

Calculation of scalar nuclear spin-spin coupling in a noble-gas mixture

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Indirect spin-spin interactions between nuclei bound in a molecule are well known in nuclear magnetic resonance, but such interactions between unbound atoms are less well studied and are often assumed to be zero. We present a precision calculation of this interaction between ^{129}Xe and ^3He nuclei in a gas. Relativistic, state-of-the-art electronic structure theory is used to compute the scalar coupling constant $J(R)$ and the interatomic potential energy function $V(R)$ as functions of the Xe-He internuclear distance R . Using virial expansion we find the nuclear spin enhancement factor $\kappa = -0.0105 \pm 0.0015$, in excellent agreement with recent experiments. This interaction is particularly important for precision measurements using nuclear spin comagnetometers.

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I. INTRODUCTION

Nuclear spins interact directly via magnetic moments and indirectly via electrons. In a liquid or gas the direct magnetic dipolar and the anisotropic part of indirect interactions are averaged out, leaving only the scalar spin-spin coupling, SSC (J coupling). SSC serves as one of the main analysis tools of nuclear magnetic resonance (NMR) spectroscopy and is routinely measured and calculated in molecules [1,2]. In contrast, SSC between unbound nuclear spins, e.g., in van der Waals (vdW) complexes, has been analyzed theoretically for only a few systems [3–8]. In such cases SSC is also much harder to measure because it is normally averaged by molecular motion. SSC is expected to be significantly smaller than the direct interaction. There is an experimental observation of SSC for unbound spins, using a liquid mixture of Xe and pentane [9]. The complex nature of this system allowed only a qualitative comparison with theory. In one case, the influence of the anisotropy of SSC could be inferred in a system with Xe atoms confined to a zeolite cage [10].

In this Rapid Communication we present a precision calculation of SSC in a vdW complex, of ^{129}Xe and ^3He , which can be compared with recent experimental observations [11,12]. The calculation can be done with a precision comparable to or better than for the much larger interaction between an unpaired electron and nucleus, as has been performed for alkali-metal–noble-gas pairs, e.g., in Refs. [13,14]. We find that SSC between nuclear spins is a general feature. For example, we estimate that for the ^{129}Xe - ^{131}Xe pair, the nuclear spin enhancement factor κ of the associated frequency shift [15] is -0.35 , almost approaching the strength of the direct magnetic dipolar coupling, which in a simple classical picture would correspond to $\kappa = 1$.

While SSC between unbound spins is small, typically resulting in frequency shifts of less than 1 Hz, it has significant

impact on precision measurements using nuclear spin comagnetometers that seek to measure nHz-level shifts due to new particle physics phenomena [16]. In particular, noble-gas systems can be used to search for dark matter particles [17], long-range spin-dependent forces [18–20], as well as tests of charge-parity (CP) [21], Lorentz, and charge, parity, and time-reversal (CPT) symmetries [22]. As the signals involved are small, it is essential to reliably estimate and eliminate frequency shifts and drifts due to conventional phenomenology and instrumentation, including SSC [23].

For SSC calculations to be useful in precision magnetometry, it is essential to account well for both electron correlation and, due to heavy elements, relativistic effects [24]. In particular, in four-component relativistic theory, one single magnetic hyperfine operator [25] replaces the four interactions of the nonrelativistic (NR) approach: the Fermi contact and dipolar Hamiltonians coupling nuclear and electron spins, as well as two orbital hyperfine Hamiltonians coupling the nuclear spin(s) to electron motion. The isotropic, rank-0 tensorial component of the resulting total relativistic SSC determines the κ factor of the associated frequency shift.

Here, relativistic first-principles electronic structure theory is used to estimate the frequency shift occurring in a ^{129}Xe - ^3He comagnetometer as a result of the indirect, electron-mediated SSC between the two isotopes. The treatment is based on the leading interaction term in the semiclassical virial expansion of the SSC constant in low-pressure gas mixture [26]. The second virial coefficient, J_1 , appearing in this term is determined by SSC and potential energy (PEC) curves, $J(R)$ and $V(R)$, respectively, as functions of the interatomic distance R . These curves are calculated using state-of-the-art quantum-chemical tools. The enhancement factor κ of ^{129}Xe frequency, as well as its temperature dependence, are obtained from J_1 . The result, $\kappa = -0.0105$, agrees very well with experiments [11,12]. There is also an order-of-magnitude agreement with earlier experimental $\kappa_{\text{XeH}} = -0.0014$ [9] for ^1H - ^{129}Xe SSC over vdW bonds between Xe and the protons of pentane.

