Estimates of the relative magnitudes of the isotropic and anisotropic magnetic-dipole hyperfine interactions in alkali-metal–noble-gas systems

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We present a detailed theoretical analysis of the noble-gas nuclear spin relaxation due to the anisotropic magnetic-dipole hyperfine interaction between the noble-gas nucleus and alkali-metal valence electron vis-à-vis the already well-understood (spin-conserving) isotropic magnetic-dipole hyperfine interaction in alkali-metal–noble-gas systems. We find that, for all pairs in which the noble-gas is not helium, the predicted spin relaxation rate from the anisotropic interaction does not exceed 2.5% of the rate from the isotropic interaction, thereby not appreciably limiting the maximum noble-gas nuclear polarization attainable via spin-exchange collisions with polarized alkali-metal atoms.

For alkali–helium pairs, we predict that the anisotropic interaction has a slightly larger relative effect, perhaps limiting the nuclear polarization to ∼95% of the electronic polarization in the Rb-3He system; however, our confidence in the helium results is limited by a lack of knowledge of the interatomic potentials necessary for the calculation.

I. INTRODUCTION

Hyperpolarized noble gases [1] – gases such as $^3$He, $^{83}$Kr, or $^{129}$Xe which have had their nuclear polarizations artificially increased to tens of percent through spin-exchange with optically pumped alkali-metal vapors [2] – have recently found many new applications in areas within and outside the traditional realm of atomic physics. Hyperpolarized $^3$He has been used as a target in the scattering of polarized electrons to determine the longitudinal spin structure function of the neutron [3,4], polarized $^{129}$Xe has contributed to new developments in surface physics [5,6] and to the search for permanent EDMs [7], and both isotopes have been deployed in conjunction with conventional magnetic resonance imaging to obtain the first in vivo MRI images of the human lung [1,8]. Polarized $^{21}$Ne has been used to look for any fundamental anisotropy of space [9]. In this paper we analyze the anisotropic magnetic dipole interaction between the nucleus of a noble-gas atom and the valence electron of an alkali-metal atom. This interaction could place an important limit on the maximum degree of hyperpolarization that can be obtained with spin-exchange optical pumping.

Happer et al. [10] took the spin Hamiltonian of the interacting alkali-metal–noble-gas system to be

$$H = A_a I_a \cdot S + g_a \mu_a S \cdot B + \mu_a I_a \cdot B + \mu_b I_b \cdot B + \gamma N \cdot S + A_b I_b \cdot S,$$

(1)

where $I_a$, $I_b$, and $S$ are the spins of the alkali-metal nucleus, the noble-gas nucleus, and the alkali-metal valence electron, respectively, $N$ is the rotational angular momentum of the colliding pair, and $B$ is an external magnetic field. The first term of (1), corresponding to the magnetic-dipole interaction between electron and nuclear spin in the alkali-metal atom, and the next three terms, representing the coupling of the nuclear and electron spins to the external field, form the Hamiltonian of an alkali–noble-gas pair at infinite separation. The term $\gamma N \cdot S$, which arises from the motion of the valence electron in the electric field of the colliding atoms, contributes to the relaxation of the electron polarization, while the term $A_b I_b \cdot S$ partially accounts for the coupling of the electron spin to the magnetic field of the noble-gas nucleus and is responsible for the transfer of angular momentum between the alkali-metal electron and the noble-gas nucleus.

The full dipole field of the noble-gas nucleus at a displacement $r_b$ from the nucleus is

$$H_b(r_b) = \frac{8\pi \mu_b}{3 I_b} I_b \delta(r_b) + \frac{\mu_b}{I_b} I_b \cdot \frac{3 r_b r_b - r_b^2}{r_b^3} 1,$$

(2)

and thus, in addition to the term $A_b I_b \cdot S$ of (1), which comes from the first term of (2) and represents the interaction of the electron moment with the nuclear magnetic field “inside” the nucleus, the Hamiltonian (1) should also contain a term

$$B_b I_b \cdot (3zz - 1) \cdot S,$$

(3)
corresponding to the second term of (2) and representing the coupling of the electron spin to the long-range anisotropic piece of the nuclear dipole field. The much-studied and well-understood isotropic magnetic-dipole hyperfine interaction aligns the noble-gas spins parallel to the electron-spin polarization, but the (habitually neglected) anisotropic magnetic-dipole hyperfine interaction tends to polarize \( I_z \) antiparallel to \( \langle S_z \rangle \). Spin exchange optical pumping can produce large nuclear polarization in a noble gas only if \( A_b \gg B_b \), in which case \( \langle I_z \rangle \to \langle S_z \rangle \) (for \( I = 1/2 \)), or \( B_b \approx A_b \), in which case \( \langle I_z \rangle \to -\langle S_z \rangle/2 \), similar to the enhancements for dipolar coupling of nuclei.

In the following we present a detailed quantitative analysis of the anisotropic interaction (3), and we show that this interaction is indeed negligible for nearly all alkali-metal–noble-gas pairs. We find the ratio of the exchange rate due to the anisotropic interaction to the rate due to the isotropic interaction to be less than 2.5% for pairs in which helium is not the noble gas. However, we predict that this ratio is somewhat larger for alkali–helium pairs, perhaps appreciably limiting the \( ^3 \)He nuclear polarizations attainable via spin-exchange collisions with optically pumped alkali-metal vapors. Our confidence in the helium results is unfortunately weakened by a lack of knowledge of the interatomic potentials necessary for the calculations.

In Section II we discuss the interatomic potentials and ground-state electron wave functions employed in the analysis. Section III outlines the approach taken to describe the collisional distortion of the valence electron wave function. The derivation of the rate equations and the numerical evaluation of the rates are described in Section IV, and our results for the scalar interaction are compared with experiment (when possible) and with previous theoretical estimates in Section V.

### II. INTERATOMIC POTENTIALS AND WAVE FUNCTIONS

To carry out the collisional averages of the interactions in question, we shall need reasonable estimates of the interatomic potentials \( V_0(R) \). For the alkali–noble-gas pairs in which the noble-gas is Ar, Kr, or Xe, we adopt the modified Lennard–Jones potentials of Buck and Pauly [11], deduced from experiment. The equilibrium distance and well depth for the Rb-Ar (Rb-Xe) pair, not studied by Buck and Pauly, were taken to be the average of the corresponding parameters in the K-Ar and Cs-Ar (K-Xe and Cs-Xe) pairs.

Although no solid experimental data exists for the alkali–Ru pairs, we can adopt the functional form of the Buck-Pauly potentials and exploit the trends apparent in their parameters to arrive at a reasonable estimate of \( V_0 \) for these pairs. Noting that the equilibrium distance \( r_m \) is independent of noble-gas partner for a given alkali metal A, we take the average of the \( r_m \)-values for A–Ar, A–Kr, and A–Xe as an estimate of the equilibrium distance in the corresponding A–Ru pair, obtaining 5.01, 5.28, 5.36, and 5.47 Å for the Na–, K–, Rb–, and Cs–Ru pairs, respectively. We note also the nearly linear dependence of well depth on the nuclear charge \( Z \) of the noble-gas partner for each alkali metal. From a least-squares fit to the Ar, Kr, and Xe well depths for each alkali metal, we estimate alkali–Rn well depths of 3.03, 3.28, 3.27, and 3.24 × 10^{-14} ergs for Na, K, Rb, and Cs, respectively.

