Anisotropic Hyperfine Interactions Limit the Efficiency of Spin-Exchange Optical Pumping of ^{3}He Nuclei

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We use accurate *ab initio* and quantum scattering calculations to demonstrate that the maximum ^{3}He spin polarization that can be achieved in spin-exchange collisions with potassium (^{39}K) and silver (^{107}Ag) atoms is limited by the anisotropic hyperfine interaction. We find that spin exchange in Ag-He collisions occurs much faster than in K-He collisions over a wide range of temperatures (10–600 K). Our analysis indicates that measurements of trap loss rates of ^2S atoms in the presence of cold ^{3}He gas may be used to probe anisotropic spin-dependent interactions in atom-He collisions.

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Spin-exchange optical pumping (SEOP) is a well-established experimental technique for the production of hyperpolarized noble-gas nuclei with many applications in diverse areas of science and technology [1–4]. In particular, measurements of nuclear spin relaxation in a hyperpolarized gas of ^{3}He can be used to constrain spin-dependent interactions between nucleons [5–7]. The study of spin-exchange collisions between ^{3}He and alkali-metal atoms can yield insights into anomalous nuclear forces and short-range torsion gravity fields [6]. The spin-exchange collisions are an important source of noise and decoherence in atomic magnetometers based on alkali-metal vapor cells [4].

The SEOP technique is based on collision-induced transfer of spin polarization from optically pumped alkali-metal atoms to noble-gas atoms (typically ^{3}He and ^{129}Xe) [1]. While the efficiency of this strategy has been confirmed by numerous experiments [1], recent experimental work has established that the maximum ^{3}He spin polarization that can be achieved in SEOP experiments with alkali-metal atoms K and Rb is limited to 81% by unknown relaxation mechanisms [8–10]. Possible explanations include wall collisions, magnetic field gradients, and anisotropic hyperfine interactions in atom-He collisions [9,10]. While the first two mechanisms can be eliminated by an appropriate choice of experimental parameters, the third mechanism cannot be avoided. The anisotropic hyperfine interaction couples the nuclear spin of ^{3}He with end-over-end rotation of the collision complex, which leads to an irreversible decay of nuclear spin polarization, fundamentally limiting the efficiency of SEOP for any given alkali-metal-He pair.

Previous theoretical and experimental work provided evidence for a minor, albeit non-negligible role, of anisotropic hyperfine interactions in spin-exchange collisions [11]. Walter, Happer, and Walker estimated the maximum ^{3}He polarization attainable via K-He collisions to be $P_{\max} = 0.95$ [11], where $P_{\max}$ can be expressed via the isotropic (k_α) and anisotropic (k_β) spin-exchange rates as $P_{\max} = (k_\alpha - k_\beta/2)/(k_\alpha + k_\beta)$ [10]. The accuracy of this estimate was, however, limited by a lack of information on interaction potentials and hyperfine interactions. Walker, Nelson, and Kadlecek have recently measured $P_{\max} = 0.90 \pm 0.11$ for K-^{3}He collisions at 463.15 K [10]. These findings suggest that, while the SEOP efficiency might indeed be limited by the anisotropic hyperfine interaction, other mechanisms (such as wall relaxation) cannot be ruled out based on current experimental data. A quantitatively accurate theoretical analysis of spin-exchange and spin relaxation mechanisms would not only settle this long-standing question, it will also establish a pathway toward systematic improvement of the SEOP technology.

In this Letter, we use accurate *ab initio* calculations of molecular interactions in combination with exact quantum scattering methods [12] to quantify the role of the anisotropic hyperfine interaction in spin-exchange collisions of alkali-metal atoms with ^{3}He. Using the K-He collision system as a representative example [9–16], we show that the maximum ^{3}He spin polarization attainable in SEOP experiments with K atoms is limited by the anisotropic hyperfine interaction. Our results are in quantitative agreement with recent measurements of frequency shift enhancement factors [16] and rate constants for spin exchange in K-^{3}He collisions [10]. In addition, we show that spin exchange in Ag-He collisions occurs much faster than in K-He collisions, suggesting that it may be advantageous to perform SEOP experiments with Ag atoms at low temperatures to reduce the time scale for the production of hyperpolarized ^{3}He nuclei [1,13].