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II. THEORY

A SSC constant experienced by ^{129}Xe with the surrounding ^3He nuclei in the gas mixture can be obtained from the virial expansion at temperature T [26],

$$J_{\text{XeHe}}(n_{\text{He}}, T) = J_1(T)n_{\text{He}} + J_2(T)n_{\text{He}}^2 \dots, \quad (1)$$

where n_{He} is the number density of ^3He . In low-pressure gas, SSC can be approximated from the first term, in which the second virial coefficient (J_0 vanishes for a pair interaction quantity such as J) is obtained as

$$J_1(T) = 4\pi \int_0^\infty J(R) \exp[-V(R)/kT] R^2 dR. \quad (2)$$

The Zeeman interaction of the ^{129}Xe nucleus is described by the spin Hamiltonian $H_Z = -\gamma_{\text{Xe}} \hbar \mathbf{I}_{\text{Xe}} \cdot \mathbf{B}_{\text{Xe}}$, where $\mu_{\text{Xe}} = \gamma_{\text{Xe}} \hbar \mathbf{I}_{\text{Xe}}$ is the magnetic moment of ^{129}Xe , expressed in terms of the gyromagnetic ratio γ_{Xe} and spin vector \mathbf{I}_{Xe} of the isotope. \mathbf{B}_{Xe} is the effective field at the ^{129}Xe nucleus. The Hamiltonian of the ^{129}Xe - ^3He SSC is, in turn, $H_J = \hbar \mathbf{I}_{\text{Xe}} \cdot \mathbf{J}_{\text{XeHe}} \cdot \mathbf{I}_{\text{He}}$, with the SSC tensor \mathbf{J}_{XeHe} and ^3He spin \mathbf{I}_{He} . The rank-0 part of \mathbf{J}_{XeHe} causes an extra contribution dB_{Xe} to the effective field,

$$\begin{aligned} -\gamma_{\text{Xe}} \hbar \mathbf{I}_{\text{Xe}} dB_{\text{Xe}} &= \hbar \mathbf{I}_{\text{Xe}} \mathbf{J}_{\text{XeHe}} \langle \mathbf{I}_{\text{He}} \rangle \\ \Rightarrow dB_{\text{Xe}} &= -\frac{2\pi}{\gamma_{\text{Xe}}} \mathbf{J}_{\text{XeHe}} \langle \mathbf{I}_{\text{He}} \rangle, \end{aligned} \quad (3)$$

in an isotropic sample, with the average ^3He spin $\langle \mathbf{I}_{\text{He}} \rangle$.

The corresponding field increment can be formulated as arising from the assumed uniform magnetization M_{He} of a spherical sample of ^3He nuclei around ^{129}Xe [27],

$$dB_{\text{Xe}} = \kappa \frac{2\mu_0}{3} M_{\text{He}} = \kappa \frac{2\mu_0}{3} n_{\text{He}} \gamma_{\text{He}} \hbar \langle \mathbf{I}_{\text{He}} \rangle, \quad (4)$$

where κ represents the modification due to the electron cloud of Xe. From Eqs. (3) and (4),

$$\kappa = -\frac{3\pi}{\mu_0 \hbar} \frac{1}{\gamma_{\text{He}} \gamma_{\text{Xe}}} \frac{J_{\text{XeHe}}}{n_{\text{He}}} = -\frac{3\pi}{\mu_0 \hbar} \frac{1}{\gamma_{\text{He}} \gamma_{\text{Xe}}} J_1, \quad (5)$$

where the first term of the expansion of Eq. (1) has been used. κ is determined by the second virial coefficient of the ^{129}Xe - ^3He SSC constant J_1 .

