Searching for an Exotic Spin-Dependent Interaction between Electrons at the Nanometer Scale with Molecular Rulers

Man Jiao,1,2,3 Xing Rong,1,2,3,* Hang Liang,1,2,3 Yi-Fu Cai,4,5 and Jiangfeng Du1,2,3,†

1Hefei National Laboratory for Physical Sciences at the Microscale and Department of Modern Physics, University of Science and Technology of China, Hefei 230026, China
2CAS Key Laboratory of Microscale Magnetic Resonance, University of Science and Technology of China, Hefei 230026, China
3Synergetic Innovation Center of Quantum Information and Quantum Physics, University of Science and Technology of China, Hefei 230026, China
4CAS Key Laboratory for Research in Galaxies and Cosmology, Department of Astronomy, University of Science and Technology of China, Hefei 230026, China
5School of Astronomy and Space Science, University of Science and Technology of China, Hefei 230026, China
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We propose a novel method to search for exotic spin-dependent interactions between electrons at the nanometer scale. Such interactions can be investigated using various techniques, including single-atom Electron Spin Resonance (ESR-STM) [9, 10], trapping ions[8], single-atom Electron Spin Resonance (ESR-STM) experiments. Then we established a constraint on the axial-vector mediated interaction between electrons at the nanometer scale, which considerably improves on previous experimental bounds.

In this paper, we propose a novel method to search for exotic spin-dependent interaction between electrons at the nanometer scale. A type of molecular rulers, which contains two electron spins with precisely adjustable distance by varying the length of the shape-persistent polymer chains, can be utilized to constrain the axial-vector mediated interaction between electrons at the nanometer scale. With measurements of the coupling strengths between two electron spins within different molecular rulers, an improved laboratory bound of exotic dipole-dipole interaction between electrons is established within the force range from 3 to 220 nm. The upper bound of the coupling $g_A^e g_A^e / 4\pi \hbar c$ at 200 nm is $|g_A^e g_A^e / 4\pi \hbar c| \leq 4.9 \times 10^{-13}$, which is about 20 times more stringent than previous limits.

Light bosons such as pseudoscalar fields (axion and the axion-like particles (ALPs)[1, 2]) and axial-vector fields (paraphotons and extra Z bosons) are hypothetically expected to address mysteries of fundamental sciences, namely, the microscopic origins of dark matter and dark energy, the resolution to the strong CP issue in quantum chromodynamics, as well as the possible connection with the hierarchy problem[3]. The exchange of such bosons may mediate exotic spin-dependent interactions between ordinary fermions, which enables laboratory searches on new particles via possible detections of new interactions[2, 4–6]. The exotic spin-dependent interactions are characterized by the dimensionless coupling constants between new bosons and fermions and the force range associated with the reduced Compton wavelength $\lambda$ of mediating bosons of mass $m$ [4, 5]. There are experiments searching for the axial-vector dipole-dipole interaction between polarized electrons [4], ranging from atomic scale to the radius of earth [6]. For the force range shorter than a millimeter, there are experiments such as Nitrogen-Vacancy (NV) centers in diamonds[7], trapped ions[8], single-atom Electron Spin Resonance with Scanning Tunneling Microscope (ESR-STM) [9, 10] and atomic spectroscopy [11], providing stringent upper limit of the exotic interaction.

In this paper, we propose a novel method to search for exotic spin-dependent interaction between electrons at the nanometer scale. A type of molecular rulers, which contains two electron spins, has been proposed to constrain the exotic spin-dependent interaction. The distance between two electron spins can be precisely set by varying the length of the shape-persistent polymer chains of the molecular rulers. The coupling strengths between the two electron spins can be obtained by Double Electron Resonance (DEER) experiments. Then we established a constraint on the axial-vector mediated interaction between electrons at the nanometer scale, which considerably improves on previous experimental bounds.