The Hamiltonian for the collision complex formed by a ^2S atom (M) and He may be written ($\hbar = 1$) [1,12,17]

$$\hat{H} = -\frac{1}{2\mu R}\frac{\partial^2}{\partial R^2}R + \frac{\hat{\boldsymbol{l}}^2}{2\mu R^2} + \hat{H}_{\rm as} + \gamma(R)\hat{\boldsymbol{l}}\cdot\hat{\mathbf{S}} + V(R) + A_F(R)\hat{\mathbf{I}}_{\rm He}\cdot\hat{\mathbf{S}} + \frac{c(R)}{3}\sqrt{\frac{24\pi}{5}}\sum_q Y^\star_{2q}(\hat{R})[\hat{\mathbf{I}}_{\rm He}\otimes\hat{\mathbf{S}}]^{(2)}_q, \quad (1)$$

where μ is the reduced mass of the complex, $\hat{\mathbf{S}}$ is the electron spin of M, $\hat{\mathbf{I}}_{\mathrm{He}}$ is the nuclear spin of ^{3}He, R is the internuclear separation, $\hat{l}$ is the collision angular momentum, and $\hat{R}$ describes the orientation of the complex in the lab frame with the quantization axis defined by the magnetic field vector $\mathbf{B}$. In Eq. (1), $\hat{H}_{\mathrm{as}}$ is the asymptotic Hamiltonian, which describes noninteracting collision partners [12,14], $V(R)$ is the interaction potential, and $Y_{2q}(\hat{R})$ are the spherical harmonics. In contrast to previous theoretical studies [12,14], our Hamiltonian explicitly includes the R dependence of the anisotropic hyperfine interaction [the last term in Eq. (1)]. The spin-rotation interaction given by $\gamma(R)\hat{\boldsymbol{l}} \cdot \hat{\mathbf{S}}$ does not affect the spin polarization of ^{3}He and will be excluded from our analysis. The spin-dependent interactions relevant for spin-exchange M-He collisions include the Fermi contact interaction $A_F(R)$ and the anisotropic hyperfine interaction $c(R)$. We neglect the weak nuclear spin-rotation interaction [18].

For the K-He interaction potential, we used the highly accurate *ab initio* results [19] fitted to analytic functions with proper long-range behavior [12]. We evaluated the hyperfine interaction constants $A_F(R)$ and $c(R)$ by using the coupled-cluster method based on an unrestricted Hartree-Fock reference wave function [20,21]. For the K atom, we constructed a large uncontracted basis set $(24s16p5d4f2g)$ from $(21s16p5d4f2g)$ primitives [22] by adding a sequence of three tight s functions with exponents forming a geometric progression. For He, we employed a modified augmented correlation-consistent valence quintuple zeta (aug-cc-pV5Z) basis [23] obtained by fully decontracting the s functions and adding a sequence of three tight s functions in the same manner as for the K atom. To construct the Ag-He interaction potential, we fitted the *ab initio* data points [24] to the analytic form [12] using the accurate long-range dispersion coefficients for AgHe [25]. The hyperfine constants for AgHe were evaluated by using quasirelativistic density functional theory [17,26]. We estimate the error of our interaction potentials and hyperfine interactions to be $<10\%$.

In order to determine the cross sections for spin exchange in atom-He collisions, we expand the total wave function of the collision complex in basis functions $|Fm_F\rangle|I_{\mathrm{He}}M_{I_{\mathrm{He}}}\rangle|\ell m_\ell\rangle$, where $|\ell m_\ell\rangle$ are the partial wave states, F is the total angular momentum of the atom, and m_F is the projection of F on the magnetic field axis. The resulting system of close-coupled Schrödinger equations is solved numerically on a radial grid extending from $R_{\mathrm{min}} = 3a_0$ to $R_{\mathrm{max}} = 60a_0$ with a grid step of $0.04a_0$. We assume that ^{39}K (^{107}Ag) atoms are initially in their fully spin-polarized hyperfine states $|22\rangle$ ($|11\rangle$). The anisotropic hyperfine interaction couples different ℓ and m_ℓ states, increasing the number of close-coupled equations for $M = \frac{1}{2}$ from 16 [12] to 1918, where $M = m_F + M_{I_{\mathrm{He}}} + m_\ell$.