III. CALCULATIONS OF POTENTIAL CURVE

First-principles calculations of J_1 as defined by Eq. (2) were pursued using a combination of electronic structure tools. $V(R)$ was calculated at 54 internuclear distances ($R = 2.4 \text{ \AA} \dots 7.3 \text{ \AA}$ in steps of 0.1 \AA , and $R = 7.3 \text{ \AA} \dots 8.1 \text{ \AA}$ in steps of 0.2 \AA) at the coupled-cluster single, double, and perturbative triple excitation [CCSD(T)] level using the MOLPRO code [28,29]. The calculations used the Gaussian augmented correlation-consistent polarized valence sextuple zeta (aug-cc-pV6Z) basis set for He [30], as well as the energy-consistent relativistic ECP28MDF pseudopotential (parameterized at the Dirac-Fock level with 28 electrons in the atomic core) and the corresponding augmented correlation-consistent polarized valence pentuple-zeta pseudopotential (aug-cc-pV5Z-PP) basis for Xe [31]. To ensure basis-set saturation in the interatomic spatial region, two measures were taken. First, Xe was furnished with three diffuse Gaussian

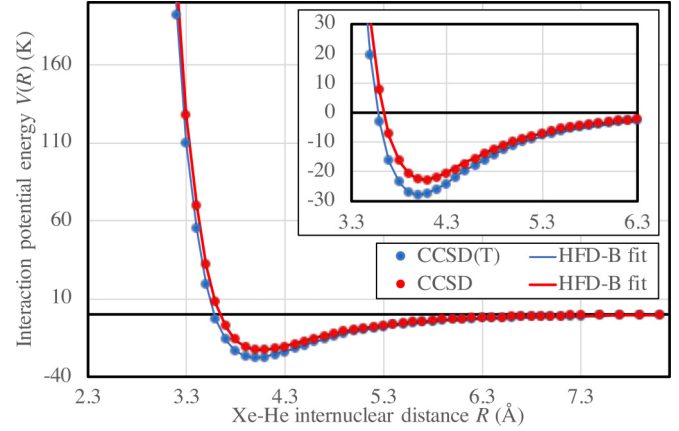


FIG. 1. Calculated CCSD(T) potential energy $V(R)$ (lower curve) for the Xe-He dimer as a function of the internuclear distance R . Fit to the HFD-B form of PEC is also shown. For comparison, $V(R)$ based on the simpler CCSD level of theory is included (upper curve). The inset shows a closeup of the well region.

exponents in each of the *spdfgh* shells. These exponents were derived by successive division by a factor of three from the most diffuse function in the aug-cc-pV5Z-PP basis in each angular momentum shell. Second, further primitive functions were added at the midpoint of the Xe-He “bond.” The bond functions (BFs) had exponents 0.9, 0.3, and 0.1 for the three *s*- and *p*-type primitives, 0.6 and 0.2 for the two *d*- and *f*-type primitives, and 0.35 for one *g*-type primitive [32]. The counterpoise correction [33] was applied to reduce the basis-set superposition error.

Figure 1 shows the calculated $V(R)$ along with its fit to the analytical Hartree-Fock-dispersion (HFD-B) form [34]. The formula and the fit parameters are given in the Supplemental Material [35]. The fitted PEC well depth is 28.0 K at 4.00 Å. The relevant temperatures for comagnetometer operation start from roughly 300 K upwards, i.e., with thermal energies significantly larger than the well depth, meaning that the semi-classical treatment of the virial coefficient in Eq. (2) is well valid [36]. The calculated well depth and minimum-energy separation are in very good agreement with the results of the analysis of high-resolution crossed molecular-beam data in Ref. [37], $28.95 \pm 0.46 \text{ K}$ and 3.975 \AA , respectively. Figure 1 also includes lower-level CCSD results (i.e., without perturbative triples) in which the potential minimum is shallower (well depth 22.7 K) and occurs at a larger internuclear distance ($R = 4.05 \text{ \AA}$) than what is seen in the CCSD(T) data. The difference between CCSD(T) and CCSD PECs is indicative of the remaining systematic error in $V(R)$.