For the lighter noble-gases neon and helium, the situation is somewhat hazier, as the experimental data is sparse or non-existent. Lapadovitch et al. [12] have conducted a spectroscopic study of the NaNe molecule, the results of which can be represented with a ground-state interatomic Morse potential of equilibrium distance 5.29 Å and well depth 1.0 meV. We shall assume that the potential form of Buck and Pauly holds for the alkali–neon pairs, and base the \( r_m \) and \( \varepsilon \) values for it on the results of Lapadovitch: Noting that for a given noble-gas, the well depth shows little dependence on the alkali-metal partner, we take 1.0 meV as the well depth for all alkali–neon pairs, and we scale up the 5.29-Å NaNe equilibrium distance according to the trend apparent in the alkali–Ar values to find \( r_m \) for the other alkali-metal neon partners. Our equilibrium distances are thus 5.29, 5.64, 5.72, and 5.81 Å for Na–, K–, Rb–, and Cs–Ne, respectively.

For the alkali–helium pairs, no results grounded in experiment stand at our disposal, and so we use the theoretically-calculated potentials of Pascale [13].

For the required wave functions of the excited orbitals in the unperturbed alkali-metal atom, we use the semipirical Coulomb wave functions of Bates and Damgaard [15], which are hydrogenic wave functions with the (typically non-integer) principal quantum numbers chosen to yield the empirical binding energies of the atom. We adopt the normalization proposed by Hartree [16], which is discussed by Bates and Damgaard.

For the core orbitals \( \phi_{0nlm} \) of the noble-gas atom and for the ground-state wave function \( \phi_{an0s} \) of the alkali-metal valence electron, also required in the following, we adopt the Roothaan–Hartree–Fock wave functions of Clementi and Roetti [17] (for atoms with \( Z \leq 54 \)) and of McLean and McLean [18] (for \( Z > 54 \)).
III. COLLISIONAL DISTORTION OF THE VALENCE ELECTRON WAVE FUNCTION

To calculate the coupling constants $A_b$ and $B_b$, we must account for the distortion of the alkali-metal valence electron wave function induced by a collision with a noble-gas atom. We parse the wave function into two pieces: an internal wave function $\psi_b$, defined in a sphere of radius $s$ centered on the nucleus of the noble-gas atom, and an external wave function $\psi_a$, defined over the rest of space. The radius $s$ separating the internal and external parts of the wave function is chosen slightly larger than the charge radius of the noble-gas atom, but the results are insensitive to the choice of $s$.

Exterior to the noble-gas atom, the effect of the Coulomb potential of the noble-gas can be treated as a perturbation to the Hamiltonian of the electron in the unperturbed alkali-metal atom, and a standard perturbative treatment yields the wave function in that region [19]. Inside the noble-gas atom, we orthogonalize the incident wave function to the occupied orbitals of the noble-gas; for the case of helium, where this orthogonalized wave approximation fails (in the absence of occupied p-orbitals), we apply a partial wave analysis to construct the internal wave function. In the following, we have neglected the small non-adiabatic correction to the wave function that arises from the rotational motion of the nuclei, as it is unimportant in calculations of the magnetic-dipole hyperfine interactions.

A. The External Wave Function $\psi_a$

Let the alkali-metal atom and the noble-gas atom be situated on the $z$ axis of a coordinate system, with unit vectors $\mathbf{x}$, $\mathbf{y}$ and $\mathbf{z}$ along the coordinate axes. The noble-gas nucleus is displaced a distance $R = \mathbf{R} z$ from the alkali-metal nucleus; the displacement of the valence electron from the nucleus of the alkali metal (noble gas) is $r_a (r_b)$. Outside the noble-gas atom, the Hamiltonian $H$ of the valence electron can be written as

$$H = H_0 + H_1,$$

where $H_0$ is the Hamiltonian for the electron in the unperturbed alkali-metal atom,

$$H_0 = \frac{\hbar^2}{2m} \nabla^2 - e U_a(r_a),$$

and $H_1$ is the perturbation due to the interaction of the electron with the Coulomb field of the noble-gas nucleus and electron cloud,

$$H_1 = -e U_b(r_b).$$

In the last two equations, $U_k(r_k)$ is the Coulomb potential of the nucleus and core-electron cloud of atom $k$. Fermi [20] demonstrated that for low-energy electrons, the Coulomb potential term $H_1$ can be replaced by the pseudopotential

$$V_F = \frac{2\pi \hbar^2 a}{m} \delta(r_b),$$

where the positive (negative) scattering length $a$ is a measure of the strength of the repulsive (attractive) delta-function potential centered on the noble-gas nucleus. The scattering lengths used in the present work are 0.63, 0.13, −0.90, −1.96, −3.4, and −6.11 Å for He, Ne, Ar, Kr, Xe, and Rn, respectively [21]. The potential (7) reproduces the perturbation of the valence electron wave function outside the core of the noble-gas atom quite well, but it cannot be used to calculate the wave function inside the core.

The solution $\psi_a^{(0)}$ to the unperturbed Schrödinger equation

$$H_0 \psi_a^{(0)} = E \psi_a^{(0)}$$

is simply the ground-state valence electron wave function $\phi_{an_{gs}}(r_a)$; $E$ is the binding energy of the electron. In the presence of the perturbation $H_1$, we can expand the first-order correction $\psi_a^{(1)}$ to the unperturbed wave function in a basis of excited orbitals of the alkali-metal atom,

$$\psi_a^{(1)} = \sum_{n > n_g} c_{ans} \phi_{ans}(r_a) + \sum_{n \geq n_g} c_{anp} \phi_{anp_z}(r_a) + ...,\quad(9)$$

neglecting terms with higher $l$ than the s- and p-waves. The orbital $\phi_{anp_z}$ is defined as
of the spherical harmonics), and retaining only the s- and p-waves, we find
\[
\phi_{bnp}(r_b) = \frac{1}{r_b} P_{bnl}(r_b) Y_{l0}(\theta_b, \phi_b).
\] (10)

The wave function (9) must be symmetric under rotations about the z axis, and therefore it contains no admixed orbitals with non-zero azimuthal quantum number. The coefficients \( c_{nl} \) are, from first-order perturbation theory,
\[
c_{nl} = -\frac{2\pi \hbar^2 a}{m(E_{nl} - E_{nl0})} \phi_{nl0}^*(\mathbf{R}) \phi_{nl0}(\mathbf{R}).
\] (11)

