Spin-rotation interaction of alkali-metal−He-atom pairs

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A treatment of the spin-rotation coupling between alkali-metal atoms and He atoms is presented. Rotational distortions are accounted for in the wave function using a Coriolis interaction in the rotating frame. The expectation value of the spin-orbit interaction gives values of the spin-rotation coupling that explain previous experimental results. For spin-exchange optical pumping, the results suggest that lighter alkali-metal atoms would be preferred spin-exchange partners, other factors being equal. [S1050-2947(97)06708-5]

I. INTRODUCTION

Spin-exchange optical pumping of ^{3}He via collisions with optically pumped alkali-metal atoms is a powerful technique for polarizing large quantities of ^{3}He. Experiments using spin-exchange optical pumping include: determination of the neutron spin structure function, measured by scattering polarized, high-energy electrons from highly polarized targets of ^{3}He [1]; magnetic resonance imaging of lungs and other organs of the human body [2]; studies of fundamental symmetries [3,4]; and neutron polarizers and polarimeters [5]. In all these experiments efficient conversion of photon spins to polarized nuclear spins is key.

Spin relaxation in collisions between the alkali-metal and ^{3}He atoms limits the efficiency of spin-exchange optical pumping [6]. Spin relaxation results from coupling of the alkali-metal electron spin **S** to the rotational angular momentum **N** of the colliding atoms by the spin-rotation coupling $\gamma\mathbf{S}\cdot\mathbf{N}$ [7], which arises from spin-orbit interactions. Experiments [8–10] established that for the heavy noble gases Ar, Kr, and Xe, γ originated from within the core of the noble-gas atom; a quantitative theory [10] has been quite successful in explaining the experimental results [11]. Helium, however, has such small spin-orbit interactions that the spin-rotation coupling must originate from within the core of the alkali-metal atom. Indeed, experimental results confirm that the spin-relaxation cross sections for Na-He [12,13] are much smaller than for Rb-He [14] as befitting the much smaller spin-orbit splittings of Na as compared to Rb. Despite the importance of these cross sections for spin-exchange optical pumping, no reliable quantitative estimates of spin-relaxation cross sections of alkali-He pairs exist in the literature.

In this paper we present a formula for the portion of the spin-rotation interaction γ_a that originates within the alkali-metal core:

$$\gamma_a(R) = \frac{4\hbar^2 \Delta E_{n_g p}}{3 E_p M_{ab}} \frac{c_{n_g p}^2(R)}{R^2}. \tag{1}$$

This formula shows that γ_a is proportional to the spin-orbit splitting $\Delta E_{n_g p}$ of the the first excited p state (excitation energy $E_{n_g p}$) of the alkali-metal atom, and to the square of the amplitude $c_{n_g p}$ of the p-state wave function, which is mixed into the ground-state wave function by the noble-gas atom. The noble-gas atom and alkali-metal atom have a reduced mass M_{ab} and they are separated by a distance R. We evaluate $c_{n_g p}$, using a simple Fermi pseudopotential [15,16], and also with wave functions used to calculate the most reliable alkali-metal–noble-gas interaction potentials [17]. The Fermi pseudopotential parametrizes the mixing, using the electron–noble-gas s-wave scattering length a, giving

$$\gamma_a = \frac{16\pi^2 \hbar^6 \Delta E_{n_g p} a^2}{3 E_p^3 M_{ab} m^2 R^2} \phi_0(R)^2 \phi_{n_g pz}(R)^2. \tag{2}$$

In this approximation the R dependence is principally determined by the exponentially decaying ground-state (ϕ_0) and the lowest p_z-state ($\phi_{n_g pz}$) wave functions of an unperturbed alkali-metal atom. This formula shows clearly the important characteristics of γ_a, namely its strong dependence on the scattering length and its proportionality to the spin-orbit splitting. This expression is comparable in principle to Eq. (15) of Herman's pioneering work [18], which also predicts that γ_a should be proportional to $\Delta E_{n_g p}$. However, Herman's expression contains other parameters that are difficult to evaluate, especially as functions of internuclear separation.