IV. CALCULATIONS OF SPIN-SPIN COUPLING CURVE

The SSC calculations were carried out at the same internuclear separations as used for $V(R)$. For $J(R)$, nor other second-order magnetic properties, there are no *ab initio* methods available that would meaningfully combine post-Hartree-Fock electron correlation and relativistic effects, however. The available four-component density-functional theory (DFT) methods for $J(R)$ based on the Dirac-Fock Hamiltonian [38,39] suffer from a significant dependence of the results on

the chosen exchange-correlation functional; indeed, J can be considered as one of the most challenging properties for DFT [40]. Instead, we followed a piecewise strategy similar to that used for $J(R)$ in the xenon dimer in Ref. [8]. In this approach, the isotropic J at each R is obtained as a sum,

$$J \approx \text{CCSD}(\text{NR})$$

$$\begin{aligned} &+ \text{SOPPA}(\text{CCSD})(\text{NR w/BF}) - \text{SOPPA}(\text{CCSD})(\text{NR}) \\ &+ \text{PBE0}(\text{R w/BF}) - \text{PBE0}(\text{NR w/BF}), \end{aligned} \quad (6)$$

of the results of distinct first-principles calculations. On the first row of Eq. (6), NR CCSD-level data are obtained using the CF4UR code [41] and the Gaussian correlation-consistent valence pentuple-zeta all-electron basis for J -couplings (ccJ-pV5Z) [42] for He, and the same completeness-optimized [43], uncontracted $27s\ 25p\ 21d\ 4f$ Xe basis as was used for the hyperfine interactions of ^{129}Xe in Refs. [14,44]. All the four NR contributions [2] to J —the para- and diamagnetic nuclear spin-electron orbit, the spin-dipole, and the Fermi contact terms, of which the last one overwhelmingly dominates in this system—were included. CCSD was adopted as the highest manageable level of theory for the present case, as CCSD(T) does not offer a similar benefit for J as it does for PEC [45,46] and the cost of even higher-level methods [45,46] is prohibitive.

On the second row of Eq. (6), an attempt is made to remedy the remaining basis-set deficiency of the CCSD calculation, by carrying out two calculations (for each R) at the second-order polarization propagator (SOPPA) level with CCSD amplitudes [SOPPA(CCSD)] [47], on the DALTON code [48,49]. A difference is taken between results obtained with (BF) and without the same set of additional BFs, as used for $V(R)$. Program limitations inhibited us from using BFs in the full CCSD calculations.

Finally, on the third line of Eq. (6), relativistic corrections are applied as the difference between the four-component Dirac-Kohn-Sham (R) DFT results using the Perdew-Burke-Ernzerhof (PBE0) hybrid functional [50,51] obtained on the DIRAC code [38] and the corresponding NR PBE0 calculation on DALTON. PBE0 was chosen as it gave, at the NR level where such a comparison can be made, the closest agreement with the *ab initio* CCSD data for the $J(R)$ curve, among the tested functionals [PBE [52], PBE0, Becke-Lee-Yang-Parr (BLYP) [53–55], Becke three-parameter Lee-Yang-Parr (B3LYP) [54,56–58], Becke three-parameter Lee-Yang-Parr with 50% exact exchange (BHandHLYP) [54,57], result not shown]. For the large component of the relativistic wave function, the ccJ-pV5Z/27s 25p 21d 4f basis (for He/Xe) was used, but with also the He basis uncontracted, as well as supplemented with BFs as discussed above. The corresponding, uncontracted small-component basis was generated using an unrestricted kinetic balance [59]. The NR PBE0 calculations used the large-component basis of the R PBE0 computations.