Figure 1a shows that two electron spins interact with each other in an external magnetic field. The magnetic dipole-dipole interaction between two electron spins is described by the following Hamiltonian:

$$H_d = -\frac{\mu_0 \gamma_1 \gamma_2 r^2}{16\pi^3} [3(\vec{\sigma}_1 \cdot \hat{r})(\vec{\sigma}_2 \cdot \hat{r}) - (\vec{\sigma}_1 \cdot \vec{\sigma}_2)],$$

(1)

where $\sigma_1$ and $\sigma_2$ stand for Pauli vectors of the two electron spins, $\gamma_1, \gamma_2$ are gyromagnetic ratios of the two electron spins, $r = |\vec{r}|$ and $\hat{r} = \vec{r}/|r|$ are the displacement and the unit displacement vector between two electron spins. $\mu_0$ is the magnetic constant, and $\hbar$ is Plank’s constants divided by $2\pi$. The axial-vector dipole-dipole interaction mediated by hypothetical axial-vector bosons can be written as [4],

$$H_2 = \frac{g_A^e g_A^e \hbar c}{4\pi \hbar c} r (\vec{\sigma}_1 \cdot \vec{\sigma}_2) e^{-\lambda r},$$

(2)

where $g_A^e g_A^e / 4\pi \hbar c$ is dimensionless axial-vector coupling constant between electrons, $\lambda = \hbar/(mc) = \hbar/c$ is the force range, $m$ is the mass of the hypothetical particle and $c$ is the speed of light.

To constrain the exotic interaction described by equation 2 within micrometer scale, several state-of-art methods have been developed to place two electron spins with precise distance and to measure the coupling strength between them. The coupling between two $^{88}S_2^+$ ions, each with a single electron spin, has been measured with high resolution [12], and the interaction can be constrained with micrometer scale [8]. Single NV centers can be uti-
A type of molecular rulers connecting two \( \text{Gd}_{(111)} \) labels (Gd-rulers) have been chosen as the system for constraining the exotic interaction. \( \text{Gd}_{(111)} \) complex is a type of spin label with half integral high-spin (\( S=7/2 \)), while the electron spin is in a \( ^8S \) ground state with 7 unpaired electrons in its f orbital \([15]\). The chemically synthesized Gd-spacer-Gd compounds have a rodlike moiety consisting of PP and E units, acting as spacers which connect the two \( \text{Gd}_{(111)} \) spin labels as shown in Figure 1b. The synthesis of these geometrically well-defined Gd-rulers is reported\([16]\). Precise DEER measurements of a series of Gd-rulers with different Gd-Gd distances are reported \([15]\). As shown in Figure 1b, five Gd-rulers with lengths ranging from 4.25-8.78 nm are chosen to constraint the exotic interaction, and the \( \text{Gd}_{(111)}-\text{Gd}_{(111)} \) pair can be treated as a pair of weakly coupled spin-half electron spins \([15]\). These molecules are denoted as Gd-rulers \( 1_n \) (\( n = 5,7,9,11 \)) and \( 2_2 \), which have different sequences of repeating units of PP and E as shown in Figure 1b.

Our method is to measure the coupling between two electron spins located on two ends of a molecular ruler, and to constrain the exotic dipole-dipole interaction at the nanometer scale. Molecular rulers is a type of shape-persistent molecules, which contains several repeating units, such as p-phenylene (PP) and ethynylene (E). The PP and E units have geometrically unambiguous structure and high stiffness \([14]\). The lengths of molecular rulers can be precisely tuned by changing the number of repeating units. A pair of spin labels with electron spins, can be attached on both ends of the molecular ruler. Thus the distance between electron spins can be adjusted in the nanometer scale by varying the length of shape-persistent polymer chain. DEER experiments can be utilized to measure the coupling between the electron spins.