II. DERIVATION OF SPIN-ROTATION INTERACTION

We consider an alkali-metal atom at rest at the center of a laboratory-fixed coordinate system, with a noble-gas atom displaced from it at a distance **R**. The noble-gas atom distorts the normally spherically symmeteric ground-state wave function ϕ_0 of the alkali-metal valence electron. We represent the distorted wave function $\psi(\mathbf{r};\mathbf{R})$ by a mixture of ϕ_0 and the various excited-state orbitals ϕ_{nlm} (with center-of-gravity excitation energies E_{nl}) of the alkali-metal atom, these orbitals forming a complete set of states:

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$$\psi(\mathbf{r}) = \phi_0(\mathbf{r}) + \sum_{nlm} c_{nlm}(\mathbf{R})\phi_{nlm}(\mathbf{r}). \qquad (3)$$

For now we assume that the mixing coefficients $c_{nlm}(\mathbf{R})$ are known. The free-atom orbitals have the common central-potential form

$$\phi_{nlm}(\mathbf{r}) = P_{nl}(r)Y_{lm}(\theta,\phi)/r, \qquad (4)$$

where $P_{nl}(r)$ is a radial wave function of the displacement $\mathbf{r}$ of the valence electron from the nucleus of the alkali-metal atom, and $Y_{lm}(\theta,\phi)$ is a spherical harmonic of the angular coordinates θ, ϕ.

The spin-orbit interaction, which vanishes for the undistorted wave function, arises from the terms with $l \geq 1$ in Eq. (3). However, the spin-orbit splittings for $l=1$ greatly exceed those for $l \geq 2$, so we focus only on the terms of Eq. (3) with $l=1$ and define a vector p orbital by

$$\boldsymbol{\phi}_{np} = \phi_{npx}\hat{\mathbf{x}} + \phi_{npy}\hat{\mathbf{y}} + \phi_{npz}\hat{\mathbf{z}} = \sum_m (-1)^m \phi_{n1m}\hat{\mathbf{u}}_{-m}, \qquad (5)$$

depending on whether Cartesian or spherical basis unit vectors $(\hat{\mathbf{u}}_{\pm 1} = \mp(\hat{\mathbf{x}}\pm i\hat{\mathbf{y}})/\sqrt{2}, \; \hat{\mathbf{u}}_0 = \hat{\mathbf{z}})$ are used. The distorted wave function (3) becomes

$$\psi(\mathbf{r}) \approx \phi_0(\mathbf{r}) + \sum_n c_{np}(\mathbf{R})\hat{\mathbf{R}}\cdot\boldsymbol{\phi}_{np}(\mathbf{R}). \qquad (6)$$

This assumes symmetry about the internuclear axis, consistent with the Σ character of the lowest molecular state of the atom pair.

We now treat the rotation of the atoms about each other at the frequency

$$\boldsymbol{\omega} = \frac{\hbar\mathbf{N}}{M_{ab}R^2} \qquad (7)$$

by transforming to a rotating coordinate system [19], in which the electron experiences a Coriolis interaction [20]

$$V_\omega = -\hbar\boldsymbol{\omega}\cdot\mathbf{L}. \qquad (8)$$

Since this interaction involves the angular momentum $\mathbf{L}$ of the electron, it would vanish to first order were it not for the p-state admixture produced by the noble-gas atom in the adiabatic wave function [Eq. (6)].

Using first-order perturbation theory, the wave function including the Coriolis interaction becomes

$$\Psi(\mathbf{r}) = \psi(\mathbf{r}) - i\sum_n \frac{\hbar^2 c_{np}(\mathbf{R})}{M_{ab}R^2 E_{np}}\hat{\mathbf{R}}\times\mathbf{N}\cdot\boldsymbol{\phi}_{np}(\mathbf{r}). \qquad (9)$$

The spin-orbit interaction of the valence electron is $V_{SO} = \xi(r)\mathbf{S}\cdot\mathbf{L}$, where $\xi(r)$ is proportional to the magnitude of the electric field, experienced by the valence electron at a distance r from the nucleus of the alkali-metal atom. Using the identity $\mathbf{L}(\mathbf{A}\cdot\boldsymbol{\phi}_{np}) = i\mathbf{A}\times\boldsymbol{\phi}_{np}$, we find the expectation value of the spin-orbit interaction to be
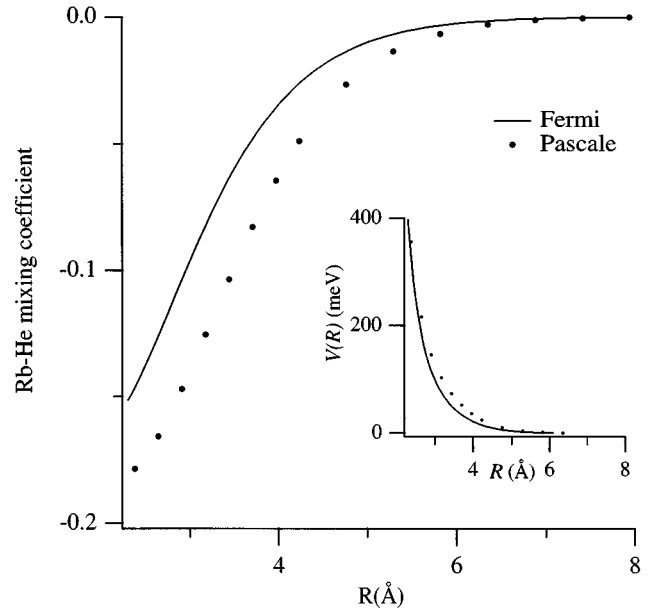