**B. The Internal Wave Function \( \psi_b \)**

A good approximation to the wave function \( \psi_b \) internal to the noble-gas atom can be attained by orthogonalizing the external wave function \( \psi_a \) to the occupied core orbitals of the noble-gas [22, 23], to wit:
\[
\psi_b(r_b) = \psi_a(\mathbf{R} + r_b) - \sum_{nlm} \phi_{nlm}(r_b) \int d^3r'_b \phi_{nlm}^*(r'_b) \psi_a(\mathbf{R} + r'_b).
\] (12)

Expanding the external wave function in a Taylor series about \( \mathbf{R} \), we obtain
\[
\psi_a(\mathbf{R} + r_b) = \psi_a(\mathbf{R}) + \nabla \psi_a(\mathbf{R}) \cdot r_b
\]
\[= \psi_a(\mathbf{R}) + \hat{z} \cdot \nabla \psi_a(\mathbf{R}) \cdot z_b,
\] (13)

where, in writing the second of the above equations, we have exploited the symmetry of \( \psi_a \) apparent in (9). Substituting (14) into (12), performing the integration (noting that all terms in the sum with \( m \neq 0 \) vanish by the orthogonality of the spherical harmonics), and retaining only the s- and p-waves, we find
\[
\psi_b(r_b) = \psi_a(\mathbf{R} + r_b) + \sum_{n} c_{bnl} \phi_{bnl}(r_b) + \sum_{n} c_{bnp} \phi_{bnp}(r_b),
\] (15)

where
\[
c_{bnl} = -\psi_a(\mathbf{R}) \int d^3r_b \phi_{bnl}(r_b)
\] (16)
\[
c_{bnp} = -\hat{z} \cdot \nabla \psi_a(\mathbf{R}) \int d^3r_b \, z_b \phi_{bnp}(r_b).
\] (17)

The first term of (15), representing the incident wave from the alkali-metal, is much smaller than the distortion caused by the noble-gas atom; we will therefore neglect it when using the above result in subsequent calculations.

The orthogonalized wave approximation fails for the case of helium, which has no occupied p-orbitals. In its stead, we use a partial wave approximation to estimate \( \psi_b \) when the noble-gas is helium. Following Walker et al. [24], we write the internal wave function as the sum of an s- and p-wave,
\[
\psi_b(r_b) = \eta_0 \psi_a(\mathbf{R}) \frac{P_{b0}(r_b)}{r_b} + 3\eta \nabla \psi_a(\mathbf{R}) \cdot r_b \frac{P_{b1}(r_b)}{r_b^2},
\] (18)

where the functions \( P_{bl} \) satisfy the radial Schrödinger equation
\[
-\frac{\hbar^2}{2m} \frac{d^2 P_{bl}}{dr_b^2} + \left\{ -eU_b + \frac{\hbar^2(l + 1)}{2mr_b^2} \right\} P_{bl} = 0,
\] (19)

subject to the boundary conditions
\[
\lim_{r_b \to 0} P_{bl}(r_b) = \frac{s^{l+1}_b}{(2l + 1)!!} \quad \text{and} \quad P_{bl}(s) = \frac{s^{l+1}}{\eta(2l + 1)!!}.
\] (20)

The first of the boundary conditions ensures that \( \eta = 1 \) for \( U_b = 0 \), and the second is necessary to preserve the continuity of the external and internal wave functions. We note that \( \eta_0 \) is the enhancement of the wave function at
the noble-gas nucleus (due to the potential $U_b$), while $\eta_1$ is the enhancement of the derivative of the wave function at the noble-gas nucleus. Writing the internal wave function as
\[
\psi_b(r_b) = c_{bs}\phi_{bs}(r_b) + c_{bp}\phi_{bp}(r_b)
\]
(21)
to bring it into agreement with the form (15), we find
\[
c_{bs} = \sqrt{4\pi\eta_0}\psi_a(R)
\]
(22)
\[
c_{bp} = \sqrt{12\pi\eta_1}\hat{z} \cdot \nabla\psi_a(R).
\]
(23)
Walker et al. [24] have theoretically estimated the enhancement factor $\eta_0$, finding $\eta_0 = -5.3$ via a partial wave method and $\eta_0 = -9.5$ via an orthogonalized-plane-wave method. Instead of attempting our own theoretical calculation of $\eta_0$, we deduce it from the experimentally determined alkali-metal EPR frequency shift enhancement factor $\kappa_0$, which is a measure of the additional energy splitting between the magnetic spin sublevels of the electron due to the presence of a polarized noble-gas nucleus. The $\kappa_0$ parameter is proportional to the square of the electron wave function at the noble-gas nucleus, and hence to $\eta_0^2$; indeed, Schaefer et al. [25] have shown that $\kappa_0$ is given by
\[
\kappa_0 = \eta_0^2 \int_0^\infty dR 4\pi R^2 |\phi_{an} (R)|^2 e^{-V_0(R)/k_B T},
\]
(24)
where $\phi_{an}(R)$ is the ground-state valence-electron wave function of the unperturbed alkali-metal atom, and $V_0(R)$ is the interatomic potential between the alkali-metal atom and noble-gas atom.

Scaling the $\kappa_0$ of Barton et al. [26] (5.13 at 74.5°C) to 100°C via the empirical relation [27]
\[
\kappa_0(T) = \kappa_0(T_0)[1 + \beta(T - T_0)],
\]
(25)
where $\beta = 1/(563^\circ C)$, we find $\kappa_0 = 5.36$. Then (24) gives, using the interatomic potential of Pascale, $|\eta_0| = 6.0$. However, the integral of (24) is quite sensitive to the location and slope of the repulsive wall of $V_0(R)$, and as a result the value of $\eta_0$ thus derived is subject to the uncertainty in the interatomic potential. We shall return to this problem in Section IV.

C. The Coupling Constants

With the electron wave function in hand, we can readily determine the coupling constants $A_b$ and $B_b$. They are given by
\[
A_b = \frac{8\pi g_s \mu_B \mu_b}{3I_b} |\psi_b(0)|^2
\]
(26)
and
\[
B_b = \frac{g_s \mu_B \mu_b}{I_b} (d_{ba} + d_{bb}),
\]
(27)
where $d_{ba}$ and $d_{bb}$, the scalar parts of the expectation of the dipole tensor of (2) external and internal to the noble-gas atom, respectively, are
\[
d_{ba} = \frac{1}{2} \int_{\Gamma_a} d^3r_a \frac{3\cos^2 \theta_b - 1}{r_b^3} |\psi_a(r_a)|^2
\]
(28)
and
\[
d_{bb} = \frac{1}{2} \int_{\Gamma_b} d^3r_b \frac{3\cos^2 \theta_b - 1}{r_b^3} |\psi_b(r_b)|^2.
\]
(29)
In the above equations, the region $\Gamma_b$ is a sphere of radius $s$ (slightly larger than the charge radius of the noble gas) centered on the noble-gas nucleus, and $\Gamma_a$ is all space except $\Gamma_b$. 