Our *ab initio* results for the isotropic and anisotropic hyperfine interaction constants for K-He and Ag-He are shown in Fig. 1 as a function of the interatomic separation. The isotropic hyperfine interaction decreases exponentially with R [1] and is much larger for Ag-He than for K-He as a consequence of the interaction potential for K-He being more repulsive at short R. The anisotropic hyperfine interaction does not exhibit such a dramatic dependence on R and is of comparable magnitude in both K-He and Ag-He complexes. This difference has important consequences for the mechanisms of spin exchange and spin relaxation in K-He and Ag-He collisions, as described below.

To verify the accuracy of our *ab initio* interaction potentials and hyperfine interactions, we calculated the frequency shift enhancement factors $\kappa_0(T) = \int_0^\infty \varrho_{\mathrm{He}}(R) e^{-V(R)/k_B T} 4\pi R^2 dR$, where ϱ_{He} is the electron spin density of the K-He complex at the He nucleus [1,12] and μ_B is the Bohr magneton. Since $\kappa_0(T)$ is exponentially sensitive to $V(R)$, experimental measurements of $\kappa_0(T)$ can be used as a sensitive probe to assess the quality of *ab initio* interaction potentials and hyperfine interactions. Figure 2 compares the calculated $\kappa_0(T)$ with the highly accurate polarimetry measurements [16]. Our results agree with experiment to within 3% over the whole range of temperatures, providing an independent verification of the high accuracy of our *ab initio* calculations.

Figure 3 shows the total rate constant for spin exchange $k = k_\alpha + k_\beta$ in K-He collisions as a function of temperature. To facilitate comparison with experiment, we distinguish between the rate constants for ^{3}He spin exchange induced by the isotropic (k_α) and anisotropic (k_β) hyperfine interactions [9,10]. Specifically, if we define k_2 as the rate constant for the transition $|Fm_F\rangle \otimes |M_{I_{\mathrm{He}}} = -1/2\rangle \rightarrow |F'm'_F\rangle \otimes |M'_{I_{\mathrm{He}}} = 1/2\rangle$, summed over all energetically accessible final states $|F'm'_F\rangle$, and we define k_1 as the rate constant for ^{3}He nuclear spin depolarization

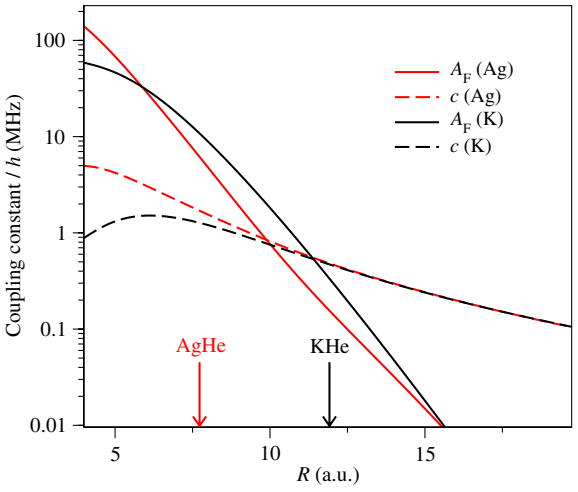

FIG. 1 (color online). Spin-dependent interactions for K-He (black lines) and Ag-He (red lines) vs R. Full lines, isotropic (Fermi contact) interaction constant $|A_F(R)|$; dashed lines, anisotropic hyperfine constant $|c(R)|$. The arrows mark zero-energy turning points of the K-He and Ag-He interaction potentials.

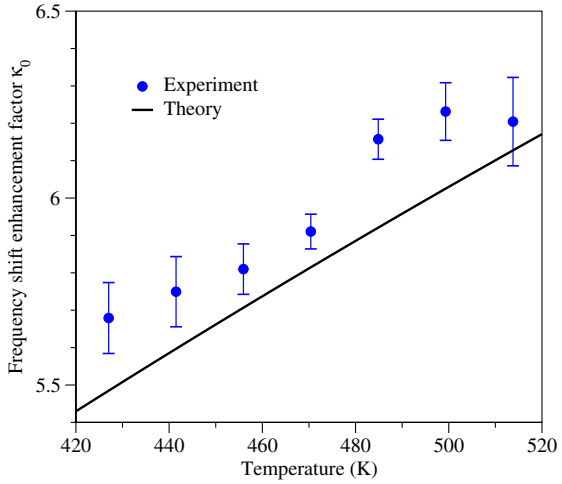

FIG. 2 (color online). Frequency shift enhancement factors for K-He vs temperature: experimental data from Ref. [16] and present *ab initio* calculations (full line).