FIG. 1. Mixing coefficients c_{5p} calculated for Rb-He as a function of interatomic separation using the Fermi and Pascale methods described in the text. Inset: calculated potential curves.

$$\langle\Psi|V_{SO}|\Psi\rangle = \sum_{nn'} \frac{\hbar^2 c_{np}(\mathbf{R})c_{n'p}(\mathbf{R})}{M_{ab}R^2}\left(\frac{1}{E_{np}} + \frac{1}{E_{n'p}}\right)$$
$$\times\langle\phi_{np}|\xi(r)|\phi_{n'p}\rangle\mathbf{S}\cdot\mathbf{N} = \gamma_a\mathbf{S}\cdot\mathbf{N}. \qquad (10)$$

The terms in the sum of Eq. (10) are weighted by the spin-orbit matrix $\langle\phi_{np}|\xi(r)|\phi_{n'p}\rangle$ and by the products of admixture coefficients $c_{np}(\mathbf{R})c_{n'p}(\mathbf{R})$. These decrease sufficiently rapidly with increasing n that a reasonable first approximation is to retain only the first term in the sum with $n = n' = n_g$, which gives Eq. (1), since $\langle\phi_{np}|\xi(r)|\phi_{np}\rangle = 2\Delta E_{np}/3$.

III. RESULTS

In order to evaluate the expression (1), we require knowledge of the mixing coefficients $c_{n_gp}(\mathbf{R})$. We present two methods for calculating these coefficients. In the first case, we extract the mixing coefficients from wave functions obtained by Pascale [27] in the course of his pseudopotential calculations of alkali-metal–He potential curves [17]. These well-regarded potential curves have been successful in explaining many phenomena, so we expect reliable values of the mixing coefficients obtained this way. Figure 1 shows values of the mixing coefficients so obtained.

The Pascale wave functions for alkali-He pairs are not widely available, and do not exist for the heavy noble gases. Thus it is important that another method of estimation be available for making quantitative estimates. Following Fermi [15,16], we represent the interaction of the valence electron with the noble gas atom with the pseudopotential

$$V_F(\mathbf{r};\mathbf{R}) = \frac{2\pi\hbar^2 a}{m}\delta(\mathbf{r}-\mathbf{R}), \qquad (11)$$

which was first introduced to account for pressure shifts of the spectral lines of Rydberg states in dense noble gases. It
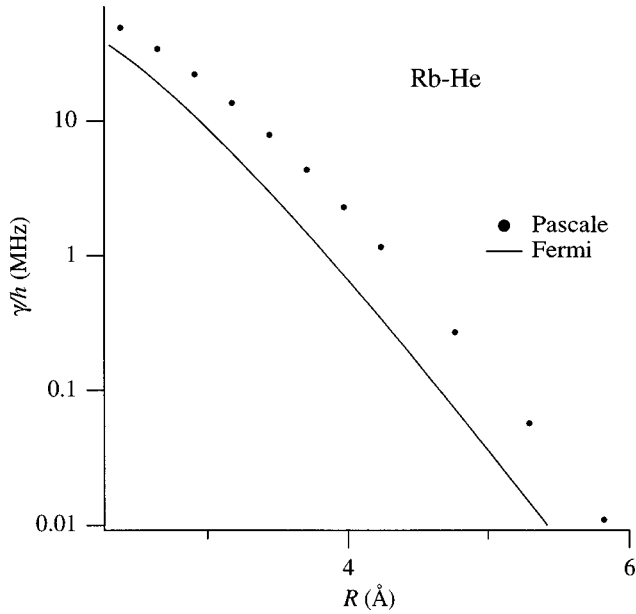
FIG. 2. Spin-rotation coupling strength as a function of interatomic separation.