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dent on the angle $\theta$ between external magnetic field and the displacement vector between of two spin labels in Gd-rulers. Because the Gd-rulers are randomly oriented, the splitting due to the magnetic dipole-dipole interaction is the Pake patterns [17]. If the additional splitting due to the possible $H_{2}^{\text{exchange}}$ is taken into account, the strength of the coupling $\omega_{\perp} (\theta = 90^\circ)$ is half of the splitting of the two prominent features,

$$\omega_{\perp} = \frac{\mu_0^2 \gamma_{\text{Gd(III)}}^2 \hbar^2}{4\pi} \frac{1}{r^3} + \frac{g_A^e g_A^e}{4\pi \hbar} \frac{4\hbar c}{r} e^{-\frac{r}{2}}. \tag{4}$$

Figure 2 shows the DEER results in frequency domain. The value of the coupling, $\omega_{\perp}$, increases when the distance of two electron spins decreases. The linewidths of the spectrum are partly due to the distributions of the distance, which are from the flexibility of the molecular building blocks [14, 15]. The linewidths caused by flexibilities of the molecular rulers are less than one tenth of those of the experimental results [18]. The decoherence of the electron spin labels also contributes to the experimental linewidths.

The experimental results and a fitting of the couplings, $\omega_{\perp}$, between spin-labels with distance from 4.25-8.78 nm are presented in Figure 3. Black squares with error bars are the experimental coupling strength between Gd-Gd spin-labels with different Gd-Gd distances. Error bars are obtained from the resolution of DEER spectrum which are essentially limited by the experimental linewidths. Red line is the fit for coupling strength with Equation 4 when $\lambda = 200\ nm$.

The experimental results of the couplings, $\omega_{\perp}$, between spin-labels with distance from 4.25-8.78 nm are presented in Figure 3. Black squares with error bars are the experimental values of the couplings $\omega_{\perp}$, which are half of the splitting of the peaks in Figure 2. Due to the geometrically unambiguous and high stiffness of the Gd-ruler’s backbone at low temperatures, the distance between Gd(III) can be estimated from density functional theory (DFT). We used scalar relativistic DFT as implemented in the Gaussian software package [19] and performed full geometry optimizations for all structures. In our DFT calculations, the three-parameter hybrid exchange functional of Becke and the exchange functional of LeeYangCParr (B3LYP) [20–22] was employed. More precisely, to ensure a correct approach for the open-shell species, we employed the spin-unrestricted open-shell version of this functional (UB3LYP). The standard basis set 6-31G(d) is used for C, H and N atoms while the Stuttgart RSC 1997 ECP basis set [23] is used for Gd atom. The DFT results shows that Gd-Gd distance for Gd-rulers 2.2, 1.5, 1.7, 1.0 and 1.11, are 4.25, 4.70, 6.05, 7.41 and 8.78 nm, respectively. The red line in Figure 3 is a fitting to the experimental data with Equation 4 when the force range $\lambda = 200\ nm$. The gyromagnetic ratio of the Gd(III) spin obtained by this fit is $\gamma_{\text{Gd(III)}} = (0.92 \pm 0.01) \gamma_e$, where $\gamma_e = 2\pi \times 2.8\ MHz/Gauss$. The coupling constant of the exotic axial-vector-mediated interaction for $\lambda = 200\ nm$ is obtained to be $g_A^e g_A^e / 4\pi \hbar c = (-1.42 \pm 1.80) \times 10^{-13}$. The value of the axial-vector field induced interaction is less than its errors showing no evidence of the exotic interaction observed in these measurements. The constraint for other given force range $\lambda$ can be obtained with the same procedure.