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IV. ESTIMATES OF THE SPIN-EXCHANGE RATES DUE TO THE MAGNETIC-DIPOLE HYPERFINE INTERACTIONS

Although the anisotropic magnetic-dipole hyperfine interaction can change both the magnitude and direction of the rotational angular momentum $\mathbf{N}$ during an alkali-metal–noble-gas collision, to first order by $\Delta N = 0, \pm 1, \pm 2$, the experimental conditions for spin-exchange optical pumping are almost always such that $N \gg 1$, so that it is a good approximation to assume $\mathbf{N}$ is a conserved classical vector during a collision. The motion of the colliding atoms can then be described by a classical collision trajectory, along which the spin-dependent hyperfine interactions act as a perturbation. As shown in the Appendix, the full rate equation which describes the rate of change of the longitudinal spin polarization of the noble-gas nucleus due to the magnetic-dipole hyperfine interactions is

$$\frac{d^{(2)}}{dt} \langle I_{bz} \rangle = n_a \Gamma_b(A_b A_b) [2(\mathbf{I}_b \cdot I_b - I_{bz}^2) \langle S_z \rangle - \langle I_{bz} \rangle]$$

$$- n_a \Gamma_b(B_b B_b) [\langle \mathbf{I}_b \cdot I_b - I_{bz}^2 \langle S_z \rangle + \langle I_{bz} \rangle],$$

where $n_a$ is the alkali-metal number density the rates $\Gamma_b(A_b A_b)$ and $\Gamma_b(B_b B_b)$ are given by

$$\Gamma_b(A_b A_b) = \frac{\pi}{2} \int_0^\infty db \int_0^\infty dw \ p(w) \ w^2 \varphi(A_b)$$

and

$$\Gamma_b(B_b B_b) = \pi \int_0^\infty db \int_0^\infty dw \ p(w) \ w^2 \sum_{n=-2}^{2} \varphi_{2n}(B_b) \varphi_{2n}(B_b).$$

In the above rate expressions, $p(w)$ is the probability density of the initial relative impact velocity $w$, as given by the Maxwell–Boltzmann distribution $(A20)$. The phase angles are

$$\varphi(A_b) = \frac{2}{\hbar} \int_{R_0}^\infty dR \left[ \frac{dR}{dt} \right]^{-1} A_b(R)$$

and

$$\varphi_{2n}(B_b) = \begin{cases} \frac{2}{\hbar \omega} \int_0^\infty d\psi \ B_b(R) \ R^2 \ d^2 m_0(\psi), & \text{if } m = 0, \pm 2; \\ 0, & \text{if } m = \pm 1. \end{cases}$$

The Wigner D-functions $D_{m0}^2(0, \theta, 0) = d_{m0}^2(\theta)$ are necessary to rotate the co-ordinate system of an arbitrary collision into the frame where $z$-axis is directed along the internuclear axis.

Denoting the impact parameter $b$, the initial relative velocity $w$, and the reduced mass of the colliding pair $M$, assumption of the conservation of energy and of angular momentum during an alkali-metal–noble-gas collision leads to the equations

$$\frac{dR}{dt} = \pm w \sqrt{1 - \frac{b^2}{R^2} - \frac{2V_0(R)}{Mw^2}}$$

and

$$\frac{dR}{d\psi} = \pm \frac{R^2}{b} \sqrt{1 - \frac{b^2}{R^2} - \frac{2V_0(R)}{Mw^2}},$$

from which the collision trajectories and phase angles can be found. We have calculated the rates $\Gamma_b(A_b A_b)$ and $\Gamma_b(B_b B_b)$ in the above framework for the 24 alkali-metal–noble-gas pairs drawn from the alkali metals Na, K, Rb, Cs and noble gases $^3$He, $^{21}$Ne, $^{37}$Ar, $^{83}$Kr, $^{129}$Xe, and $^{209}$Rn. The results are listed in Table I.

The results for the alkali–helium pairs given in Table I were found using the Pascale potentials and an $\eta_0$ of $-6.0$. To investigate the uncertainty in our results caused by the uncertainty in the alkali–helium interatomic potentials, we have also calculated $\eta_0$ ($\eta_0$ from (24), with $\kappa_0 = 5.36$) and the spin-exchange rates for Rb–$^3$He using the Morse potential

$$V_0(R) = D(e^{-2a(R-R_0)} - 2e^{-a(R-R_0)}),$$
rates calculated using the Pascale potentials yields example, as illustrated in Figure 1, a least-squares linear fit (valid over the range from 25 energy of the colliding atoms. However, we do predict some temperature dependence for the alkali–helium pairs. For helium, where the repulsive wall is so steep so as to fix the distance of closest approach, regardless of the kinetic above) is temperature independent. We have found that this assumption is valid for the noble-gases heavier than assumed that the velocity-averaged binary spin-exchange cross section rates are sparse. A few results are listed in Table III. In interpreting experimental data, most investigators have considering these substantial differences, our results are in good agreement with Walker’s, within a factor of 7 in all cases, and often much less.

V. COMPARISON OF RESULTS WITH EXPERIMENT AND WITH PREVIOUS ESTIMATES

To date, no experimental observation of the effect of the anisotropic magnetic-dipole hyperfine interaction has been reported, nor have any previous theoretical estimates been undertaken. However, Walker [28] has estimated the spin-exchange rates due to the isotropic interaction, and experimental results (of varying quality) exist for some of the pairs. Table III shows a comparison of our results with those of Walker and with experiment.

The expression for the rate \( \Gamma_b(A_bA_b) \) in [28] – defined for the same rate equation as (30) – contains an extra (erroneous) factor of two; the values from [28] listed in Table III have been corrected for this factor. The remaining differences between our and Walker’s results can be attributed to the facts that he assumed different interatomic potentials for all pairs not involving helium, and that he used Coulomb wave functions for the ground state of the alkali–metal valence electron, where we have instead chosen Roothaan–Hartree–Fock wave functions. Most significantly, Walker handled the distortion of the valence-electron wave function in the framework of the partial-wave approximation, calculating (or selecting, based on experimental results) an enhancement factor \( \eta_0 \) for all alkali–noble-gas pairs, while we have worked in the orthogonalized-wave approximation for all pairs except the alkali–helium. Considering these substantial differences, our results are in good agreement with Walker’s, within a factor of 7 in all cases, and often much less.

Because of the difficulties inherent in the measurement, reliable experimental results for the isotropic spin-exchange rates are sparse. A few results are listed in Table III. In interpreting experimental data, most investigators have assumed that the velocity-averaged binary spin-exchange cross section \( \langle \sigma_{SEV} \rangle \) (which we have called \( \Gamma_b(A_bA_b) \) in the above) is temperature independent. We have found that this assumption is valid for the noble-gases heavier than helium, where the repulsive wall is so steep so as to fix the distance of closest approach, regardless of the kinetic energy of the colliding atoms. However, we do predict some temperature dependence for the alkali–helium pairs. For example, as illustrated in Figure 1, a least-squares linear fit (valid over the range from 25°C to 200°C) to the Rb-3He rates calculated using the Pascale potentials yields

\[
\Gamma_b(T) = \Gamma_b(100°C) \left(1 + \frac{T - 100°C}{T_0}\right),
\]

where \( \Gamma_b(100°C) = 4.543 \times 10^{-20} \text{ cm}^3/\text{s} \) and \( T_0 = 387.6°C \). Of course, the slope of the temperature dependence is sensitive to the steepness of the repulsive wall of the interatomic potential. Given the uncertainty in our potentials for the helium systems, it is quite possible that the actual slope is considerably smaller or even vanishingly small. In recent experiments with Rb-3He, Baranga et al. [29] have observed no measurable temperature dependence of the spin-exchange rate.