FIG. 3. Energy and temperature dependences for Rb-He spin-relaxation cross sections.

has since been used for a variety of problems, including neutron scattering [21] and interactions in degenerate Bose gases [22]. Using the Fermi pseudopotential in first-order perturbation theory then gives

$$c_{np}(\mathbf{R}) = -\frac{2\pi\hbar^2 a}{mE_{np}} \phi_0(\mathbf{R})\phi_{npz}(\mathbf{R}), \qquad (12)$$

and Eq. (2) follows from this.

To obtain numerical values of $c_{np}(\mathbf{R})$ with the Fermi method, we used parametrized Hartree-Fock wave functions [23,24] for ϕ_0 and Coulomb approximation wave functions [25] for $\phi_{n_g p}$. Values of the scattering length are [26] He, 0.63 Å; Ne, 0.13 Å; Ar, -0.90 Å; Kr, -1.96 Å; Xe, -3.4 Å. Figure 1 shows that the Fermi pseudopotential gives smaller mixing coefficients than do the Pascale wave functions. One may object that the Fermi method neglects important effects, especially the core-polarization interaction between the electrons and the He atom. Despite this, Fig. 1 shows that the Fermi method gives reasonable results. As a further comparison, the inset to Fig. 1 shows a remarkable agreement between the Pascale Rb-He potential and the potential that results from adding the experimentally derived Rb$^+$-He interaction [17] to the Fermi pseudopotential. Thus, while it is clearly desirable where possible to use the Pascale wave functions, the figure demonstrates that reasonably reliable estimates are given by the Fermi method. The Fermi method has the additional advantage of requiring only experimental data and readily accessible wave functions for its evaluation.

Calculated values of $\gamma_a(R)$ for Rb-He are shown in Fig. 2. The strong R dependence comes from the exponentially decreasing wave functions. To compare to experiment, we calculate spin-relaxation cross sections [11] using classical collision trajectories. We use the interatomic potentials of Pascale to calculate the trajectories, but use both the Fermi
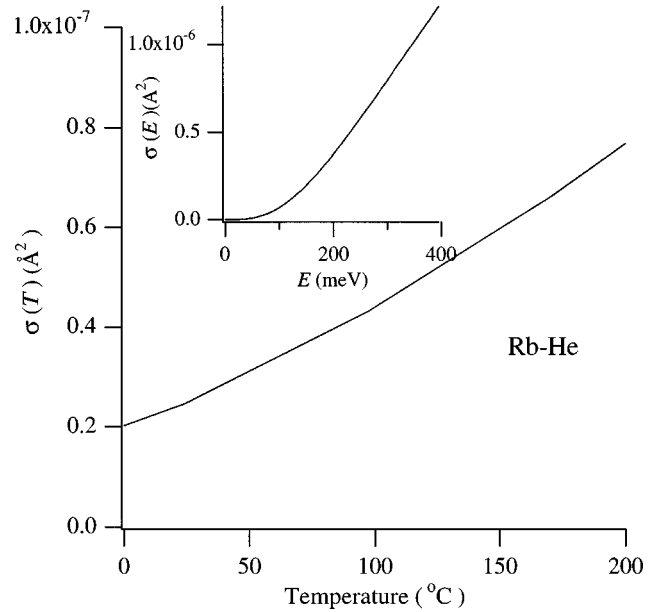
pseudopotential and the Pascale mixing coefficients in evaluating $\gamma_a(R)$. For a fixed collision energy E we define a cross section

$$\sigma(E) = \frac{8\pi M_{ab}^2}{3\hbar^4} \int b^3 db \left| \int_{r_o}^{\infty} \frac{\gamma(R)dR}{\sqrt{(1-b^2/R^2)-V(R)/E}} \right|^2, \qquad (13)$$

whose strong energy dependence produces a marked temperature dependence of the cross section. In terms of $\sigma(E)$ the thermally-averaged cross section for temperature T is

$$\sigma(T) = (kT)^{-2} \int_0^{\infty} E e^{-E/kT} \sigma(E) dE. \qquad (14)$$

Figure 3 shows that $\sigma(E)$ increases approximately linearly with energy, giving a linear increase of $\sigma(T)$ with T.