Figure 4 shows the new constraint obtained from this work together with recent constraints from experimental searches for axial-vector-mediated dipole-dipole interactions. The horizontal axis shows the force range of the interaction, inversely proportional to the mass of the boson communicating the interaction. The vertical axis shows the dimensionless coupling parameter $g_A^e g_A^e / 4\pi \hbar c$ between electrons. Filled areas correspond to...
excluded values. For the force range $0.22 < \lambda < 10 \mu m$, the constraint was established by Kotler et al.\cite{8}. For the force range $\lambda < 3 \text{ nm}$, the upper limit was obtained from Ref.\cite{11}. For the force range from 10 to 200 nm, a previous limit was set by Luo et al.\cite{10} with data from ESR-STM experiments \cite{9}. The line widths of the ESR-STM experiments are about several Megahertz, which are due to the short coherence time of the ions. Electron spin labels in molecular rulers have longer coherence times than those of metal ions in ESR-STM experiments. The line widths of the DEER experiments for Gd-rulers are about sub-Megahertz. The method here can provide better precision of detection for coupling between two electrons compared with ESR-STM experiments. The red line is the constraint established in this work, which clearly shows that more stringent constraints in the range from 3 to 220 nm. Specifically, the obtained upper limit of the exotic dipole-dipole interaction at 200 nm is about a factor of 20 more stringent than the one obtained from Ref.\cite{10}.

In summary, we provide a novel method to search for an exotic spin-dependent interaction at the nanometer scale. An improved constraint on axial-vector mediated interaction between electron spins has been established at the nanometer scale. DEER measurements have been carried on molecule with triple spin labeling with Gd$^{3+}$, Mn$^{2+}$, and a nitroxide \cite{25}, these measurements based on chemically synthesized molecules may provide new possibilities for searching for exotic spin-dependent interactions. We also expect that spin labels of molecular rulers with longer coherence times can be synthesized for this study. Since longer coherence times ensure longer observation times, better frequency resolutions can be achieved and the constraint can be further improved.

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We noticed that a revision of spin-dependent interactions have recently been proposed \cite{5}. We provide the constraints on the revisited interactions in the Supplemental Material \cite{18}.
[20] Lee, C., Yang, W. & Parr, R. G. Development of the
colle-salvetti correlation-energy formula into a functional of the electron density. *Phys. Rev. B* **37**, 785 (1988).

[21] Becke, A. D. Density-functional thermochemistry. iii. the
role of exact exchange. *The Journal of Chemical Physics* **98**, 5648 (1993).

[22] Becke, A. D. Density-functional exchange-energy approx-
imination with correct asymptotic behavior. *Phys. Rev. A* **38**, 3098 (1988).

[23] Andrae, D., Häußermann, U., Dolg, M., Stoll, H. & Preuß, H. Energy-adjusted ab initio pseudopotentials for
the second and third row transition elements. *Theoretica chimica acta* 123.

[24] Ritter, R. C. Experimental test of equivalence principle
with polarized masses. *Physical Review D* **42**, 977 (1990).

[25] Wu, Z. *et al.* Selective distance measurements using triple spin labeling with gd3+, mn2+, and a nitrooxide. *The Journal of Physical Chemistry Letters* 5277.

[26] Karshenboim, S. G. Precision physics of simple atoms
and constraints on a light boson with ultraweak coupling. *Physical Review Letters* **104**, 220406 (2010).

[27] Leslie, T., Weisman, E., Khatiwada, R. & Long, J.
Prospects for electron spin-dependent short-range force experiments with rare earth iron garnet test masses. *Physical Review D* **89**, 114022 (2014).
Supplementary Material for
Searching for an Exotic Spin-Dependent Interaction between Electrons at the Nanometer Scale with Molecular Rulers

FIG. S1. (a) Histogram of distance distribution of the backbone of Gd-ruler 111. (b) The Black square is the experimental result of Gd-ruler 111 and the gray histogram is the distribution of the coupling strength due to the flexibility of the molecular ruler.