In general our estimates for the isotropic spin-exchange rate are somewhat lower than the experimental values, usually by a factor of 2 to 3. However, we note that for the case of Rb-3He, where we have relied on accurate \( \kappa_0 \) measurements to deduce \( \eta_0 \), our result is in much better agreement with the measurement reported in [30] than with the result of [31]. A very recent measurement [29] agrees with both [30] and our calculation.
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APPENDIX: DERIVATION OF THE RATE EQUATIONS

1. Classical collision trajectories

The initial state of the atoms before the collision can be characterized by the angular momentum $N$, and by the initial relative velocity $w = dR/dt$ of the noble-gas atom with respect to the alkali-metal atom at a time $t = -\infty$ before the pair is close enough to interact. Because of the constraint $N \cdot w = 0$ the three components of $N$ and the three components of $w$ are not independent, and only five independent parameters are needed to characterize the collision. We choose the five independent parameters to be the magnitude $b$ of the impact parameter, the magnitude $w$ of the initial velocity, and the three Euler angles $\alpha$, $\beta$ and $\gamma$, which rotate a collision with a “reference orientation” to a collision with an arbitrary orientation but with the same values of $b$ and $w$.

As sketched in Figure 2, the collision with the reference orientation takes place in the $zx$ plane. The magnitude of the internuclear separation is $R$ and the internuclear axis makes an angle $\theta$ with the $z$ axis. The scattering angle is $\theta_s = \pi - 2\psi_s$. The symmetries of the scattering are more easily exploited with the angular coordinate

$$\psi = \theta_s + \psi_s - \theta.$$  \hspace{1cm} (A1)

At the point of closest approach, we have $\theta = \theta_s + \psi_s$ or $\psi = 0$. For a collision of arbitrary orientation, the entire trajectory of the reference orientation is rotated by the Euler angles $\alpha$, $\beta$ and $\gamma$.

Since we assume that the angular momentum and energy are conserved during the collision, we may write the angular velocity as

$$\frac{d\psi}{dt} = \frac{bw}{R^2},$$  \hspace{1cm} (A2)

and the radial velocity as

$$\frac{dR}{dt} = \pm w \sqrt{1 - \frac{b^2}{R^2} - \frac{2V_0(R)}{Mw^2}}.$$  \hspace{1cm} (A3)

The plus and minus signs refer to the receding and approaching segments of the orbital trajectory. A differential equation for the trajectory $R(\psi)$ of the collision is given by the ratio of (A3) to (A2)

$$\frac{dR}{d\psi} = \pm \frac{R^2}{b} \sqrt{1 - \frac{b^2}{R^2} - \frac{2V_0(R)}{Mw^2}}.$$  \hspace{1cm} (A4)

2. The density matrix

We will describe the spin state of the alkali-metal atoms with a density matrix $\rho_a$ and the spin state of the noble-gas atoms with a density matrix $\rho_b$. For the usual conditions of spin-exchange optical pumping, the alkali-metal density matrix is well described by a spin temperature $\beta^{-1}$, and is given by

$$\rho_a = c_a e^{\beta F_z} = c_a e^{\beta S_z} e^{\beta I_{az}}$$  \hspace{1cm} (A5)

where $c_a = \frac{1}{Tr e^{\beta F_z}}$.

The inverse spin temperature $\beta$ will normally be a slowly changing function of position in the vapor and of time. The density matrix (A5) is a simple product of electronic and nuclear density matrices. It is axially symmetric, that is, it commutes with the total spin operator $F_z$ of the alkali-metal atoms, and it is invariant to spin-exchange...
collisions between alkali-metal atoms. It also commutes with the spin interaction between the pair of atoms at infinite separation

\[ V_1(\infty) = A_a(\infty)I_a \cdot S + g_s \mu_B S_z H_0 - \frac{\mu_a}{I_a} I_{sz} H_0 - \frac{\mu_b}{I_b} I_{bz} H_0. \]  

(A6)

We will assume that the density matrix of the noble-gas atoms is also axially symmetric, that is,

\[ \langle m | \rho_b | m' \rangle = \delta_{mm'} \langle m | \rho_b | m' \rangle, \]  

(A7)

where \(|m\rangle\) denotes an eigenstate of \(I_{bz}\).

When the atoms are well separated, the spins of each of the two atomic species \(k\) will evolve under the influence of the spin-dependent potential of the free atoms according to

\[ i\hbar \frac{d}{dt} \rho_k = [V_1(\infty), \rho_k]. \]  

(A8)

To isolate the evolution due to collisions we work in the interaction picture. Operators \(\tilde{X}\) of the interaction picture are defined in terms of operators \(X\) of the laboratory picture by

\[ \tilde{X} = e^{iV_1(\infty)t/\hbar} X e^{-iV_1(\infty)t/\hbar}. \]  

(A9)

The interaction-picture density matrices \(\tilde{\rho}_k\) would be constant in time if there were no collisions, as one can verify by differentiating \(\tilde{\rho}_k\) and using (A8).

Consider atomic pairs that collide in the time interval \(t - dt/2\) to \(t + dt/2\). After a collision the initial spin state, a simple product \(\tilde{\rho} = \tilde{\rho}_a \tilde{\rho}_b\), will evolve to \(\tilde{\rho} + \Delta \tilde{\rho}\), where

\[ \Delta \tilde{\rho} = \tilde{U} \tilde{\rho} \tilde{U}^\dagger - \tilde{\rho} = \Delta^{(1)} \tilde{\rho} + \Delta^{(2)} \tilde{\rho} + \ldots \]  

(A10)

The time evolution operator is

\[ \tilde{U} = 1 + \tilde{U}^{(1)} + \tilde{U}^{(2)} + \ldots, \]  

(A11)

where the antihermitian first-order part is

\[ \tilde{U}^{(1)} = \frac{1}{i\hbar} \int_{-\infty}^{\infty} dt' \Delta \tilde{V}_1(R') = -\tilde{U}^{(1)\dagger}, \]  

(A12)

and the second-order part is

\[ \tilde{U}^{(2)} = \frac{1}{(i\hbar)^2} \int_{-\infty}^{\infty} dt' \Delta \tilde{V}_1(R') \int_{-\infty}^{t'} dt'' \Delta \tilde{V}_1(R''). \]  

(A13)

The increment of the spin-dependent potential due to collisions is

\[ \Delta \tilde{V}_1(R') = \tilde{V}_1(R') - \tilde{V}_1(\infty). \]  

(A14)

We use the notation \(R' = R(t')\) and \(R'' = R(t'')\) for these classical-path collisions. In (A14) we assume that \(|R(t)| = R_0\); that is, the distance of closest approach of the classical-path collision occurs when \(t' = t\). Since the magnitudes of the spin interactions have sharp maxima at the distance of closest approach, the contributions to the integrals of (A12) and (A13) are negligible a few picoseconds before or after \(t' = t\).