Table I compares the calculated spin-relaxation cross sections, using the single-excited-state approximation of Eq. (1) and the Pascale mixing coefficients, with existing

TABLE I. Measured and calculated spin-relaxation cross sections for alkali-metal atoms colliding with noble-gas atoms. The Na-He experimental results did not originally account for nuclear-spin effects, and have been multiplied by a factor of 6 (assuming spin-temperature equilibrium) to convert the reported cross sections to electron randomization cross sections [29]. The calculated cross sections use Eq. (1) with Pascale's wave functions and interatomic potentials [17,27].

Atom pair	Ref.	Temp. (°C)	Experiment (Å^2)	Calculated
Na-He	[12]	155	1.3×10^{-9}	1.2×10^{-10}
	[13]	150	1.4×10^{-9}	
K-He		186		6.5×10^{-9}
Rb-He	[14]	186	1.3×10^{-7}	7.5×10^{-8}
Cs-He		150		6.0×10^{-7}

experiments.[1] For Na-He, the calculated results are a factor of 10 smaller than experiment, while for Rb they are smaller by a factor of 1.7. We note, however, that the neglect of the higher excited states of Eq. (10) systematically underestimates the cross sections. Using the Fermi method we have estimated the excited-state contributions from states $n = n_g + 1$ to 10. In particular, terms with either $n = n_g, n' > n$ or $n' = n_g, n > n'$ make a significant contribution, and bring the theory for Rb-He into excellent agreement with experiment. From this we conclude that the underlying physics is likely correctly represented by Eq. (10). In practice, the use of the single-state Fermi approximation [Eq. (2)] leads to underestimates of the spin-relaxation cross sections by up to a factor of 10. Considering that the cross section depends on the fourth power of the mixing coefficients, this represents a reasonable accuracy for such a simple formula.

IV. CONCLUSIONS

The spin-rotation interaction also includes a contribution γ_b that arises from spin-orbit interactions inside the noble-gas core. Wu *et al.* [10] gave a formula for γ_b analogous to Eq. (2) above:

$$\gamma_b(R) = -\frac{mG}{MR}\frac{d|\phi_0|^2}{dR}, \tag{15}$$

where the factor G reflects both the strength of the spin-orbit interaction and the distortion of the wave function inside the noble-gas core. Figure 4 shows that for Xe $\gamma_b \gg \gamma_a$, except at quite small interatomic separations. For alkali-metal–He pairs γ_a always dominates over γ_b.

Finally, we emphasize that the spin-relaxation cross sections for alkali-metal–He pairs depend strongly on the spin-orbit splitting of the alkali-metal atom. For applications of ^{3}He spin-exchange optical pumping that require intense light

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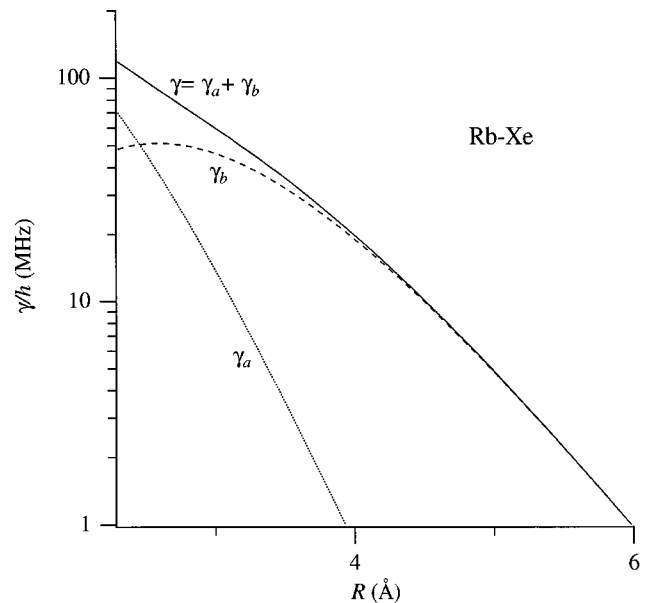[1]Other experiments done before 1970 suffer from lack of accounting for nuclear spin effects [28].

FIG. 4. The relative contributions of spin-orbit interactions in the alkali-metal core (γ_a) and the noble-gas core (γ_b) to determining the spin-rotation coupling for Rb-Xe.

sources, replacement of rubidium with a lighter alkali-metal atom such as potassium may lead to significantly enhanced conversion efficiency of spin-polarized photons into spin-polarized ^{3}He nuclei. Potassium has only a slightly smaller vapor pressure than Rb, and it is possible to use diode lasers for the optical pumping. Thus there may be significant advantages to using potassium as the spin-exchange partner for ^{3}He.

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