Figure 2 shows the internuclear $J(R)$ curve as obtained using Eq. (6), as well as deviations thereof resulting from selected, more approximate levels of theory. The calculated data have been least-squares fitted to

$$J(R) = \frac{C}{R^{p(R)}}, \quad p(R) = p_0 + p_1 R. \quad (7)$$

No physical interpretation of this form or the numerical parameters is implied—Eq. (7) is merely used as a convenient

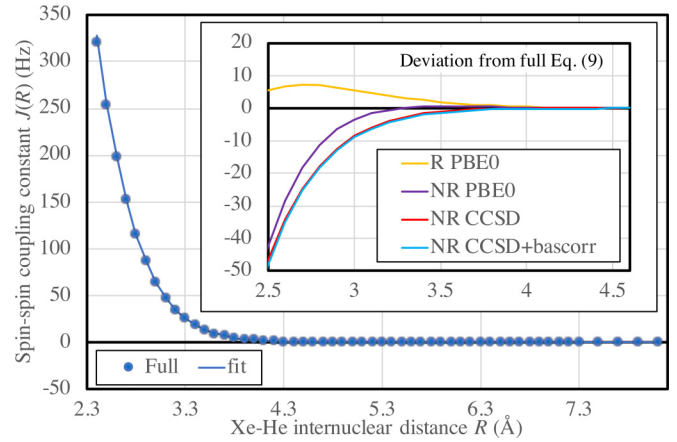


FIG. 2. Calculated ^{129}Xe - ^3He spin-spin coupling constant as a function of the internuclear separation R . The main panel shows the CCSD curve including both basis-set and relativistic corrections (Full) according to Eq. (6). The inset illustrates the difference from those data resulting from (lines from bottom to top) omitting the relativistic correction [last line of Eq. (6), “NR CCSD + basccorr”], and also the basis-set deficiency correction [second line of Eq. (6), “NR CCSD”]. Corresponding deviations from the Full data resulting from DFT/PBE0 calculations at the nonrelativistic (NR PBE0) and relativistic (R PBE0) levels are also shown.

form for interpolating the data. To emphasize the physically relevant internuclear distance range, the magnitude of the function $w(R) = R^2 J(R) \exp[-V(R)/kT]$ was used as the weighting factor, with the experimentally relevant temperature parameter $T = 120^\circ\text{C}$. The fit parameters are listed in the Supplemental Material [35].

The SSC constant increases very steeply at small intermolecular distances, well below the minimum of the PEC. Frequency shifts due to interatomic SSC arise in deep-impact collisions of the interacting species. Both electron correlation and relativistic influences on $J(R)$ are very significant in our best data, as specified by Eq. (6). The former aspect is seen from the comparison of the NR CCSD and PBE0 results, with DFT producing a larger SSC over the relevant range of internuclear distances R . The magnitude of the difference is about 4 Hz at $R = 3.1 \text{ \AA}$, which coincides with the maximum of the function $w(R)$. The relativistic contribution to SSC is positive and increases steeply towards smaller R . Its magnitude at $R = 3.1 \text{ \AA}$ is over 6 Hz. The role of the basis-set correction obtained on the second line of Eq. (6) is very small, as the data show a very small difference between the “NR CCSD” and “NR CCSD + basccorr” results. This implies that already our original basis set (without the additional BFs) is quite well converged for $J(R)$.

V. FINAL RESULTS AND DISCUSSION

Table I reports the the calculated $J_1(T)$ according to Eq. (2), as well as κ resulting from Eq. (5). Here, the CCSD(T) PEC and the piecewise approximated $J_1(R)$ from Eq. (6) were used, as best results available to us. In addition, the effects of systematic error in the computations of $V(R)$ and $J(R)$ were very conservatively estimated by repeating the calculations with the CCSD PEC and NR CCSD function for

TABLE I. Second virial coefficient J_1 of the ^{129}Xe - ^3He spin-spin coupling and the enhancement factor of ^{129}Xe frequency κ .

Quantity	This work	Experiment
J_1 (10^{-27} Hz m^3)	$2.24 \pm \begin{smallmatrix} 0.10^a \\ 0.21 \end{smallmatrix}$	
κ	$-0.0105 \pm \begin{smallmatrix} 0.0005^a \\ 0.0010 \end{smallmatrix}$	-0.011 ± 0.001^b -0.009 ± 0.0004^c

^aError margins due to the choice of $V(R)$ and $J(R)$ are given as super- and subscripts, respectively (see text). At $T = 120^\circ\text{C}$.

^bReference [11]. Measurement at 120°C .