The first-order collisional increment in (A10) is given by the commutator

\[ \Delta^{(1)} \tilde{\rho} = [\tilde{U}^{(1)}, \tilde{\rho}], \]  

(A15)

and the second-order increment is

\[ \Delta^{(2)} \tilde{\rho} = \tilde{U}^{(1)} \tilde{\rho} \tilde{U}^{(1)\dagger} + \tilde{U}^{(2)} \tilde{\rho} + \tilde{\rho} \tilde{U}^{(2)\dagger}. \]  

(A16)

The global evolution of the density matrix for the atomic species \(k\), due to collisions with atoms of the other species \(\bar{k}\) of number density \(n_{\bar{k}}\), is given by the statistical average
\[
\frac{d}{dt} \tilde{\rho}_k = n_\bar{k} Z \text{ Eu Tr}_{\bar{k}} \Delta \tilde{\rho}.
\]  
(A17)

Here the symbol \(\text{Tr}_{\bar{k}}\) means a trace over a complete set of spin sublevels of the atomic species \(\bar{k}\). The average of an operator \(X\) over all possible Euler angles of a collision is denoted by

\[
\text{Eu } X = \frac{1}{8\pi^2} \int_0^{2\pi} d\alpha \int_0^\pi d\beta \sin \beta \int_0^{2\pi} d\gamma X.
\]  
(A18)

The rate integral \(ZX\) of an operator \(X\) is defined to be

\[
ZX = \int_0^\infty db \ 2\pi b \int_0^\infty dw \ p(w) w X,
\]  
(A19)

where \(p(w)\) is the probability density of initial velocities. We assume a Maxwell–Boltzmann distribution, with density

\[
p(w) = 4\pi w^2 \left( \frac{M}{2\pi kT} \right)^{3/2} e^{-Mw^2/2kT}.
\]  
(A20)

It is sufficient to consider the rates of evolution from (A17) that are first-order and second-order in \(V_1\). The first-order rate is given by

\[
\frac{d^{(1)}}{dt} \tilde{\rho}_k = n_\bar{k} Z \text{ Eu Tr}_{\bar{k}} \Delta^{(1)} \tilde{\rho} = \frac{1}{i\hbar} [\delta \tilde{\mathcal{E}}_k, \tilde{\rho}_k],
\]  
(A21)

where the collisional energy-shift operator which occurs in the commutator is

\[
\delta \tilde{\mathcal{E}}_k = i\hbar n_\bar{k} Z \text{ Eu Tr}_{\bar{k}} \tilde{U}^{(1)} \tilde{\rho}_k.
\]  
(A22)

The small energy-shift operators have no effect on the efficiency of spin-exchange optical pumping and will not be discussed further. The second-order rate is

\[
\frac{d^{(2)}}{dt} \tilde{\rho}_k = n_\bar{k} Z \text{ Eu Tr}_{\bar{k}} \Delta^{(2)} \tilde{\rho}.
\]  
(A23)

We can use (A23) to show that the second-order rate of change of the expectation value \(\langle X_k \rangle\) of any spin operator \(X_k\) for the atomic species \(k\) is

\[
\frac{d^{(2)}}{dt} \langle X_k \rangle = \text{Tr}_k \tilde{X}_k \frac{d^{(2)}}{dt} \tilde{\rho}_k = n_\bar{k} Z \text{ Eu Tr } \tilde{\rho} \{\tilde{U}^{(1)*} \tilde{X}_k \tilde{U}^{(1)} + \tilde{U}^{(2)*} \tilde{X}_k + \tilde{X}_k \tilde{U}^{(2)*}\},
\]  
(A24)

The trace extends over the spin sublevels of both atomic species.

3. The isotropic magnetic-dipole hyperfine interactions

We assume that the collision is over in a few picoseconds, so the time variation of the exponentials in (A9) can be ignored and we can write

\[
\Delta \tilde{V}_1(R') \approx \sum_p A_p(R') \tilde{I}_p \cdot \tilde{S}
\]  
(A25)

for the isotropic magnetic-dipole hyperfine interaction of the atomic species \(p = a\) or \(b\), where the interaction-picture spin operators

\[
\tilde{I}_p = e^{iV_1(\infty)t/\hbar} I_p e^{-iV_1(\infty)t/\hbar}
\]  
(A26)

and

\[
\tilde{S} = e^{iV_1(\infty)t/\hbar} S e^{-iV_1(\infty)t/\hbar}
\]  
(A27)
are evaluated at the time \( t' = t \) of closest approach and are therefore independent of \( t' \). From (A12) and (A13) we obtain

\[
\tilde{U}^{(1)} = \frac{1}{i} \sum_p \varphi(A_p) \tilde{I}_p \cdot \tilde{S} \quad (A28)
\]

and

\[
\tilde{U}^{(2)} = -\frac{1}{2} \sum_{pq} \varphi(A_p) \varphi(A_q) \tilde{I}_p \cdot \tilde{S} \tilde{I}_q \cdot \tilde{S}, \quad (A29)
\]

where the phase angle is

\[
\varphi(A_p) = \frac{1}{\hbar} \int_{-\infty}^{\infty} dt' \ A_p(R') = \frac{2}{\hbar} \int_{R_0}^{\infty} dR \left[ \frac{dR}{dt} \right]^{-1} A_p(R). \quad (A30)
\]

Substituting (A28) and (A29) into (A24), we find

\[
d^{(2)} \langle X_k \rangle = -\frac{1}{2} \eta_k Z E_u \sum_{pq} \varphi(A_p) \varphi(A_q) \text{Tr} \left[ \tilde{I}_p \cdot \tilde{S}, [\tilde{I}_q \cdot \tilde{S}, \tilde{X}_k] \right] \hat{\rho} \quad (A31)
\]

Using the commutation relations \( \tilde{I}_p \times \tilde{I}_q = i \delta_{pq} \tilde{I}_q \) along with the dyadics formed from the spin operators

\[
\tilde{I}_p \tilde{I}_q = \sum_{ij} \tilde{I}_{pi} \tilde{I}_{qj} x_i x_j \quad \text{and} \quad (\tilde{I}_p \tilde{I}_q)^\dagger = \sum_{ij} \tilde{I}_{qj} \tilde{I}_{pi} x_i x_j, \quad (A32)
\]

with analogous relations for \( S \), we find

\[
\left[ \tilde{I}_p \cdot \tilde{S}, [\tilde{I}_q \cdot \tilde{S}, \tilde{I}_k] \right] = \frac{\delta_{pq}}{2} \left( 2\tilde{S} \cdot \tilde{S} - \tilde{S} \tilde{S} - (\tilde{S} \tilde{S})^\dagger \right) \cdot \tilde{I}_k - \{2\tilde{I}_p \cdot \tilde{I}_q - \tilde{I}_p \tilde{I}_q - (\tilde{I}_p \tilde{I}_q)^\dagger \} \cdot \tilde{S} \quad (A33)
\]