$|Fm_F\rangle \otimes |M_{I_{\mathrm{He}}} = 1/2\rangle \rightarrow |F'm'_F\rangle \otimes |M'_{I_{\mathrm{He}}} = -1/2\rangle$, then $k_\alpha = k_2 - k_1/3$ and $k_\beta = 4k_1/3$ [27]. The calculated spin-exchange rate for Ag-He is notably larger than for K-He, due to the large magnitude of the Fermi contact interaction in Ag-He as compared to K-He (see Fig. 1).

Our calculations for K-He yield $k = 6.7 \times 10^{-20}$ cm^3/s at 463.15 K, in quantitative agreement with the measured value of $(6.1 \pm 0.7) \times 10^{-20}$ cm^3/s [10]. The anisotropic contribution to the total spin-exchange rate amounts to 1.8×10^{-21} cm^3/s or 2.7%, demonstrating that the effect of anisotropic hyperfine interaction on K-He spin exchange is weak. From Fig. 3, we observe that the rate constant k_α starts to deviate significantly from k at temperatures below ~200 K and becomes too low by a factor of ~4 at 10 K. This observation suggests that the anisotropic hyperfine interaction has a dramatic effect on K-He collision dynamics at low temperatures, as expected in the limit of large R, where $A_F(R)$ decreases exponentially but $c(R)$ approaches zero as R^{-3} [11].

To elucidate the role of the anisotropic hyperfine interaction in low-temperature K-He collisions, we evaluated the rate constants for K electron spin depolarization induced by collisions with ^{3}He atoms at $T = 320$ mK and $B = 1$ T. This rate constant can be measured by observing collision-induced loss of spin-polarized K atoms from a magnetic trap [14]. The calculated spin depolarization rate is 1.1×10^{-20} cm^3/s, consistent with the measured upper limit of 1.0×10^{-18} cm^3/s [14]. If the anisotropic hyperfine interaction is neglected, the calculated spin depolarization rate is 0.6×10^{-21} cm^3/s, more than an order of magnitude smaller than the exact result. We conclude that the anisotropic hyperfine interaction, neglected in all previous theoretical analyses [12,14], is the dominant spin relaxation mechanism of spin-polarized K atoms trapped in cold ^{3}He gas [14]. This conclusion implies that measurements of trap loss rates of alkali-metal atoms in cold He gas may be used to probe anisotropic spin-exchange interactions in alkali-metal-He collisions. Such measurements would be particularly helpful for systems in which anisotropic spin-exchange rates are difficult to obtain experimentally, such as Rb-He.

Figure 4 shows the temperature dependence of the polarization factor P_{max} [10], which determines the maximum attainable polarization of ^{3}He that can be achieved in SEOP experiments. A falloff of P_{max} with decreasing temperature reflects the increasing role of the anisotropic hyperfine interaction shown in Fig. 3. At $T = 463.15$ K, we obtain $P_{\mathrm{max}} = 0.96$, in agreement with the experimental value of 0.90 ± 0.11 [10] and not far from the previous estimate of 0.95 [11]. The temperature dependence of P_{max} for Ag-He is almost identical to that for K-He at $T > 400$ K but differs significantly from the latter at lower

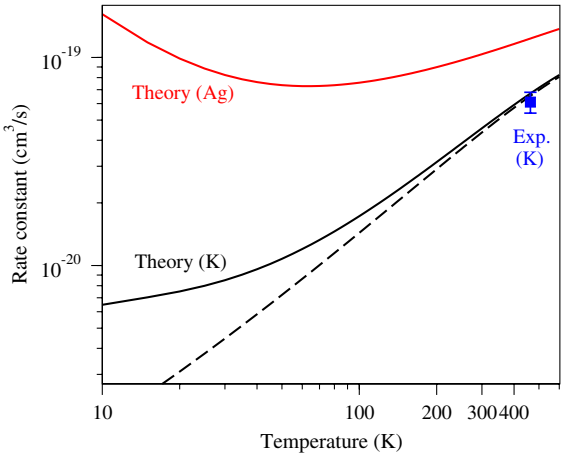

FIG. 3 (color online). Rate constants for spin exchange in K-^{3}He collisions vs temperature at $B = 1$ G: k_α (dashed line), $k = k_\alpha + k_\beta$ (full line); symbol, experimental result [10]. Also shown (red line) is the calculated $k(T)$ for Ag-He.

