delta E_{\text{s.r.}}(R)+\Lambda\bar{E}=0, \quad \text{(A4)}$$

or simply

$$\Lambda(R)=-c(R)(\Delta E_{\text{s.r.}}(R)/\bar{E}). \quad \text{(A5)}$$

To find $c(R)$, we employ the following arguments. Consider the sum

$$\sum_k\langle 0|p_z|k\rangle\langle k|z|0\rangle=\langle 0|p_zz|0\rangle, \quad \text{(A6)}$$

where now $|0\rangle$ and $|k\rangle$ represent undeformed ground and excited states of the isolated alkali. Because p_z is Hermitian and $|0\rangle$ real, we have

$$\langle 0|p_zz|0\rangle=(i\hbar/2). \quad \text{(A7)}$$

Moreover, since

$$p_z=-(i/\hbar)m[\mathcal{H},z], \quad \text{(A8)}$$

we obtain, using Eqs. (A6) and (A7),

$$\sum_k E_{k0}\langle 0|z|k\rangle^2=(\hbar^2/2m). \quad \text{(A9)}$$

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

[15] L. B. Robinson, Phys. Rev. **117**, 1275 (1960).

Because the oscillator strength associated with the resonant transition is nearly unity for the alkalis, Eq. (A9) is virtually equivalent to

$$\langle 0|z|k\rangle^2 = (\hbar^2/2m\bar{E}), \quad k=1_z \qquad \text{(A10)}$$
$$=0, \qquad k\neq 1_z.$$

Consequently, the relation

$$z|0\rangle \approx ((\hbar^2/2m\bar{E}))^{1/2}|1_z\rangle \qquad \text{(A11)}$$

holds in regions where $|0\rangle$ is appreciable. Accordingly, for $z=R$, the ratio of $|1_z\rangle$ to $|0\rangle$ is

$$c(R)=R\left(\frac{2m\bar{E}}{\hbar^2}\right)^{1/2}=\left(\frac{R}{a_0}\right)\left(\frac{\bar{E}}{E_H}\right)^{1/2}. \qquad \text{(A12)}$$

Combining Eqs. (A12) and (A5), we finally obtain for Λ

$$\Lambda(R)=-\frac{R}{a_0}\frac{\Delta E_{\mathrm{s.r.}}(R)}{(\bar{E}E_H)^{1/2}}. \qquad \text{(A13)}$$

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One-Dimensional Electron-Phonon Model*

STANLEY ENGELSBERG AND B. B. VARGA†
Palmer Physical Laboratory, Princeton University, Princeton, New Jersey

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The properties of a one-dimensional system of degenerate electrons coupled to long-wavelength phonons are investigated. The equivalent model Hamiltonian of Tomonaga, which describes the electrons by density waves, is diagonalized to normal modes. These are calculated for the Einstein model and constant coupling, and used to get the ground-state energy. A physical interpretation of the model is given. The breakdown of the system for strong coupling is discussed. The many-body perturbation theory is used to assess the validity of the Tomonaga model. The electron-phonon ground-state energy diagrams may be grouped in two sets as Tomonaga and non-Tomonaga. The latter cancel among themselves exactly to a high order. The extent of the cancellation in three dimensions is treated in fourth order and found to be significant, but not exact.

1. INTRODUCTION

THE properties of an electron-phonon system are investigated for the case when the electrons are degenerate and the shortest wavelength coupled phonon has wave vector k_c much smaller than the Fermi momentum k_f. For these phonons the wavelength is large compared to the average electron spacing, and the electron density fluctuations which couple to the phonons are well-defined collective "sound" waves. Most of the work is on a one-dimensional model; Sec. 10 discusses the possibility of extending the results to three dimensions.

The method of Tomonaga[1] is used in Sec. 2 to derive an equivalent Hamiltonian for the system where the electron kinetic energy for momentum p is $v_f|p|$. The electron kinetic energy operator is expressed in terms of boson operators which create and annihilate electron density waves. The validity of the description of the electron-phonon system by the Tomonaga Hamiltonian is discussed using Tomonaga's results, and an extension is given which is proved by perturbation methods in Sec. 7. The physical interpretation of the boson kinetic operator in Sec. 3 splits the operator into two parts. The first gives the Fermi-Thomas energy of degenerate electrons with long-wavelength density oscillations; the second is the energy of the collective motion in these oscillations. We may consider the description to be a dynamical Fermi-Thomas method which accounts for the correlations in the long-wavelength motions of the electron gas.

The Tomonaga Hamiltonian is diagonalized by a canonical transformation in Sec. 4 into a set of independent harmonic oscillators, three for each wave vector when the electron spin is included as a variable. One of the independent modes is a spin density wave whose frequency is unaffected by the phonons, because it leads to no change in the electron density in space. The dispersion curves of the oscillators are calculated in a specific model: Einstein-model phonons of frequency ω, and the electron-phonon vertex matrix elements g_k taken as constant $=g$ for $|k|<k_c$ and zero for $|k|>k_c$. When $\Omega_k=v_f|k|$ is not close to ω, the two other displaced normal modes contain a phonon and a density wave with no spin wave, one of the modes being mainly a phonon and the other mainly a density wave. For $v_f|k|$ close to ω, neither mode is mainly phonon or density fluctuation. The mode which is a phonon (density wave) for $\Omega_k\ll\omega$ becomes a density wave (phonon) for $\Omega_k\gg\omega$.

The ground-state energy E_T of the system is plotted against the coupling strength g and the cutoff momentum k_c. It is shown that in the general case, E_T is analytic in the coupling constant, so that perturbation

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† Leeds and Northrup Foundation Predoctoral Fellow.

[1] S. Tomonaga, Progr. Theoret. Phys. (Kyoto) 5, 544 (1950).