Substituting (A33) into (A31) and assuming a spin-temperature limit we find

\[
d^{(2)} \langle I_{bz} \rangle = \eta_a \Gamma_b(A_b A_b) \left[ 2 \langle I_b \cdot I_b - I_{bz}^2 \rangle \langle S_z \rangle - \langle I_{bz} \rangle \right], \quad (A34)
\]

where the exchange rate is

\[
\Gamma_b(A_b A_b) = \frac{1}{4} Z E_u \varphi^2(A_b) = \frac{\pi}{2} \int_0^\infty db \int_0^\infty dw \ p(w) \ w \ \varphi^2(A_b). \quad (A35)
\]

4. The anisotropic magnetic-dipole hyperfine interactions

In analogy to (A25) we may write

\[
\Delta \tilde{V}_1(R') = \sum_p B_p(R') \tilde{I}_p \cdot (3z'z' - 1) \cdot \tilde{S} \quad (A36)
\]

for the anisotropic magnetic-dipole hyperfine interaction of the atomic species \( p = a \) or \( b \). The interaction-picture spin operators \( \tilde{I}_p \) and \( \tilde{S} \) are defined as in (A26) and (A27) for the time \( t' = t \) of closest approach.

The operator algebra for the anisotropic magnetic-dipole interactions and the electric-quadrupole interactions is most efficiently carried out with angular momentum recoupling. We will use the notation

\[
\{T_l T_s\}_{jm} = \sum_n T_{ln} T_{s,m-n} C(l s j; n, m - n) \quad (A37)
\]

11
to denote the coupling of the spherical tensors components $T_{lm}$ and $T_{sm}$ to a product tensor of total angular momentum $j$ and $z$ component $m$. Here $C(l; j; n, m - n)$ is a Clebsch-Gordan coefficient. The product tensor transforms under rotations with the Wigner functions $D_{mn}^j$.

We note that

$$\langle 3zz - 1 \rangle = \sqrt{6}\langle xx \rangle_{20}, \quad (A38)$$

where $\{xx\}_{jm}$ denotes a spherical basis dyadic, formed according to (A37) from the spherical unit vectors $x_{\pm 1} = \mp(x \pm iy)/\sqrt{2}$ and $x_0 = z$. Thus, for a reference collision we have

$$\langle 3\zeta\zeta - 1 \rangle = \sqrt{6}\sum_{m'}\langle xx \rangle_{2m'd_{m'0}^2(\theta)} = \sqrt{6}\sum_{m'm} \langle xx \rangle_{2m'd_{m'm}(\theta + \psi)d_{m0}^2(-\psi)}, \quad (A39)$$

where the instantaneous direction $\zeta$ of the internuclear axis for a reference collision is obtained by rotating $z = x_0$ about the $y$ axis by an angle $\theta = \theta + \psi - \psi$. Following a common convention, we denote the Wigner $D$ function for this rotation by $D_{m'0}(0, \theta, 0) = d_{m'0}^2(\theta)$. Substituting (A36) into (A12) we find for a reference collision

$$\tilde{U}^{(1)} = \frac{\sqrt{6}}{i} \sum_{m'mp} \langle \tilde{I}_p \tilde{S} \rangle_{2m'd_{m'm}(\theta + \psi)} \varphi_{2m}(B_p). \quad (A40)$$

The phase

$$\varphi_{2m}(B_p) = \frac{1}{i\hbar} \int_{-\infty}^{\infty} dt B_p(R) R^2 d_{m0}^2(-\psi) \quad (A41)$$

depends on the collisional parameters $w$ and $b$, but is independent of the Euler angles of the collision. The interaction coefficients $B_p(R)$ are implicitly even functions of $\psi$, since $R(\psi) = R(-\psi)$. The Wigner functions $d_{m0}^2(\psi)$ are even functions of $\psi$ when $n$ is even and odd functions if $n$ is odd. Therefore, we have

$$\varphi_{2m}(B_p) = \begin{cases} \left(2bw/\hbar\right) \int_0^\infty d\psi B_p(R) R^2 d_{m0}^2(\psi), & \text{if } m = 0, \pm 2; \\ 0, & \text{if } m = \pm 1. \end{cases} \quad (A42)$$

Since $\varphi_{2-2}(B_p) = \varphi_{22}(B_p)$, two independent phases $\varphi_{22}(B_p)$ and $\varphi_{20}(B_p)$ must be calculated for the tensor interactions. The rotation matrices needed are simple trigonometric functions $d_{m0}^2(\psi) = (3\cos^2 \psi - 1)/2$ and $d_{m0}^2(\psi) = \sqrt{3/8}\sin^2 \psi$. The trajectory $R(\psi)$ is the solution to (A4) subject to the boundary condition $R(\psi = 0) = R_0$.

For an arbitrary collision we find

$$\tilde{U}^{(1)} = \frac{\sqrt{6}}{i} \sum_{m'm'mp} \langle \tilde{I}_p \tilde{S} \rangle_{2m'd_{m'm}(\alpha, \beta, \gamma)} d_{m'm}(\theta + \psi) \varphi_{2m}(B_p). \quad (A43)$$

In like manner, we find that the second-order evolution operator is

$$\tilde{U}^{(2)} = -3 \sum_{m'm'm'np} \langle \tilde{I}_p \tilde{S} \rangle_{2m'd_{m'm}(\alpha, \beta, \gamma)} d_{m'm}(\theta + \psi) \varphi_{2m}(B_p)$$

$$\times \sum_{n'n'nq} \langle \tilde{I}_q \tilde{S} \rangle_{2n'd_{n'n}(\alpha, \beta, \gamma)} d_{n'n}(\theta + \psi) \varphi_{2n}(B_q). \quad (A44)$$

Making use of the orthogonality properties of the Wigner $D$ functions we find that the integral over Euler angles gives

$$\text{Eu} \tilde{U}^{(2)} = -\frac{24\pi}{5} \sum_{pqmn} \varphi_{22}(B_p) \cdot \varphi_{22}(B_q)(-1)^m \langle \tilde{I}_p \tilde{S} \rangle_{2m} \langle \tilde{I}_q \tilde{S} \rangle_{2,-m} \quad (A45)$$

where

$$\varphi_{22}(B_p) \cdot \varphi_{22}(B_q) = \sum_n \varphi_{2n}(B_p) \varphi_{2n}(B_q). \quad (A46)$$

Similarly, we find that for any operator $X$
Using the 9j recoupling coefficients, which are proportional in this case to Racah coefficients $W(1111; 2K)$ (6j coefficients times a phase factor), one can show that
\[
\left\langle \{I_p|I_{kn}\}I_q\right\rangle_Km = \sum_{m'} \tilde{I}_{p,m'}\tilde{I}_{kn}\tilde{I}_{q,m'-m'}C(11K;m',m-m').
\] (A49)