1. DISTANCE DISTRIBUTION OF THE MOLECULAR RULERS

In ESR experiments where the signal is contributed from ensemble molecules, it’s necessary to take the flexibility of molecules into account. The flexibility of molecules can be estimated by the distance distribution of the molecular backbone. The distance distribution of the backbone containing repeating units of p-phenylene (PP) and ethynylene (E) can be estimated by harmonic segmented chain model (HSC), where the distance distribution is determined by the bending potential $F$ and the thermal energy $k_B T$ [RefS1]. Here we take Gd-ruler 111 as an example, which contains 11 repeating units of PP and E. The distance distribution derived from HSC model is shown in Figure S1a with the FWHM of the distance distribution being 0.397 nm.

The linewidths of DEER spectrum caused by flexibilities can be estimated by the first term of Eqn.4 in the main text. As shown in Figure S1b, the FWHM of the coupling strength caused by flexibilities is 0.008 MHz, which is much smaller than that of the experimental result which is about 0.1054 MHz. It shows that the molecular rulers with high stiffness are good platform to investigate the spin-dependent interactions.

2. CONSTRAINTS ON REVISITED SPIN-DEPENDENT INTERACTIONS

Recently, a revision of spin-dependent interactions has been proposed, which gives nine non-relativistic potentials by the exchange of a spin-0 or spin-1 boson in coordinate-space [RefS2]. Different from the spin-dependent interactions derived in a mixed momentum and coordinate-space proposed in 2006 [RefS3], the revisited spin-dependent interactions in coordinate-space sort the spin-dependent interactions in a different way. Our result can also provide constraints on the revisited spin-dependent interactions. We consider the axial-vector potential mediated by a massive spin-1 boson of the revisited interactions, the interaction between electrons can be written as [RefS2],

$$V_{AA}(r) = -\frac{g_A g_A'}{4\pi m^2} m^2 \hbar c \sigma_1 \cdot \sigma_2 \frac{e^{-mr}}{r} - \frac{g_A g_A'}{4\pi m^2} \hbar c \left[ (\sigma_1 \cdot \sigma_2) \left( \frac{1}{r} + \frac{m}{3r} + \frac{4\pi}{3}\delta(r) \right) - (\sigma_1 \hat{r}) (\sigma_2 \hat{r}) \left( \frac{3}{r} + \frac{3m}{r} + \frac{m^2}{r^2} \right) \right] e^{-mr}$$

(S1)

where $m$ is the mass of the hypothetical particle, $g_A g_A'$ is dimensionless axial-vector coupling constant between electrons and $c$ is the speed of light. We take the combination of parameters $|g_A g_A'|/4\pi m^2$ as a constant and give constraints on it (Fig. S2).

* xrong@ustc.edu.cn
† djf@ustc.edu.cn
[RefS1] Jeschke, G. et al. Flexibility of shape-persistent molecular building blocks composed of p-phenylene and ethynylene units. Journal of the American Chemical Society 132, 10107 (2010).

[RefS2] Fadeev, P. et al. Revisiting spin-dependent forces mediated by new bosons: Potentials in the coordinate-space representation for macroscopic- and atomic-scale experiments. Phys. Rev. A 99, 022113 (2019).

[RefS3] Dobrescu, B. A. & Mocioiu, I. Spin-dependent macroscopic forces from new particle exchange. Journal of High Energy Physics 2006, 005 (2006).

[RefS4] Luo, P., Ding, J., Wang, J. & Ren, X. Constraints on spin-dependent exotic interactions between electrons at the nanometer scale. Physical Review D 96, 055028 (2017).

[RefS5] Ficek, F. et al. Constraints on exotic spin-dependent interactions between electrons from helium fine-structure spectroscopy. Physical Review A 95, 032505 (2017).

[RefS6] Kotler, S., Akerman, N., Navon, N., Glickman, Y. &
FIG. S2. Upper limit on $|g_A g_A'|/4\pi m^2$ between electrons, as a function of the force range and the mass of the axial-vector bosons, $m$. The black solid lines represent upper bounds obtained from Refs. [RefS4–RefS8]. This work provides constraints as the red line.