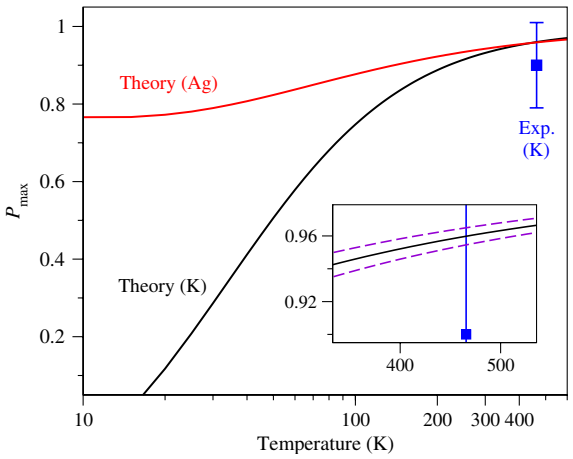

FIG. 4 (color online). Maximum attainable ^{3}He polarization as a function of temperature at $B = 1$ G: full line, present calculations for K-He; symbol, experimental result for K-He [10]; red/light gray line, present calculations for Ag-He. The inset shows the results of calculations with the original (full line) and scaled (dashed lines) K-He interaction potentials.

temperatures. Since the anisotropic hyperfine interaction in Ag-He collisions is much weaker than in K-He (Fig. 1), the calculated $P_{\max}$ for Ag-He remains high over the whole temperature range, in marked contrast to the behavior observed for K-He. Figure 4 shows that $P_{\max}(T)$ increases from 0.96 to 0.97 as the temperature is varied from 463.15 to 600 K, which reflects the diminishing role of the anisotropic hyperfine interaction.

In order to examine the robustness of our results against small variations in the K-He interaction potential, we repeated the scattering calculations with a scaled interaction potential obtained by multiplying $V(R)$ in Eq. (1) by a constant factor f_s. The calculations show that k_α at $T = 463.15$ K changes by as much as 18% over the range $f_s = 0.9$–1.1, which corresponds to the expected level of accuracy of *ab initio* calculations [19]. In contrast, the anisotropic spin-exchange rate varies only by 2% over the same range of f_s. The variation of $P_{\max}$ with f_s is shown in the inset in Fig. 4. At $T = 463.15$ K, we obtain $P_{\max} = 0.960 \pm 0.005$. The theoretical error bars are small because $k_\alpha \gg k_\beta$, so the uncertainties in k_α cancel out in the expression for $P_{\max}$.

In summary, we have presented a rigorous theoretical analysis of K-He and Ag-He collisions demonstrating that the maximum spin polarization of ^{3}He is limited by the anisotropic hyperfine interaction. Our calculations are in good agreement with the experimental measurements of frequency shift enhancement factors and rate constants for spin exchange in K-He collisions. Our results bear implications for research in several areas of physics with hyperpolarized ^{3}He nuclei. First, they demonstrate that the maximum ^{3}He spin polarization of 81% achieved so far with SEOP experiments can be significantly improved. Second, our calculations suggest that performing SEOP experiments with atomic Ag as a collision partner will increase the SEOP rate by a factor of 2 at temperatures above 400 K (Fig. 3). As shown in Fig. 4, the maximum attainable He polarization via Ag-He collisions does not fall dramatically with decreasing temperature, suggesting that it may be possible to perform SEOP experiments in the low-temperature regime, where the SEOP efficiency is higher due to the suppression of spin-destruction collisions driven by the spin-rotation interaction [13,14]. While further experimental and theoretical work is required to explore this possibility, we note that cold (1.85–20 K) and dense ($\sim 10^{12}$ cm^{-3}) Rb and Ag vapors have been produced inside a cryogenic He buffer-gas cell [28]. Third, our analysis suggests an alternative approach to probing anisotropic spin-dependent interactions by measuring collision-induced loss of alkali-metal atoms from a magnetic trap in the presence of cryogenic He gas at millikelvin temperatures. Finally, our study provides accurate reference information on the rate constants for spin exchange and spin depolarization over a wide range of temperatures, which could be used to better constrain the anomalous spin-dependent interactions between nucleons [5–7] and quantify the sources of noise and decoherence in atomic magnetometers [4].

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