Using the commutation relations for angular momenta, and Racah sum rules for products of Clebsh-Gordan coefficients we find
\[
\left\langle \{I_p|I_{kn}\}I_q\right\rangle_Km = \tilde{I}_{kn}\tilde{I}_{p\tilde{q}}\sum_{L} \left[ \{I_p\tilde{I}_q\}_{L,m+n}\sqrt{2[L]|K|} \right]
\times W(111L; 1K)C(LK1;m+n,-n)(-1)^{L+1+n}
= \left\langle \{I_p\tilde{I}_q\}_{Km}\tilde{I}_{kn} + \delta_{kq}\sum_{L} \left[ \{I_p\tilde{I}_q\}_{L,m+n}\sqrt{2[L]|K|} \right] \right.
\times W(111L; 1K)C(LK1;m+n,-n)(-1)^{K+n}
\] (A50)

where we use the notation $|J| = 2J + 1$. Substituting (A45), (A47), (A48), and (A50) into (A24), and assuming an axially symmetric density matrix in the spin-temperature limit we find
\[
\frac{d^{(2)}}{dt} \langle I_{kz} \rangle = 24\pi^2 n_k Z \sum_{pqK} \varphi_2(B_p) \cdot \varphi_2(B_q) P_{LK}\left[ \delta_{pq} + \delta_{kq}\right] \left\langle \{I_p|I_q\}_00\right\rangle \left\langle \{SS\}_K0\right\rangle,
\] (A51)

where
\[
P_{LK} = (-1)^K \sqrt{2|L||K|} W(111L; 1K)W(1111; 2K)C(LK1;00).
\] (A52)

Because of symmetries of the Clebsh-Gordan coefficient, $P_{LK}$ is zero unless $L + K$ is odd. To evaluate (A51) we note that
\[
\langle \{I_pI_q\}_00 \rangle = -\frac{1}{\sqrt{3}} \langle I_p \cdot I_q \rangle,
\] (A53)
\[
\langle \{I_pI_q\}_10 \rangle = \frac{i}{\sqrt{2}} \langle I_p \times I_q \rangle,
\] (A54)

and
\[
\langle \{I_pI_q\}_20 \rangle = \frac{1}{\sqrt{6}} \langle 3I_pzI_qz - I_p \cdot I_q \rangle.
\] (A55)

Analogous expressions for $\langle \{SS\}_K0 \rangle$ can be obtained by letting $L \rightarrow K$, $I_p \rightarrow S$ and $I_q \rightarrow S$. Substituting these into (A51), noting that $I_k \times I_k = iI_k$ and $\{SS\}_20 = 0$ since $S = 1/2$, we obtain
\[
\frac{d^{(2)}}{dt} \langle I_{bz} \rangle = -n_a \Gamma_b(B_bB_b) \left[ \langle I_b \cdot I_b - I_{bz}^2 \rangle \langle Sz \rangle + \langle I_{bz} \rangle \right],
\] (A56)

where the rate is
\[ \Gamma_b(B_b B_b) = \frac{1}{2} Z \phi_2(B_b) \cdot \phi_2(B_b) \]
\[ = \pi \int_0^\infty db \int_0^\infty dw \, p(w) \, w \phi_2(B_b) \cdot \phi_2(B_b). \quad (A57) \]


FIG. 1. Calculated temperature dependence of the isotropic spin-exchange rate \(\Gamma_B(A_B A_B)\) for the Rb-\(^3\text{He}\) pair. The solid line is a least-squares fit to the points calculated at \(10^5\) intervals.

FIG. 2. Alkali-metal–noble-gas collision geometry in the \(x\)-plane. The vector \(\mathbf{R}\) is directed from the alkali-metal nucleus (A) to the noble-gas nucleus (B). The impact parameter is \(b\) and the initial relative velocity, \(w\); the distance of closest approach is \(R_0\).
TABLE I. Estimated spin-exchange rates $\Gamma_b(A_bA_b)$ and $\Gamma_b(B_bB_b)$ from the isotropic and anisotropic magnetic-dipole hyperfine interactions, respectively. All rates were calculated at 100°C except for the alkali–helium pairs, which were calculated at 190°C. The equilibrium noble-gas nuclear polarization as a fraction of the alkali-metal electronic polarization for the alkali–helium and –xenon pairs is $\approx 1 - 3\epsilon/2$, where $\epsilon = \Gamma_b(A_bA_b)/\Gamma_b(B_bB_b)$ is the ratio of rates given in column 4.

<table>
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<tr>
<th>Alkali-Metal–Noble-Gas</th>
<th>$\Gamma_b(A_bA_b)$ ($10^{-19}$ cm$^3$/s)</th>
<th>$\Gamma_b(B_bB_b)$ ($10^{-21}$ cm$^3$/s)</th>
<th>$\epsilon$</th>
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<td>K $^{209}$Rn</td>
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<td>0.88%</td>
</tr>
<tr>
<td>Rb $^{209}$Rn</td>
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<td>130</td>
<td>0.72%</td>
</tr>
<tr>
<td>Cs $^{209}$Rn</td>
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<td>220</td>
<td>0.49%</td>
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TABLE II. Estimates of $\eta_0$, $\Gamma_b(A_bA_b)$, and $\Gamma_b(B_bB_b)$ for the Rb–$^3$He pair at 190°C, found using several different interatomic potentials $V_0(R)$. Here, Morse ($R_0,D$) denotes the potential (37), where $R_0$ is the equilibrium distance in Å and $D$ is the well depth in $10^{-14}$ ergs.

| Interatomic Potential $V_0(R)$ | $|\eta_0|$ | $\Gamma_b(A_bA_b)$ ($10^{-20}$ cm$^3$/s) | $\Gamma_b(B_bB_b)$ ($10^{-21}$ cm$^3$/s) | $\epsilon$ |
|-------------------------------|----------|----------------------------------------|----------------------------------------|----------|
| Pascale                       | 6.0      | 5.6                                    | 1.7                                    | 3.1%     |
| Morse (7.00,0.030)            | 5.8      | 5.2                                    | 1.7                                    | 3.3%     |
| Morse (7.41,0.030)            | 7.1      | 4.8                                    | 1.6                                    | 3.3%     |
| Morse (8.00,0.030)            | 10.0     | 4.4                                    | 1.4                                    | 3.2%     |
| Morse (7.00,0.060)            | 7.0      | 4.8                                    | 1.6                                    | 3.3%     |
| Morse (7.41,0.060)            | 8.8      | 4.5                                    | 1.4                                    | 3.1%     |
| Morse (8.00,0.060)            | 12.6     | 4.0                                    | 1.2                                    | 3.0%     |
TABLE III. Comparison of isotropic spin-exchange rate results with experiment and with the estimates of Walker [28].

<table>
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<tr>
<th>Alkali-Metal–Noble-Gas</th>
<th>Present</th>
<th>$\Gamma_{ab}(A_bA_b)$ (10$^{-19}$ cm$^3$/s)</th>
<th>Walker</th>
<th>Expt.</th>
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$^a$Reference [30].
$^b$Reference [31].
$^c$Reference [32].