^cReference [12]. The corresponding ^3He shift measurements give $\kappa = -0.007 \pm 0.001$. At $T = 28^\circ\text{C}$ [60].

SSC, respectively. Error margins adopted from the resulting changes of J_1 and κ are also given in Table I. Our value for κ equals -0.0105 ± 0.0015 , with one third of the error arising from $V(R)$ and two thirds from $J(R)$. There is excellent agreement with both the experiments of Refs. [11,12]; indeed, the theory and experiments agree with each other to within the reported error margins.

At the experimental conditions of Ref. [11], $T = 120^\circ\text{C}$ and $n_{\text{He}} = 4 \times 10^{19} \text{ cm}^{-3}$, the presently calculated J_1 corresponds to $J_{\text{XeHe}} = 0.09 \text{ Hz}$, retaining the first term of Eq. (1). The resulting ^{129}Xe frequency shift is orders of magnitude larger than what can be expected from novel physical phenomenology, in the nHz range [16]. This underlines the necessity of eliminating the influence of SSC in comagnetometer investigations. At the same time, such couplings are large enough to offer a potential tool to investigate weakly bound systems via NMR techniques.

Figure 3 shows the calculated temperature dependence of κ as well as the existing experimental results. In qualitative agreement with Ref. [11], κ is very modestly temperature dependent. In the depicted temperature range, κ can be fitted to a linear dependence $\kappa = \kappa_0 + \kappa_1 T$ with $\kappa_0 = -0.00453$ and $\kappa_1 = -1.51 \times 10^{-5} \text{ K}^{-1}$.

Similar methodology can be used to evaluate κ for other noble-gas pairs, e.g., ^{129}Xe - ^{131}Xe . We can use data from first-principles calculations of the corresponding $J(R)$ and $V(R)$ curves in Refs. [8] [Eq. (7) of that paper] and [61], respectively, in Eqs. (2) and (5), with $\gamma_{^{131}\text{Xe}}$ replacing $\gamma_{^3\text{He}}$ in the denominator of the latter equation. This leads to $\kappa = -0.352, -0.347$, and -0.342 at $T = 80, 100$, and 120°C , for the indirect ^{129}Xe - ^{131}Xe SSC.

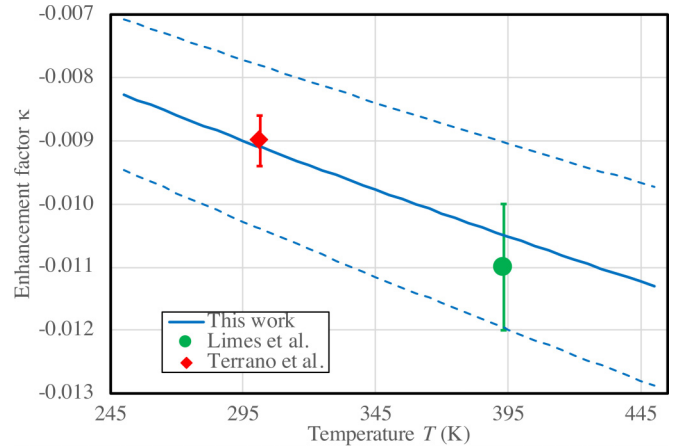


FIG. 3. Calculated temperature dependence of the enhancement factor κ of the ^{129}Xe frequency in the presence of ^3He . Experimental data by Limes *et al.* [11] and Terrano *et al.* [12] are also given. The error margins of all results are shown.

VI. CONCLUSION

We have computationally investigated the frequency shift of ^{129}Xe due to the indirect spin-spin coupling to ^3He in low-pressure gas, corresponding to recent comagnetometer experiments. Using state-of-the-art first-principles electronic structure theory, the second virial coefficient of the SSC constant between the two isotopes was calculated and converted to the enhancement factor κ , with results that are in excellent agreement with the two recent measurements. In reaching this quantitative agreement, both *ab initio* electron correlation treatment and consideration of relativistic influences were necessary. We trust that calculations of the present type are useful in eliminating the frequency shifts due to standard phenomenology in search of novel physics, as well as pave the way for precision determination of small interactions in materials NMR.

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