PHYSICAL REVIEW D **92,** 056002 (2015)

Lorentz and *CPT* tests with hydrogen, antihydrogen, and related systems

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(Received 8 June 2015; published 15 September 2015)

The potential of precision spectroscopy as a tool in systematic searches for effects of Lorentz and *CPT* violation is investigated. Systems considered include hydrogen, antihydrogen, deuterium, positronium, and hydrogen molecules and molecular ions. Perturbative shifts in energy levels and key transition frequencies are derived, allowing for Lorentz-violating operators of arbitrary mass dimensions. Observable effects are deduced from various direct measurements, sidereal and annual variations, comparisons among species, and gravitational responses. We use existing data to place new and improved constraints on nonrelativistic coefficients for Lorentz and *CPT* violation, and we provide estimates for the future attainable reach in direct spectroscopy of the various systems or tests with hydrogen and deuterium masers. The results reveal prospective sensitivities to many coefficients unmeasured to date, along with potential improvements of a billionfold or more over certain existing results.

DOI: 10.1103/PhysRevD.92.056002 PACS numbers: 11.30.Cp, 11.30.Er, 12.60.-i

I. INTRODUCTION

Hydrogen spectroscopy has been intimately linked with precision tests of the foundations of relativity since the exact solution of the Dirac equation for hydrogen [1,2] matched relativistic quantum mechanics with experiments. Indeed, a famous classic test of special relativity, the Ives-Stilwell experiment confirming time dilation [3], was first performed using a hydrogen clock. Another classic experiment, Gravity Probe A [4], verified the relativistic frequency shift in a gravitational field using a hydrogen maser launched on a suborbital rocket.

The underlying symmetry of relativity, Lorentz invariance, can naturally be broken in some approaches to the unification of gravity with quantum physics such as string theory [5]. This possibility opens the door to the experimental detection of new physics emerging from the Planck scale $M_P \simeq 10^{19}$ GeV, and it has led to numerous sensitive tests of relativity using techniques from various subdisciplines of physics [6]. In the present work we further this program, studying the prospects for signals of Lorentz violation using spectroscopy of hydrogen, antihydrogen, and related systems, including deuterium, positronium, and hydrogen molecules and molecular ions.

The methods of effective field theory offer a powerful and general approach to describing physical phenomena at accessible scales when the fundamental theory at a larger scale is unknown [7]. The general realistic effective field theory for Lorentz violation, the Standard-Model Extension (SME) [8,9], is built from general relativity and the Standard Model of particle physics by adding to the action all coordinate-independent contractions of Lorentz-violating operators with controlling coefficients. Operators of larger mass dimension d can be viewed as higher-order effects in a large-distance expansion of the underlying physics. Since *CPT* violation in effective field theory breaks Lorentz symmetry [8,10], the SME also provides a general description of *CPT* violation. The limit of the SME restricted to operators with $d \leq 4$ is called the minimal SME, and it is power-counting renormalizable in Minkowski spacetime [11,12].

The minimal-SME terms generate striking effects in the spectra of hydrogen and antihydrogen, including *CPT*-violating signals and shifts in the hyperfine and $1S$-$2S$ transitions that depend on sidereal time [13]. Published searches for these effects have measured the hyperfine splitting using a hydrogen maser [14–16] and compared the $1S$-$2S$ transition in atomic hydrogen to a cesium fountain clock [17,18]. Related experiments with antihydrogen are being developed [19–22], and experiments with hydrogen molecules and molecular ions have been proposed as well [23]. In the context of the minimal SME, theoretical modifications to the spectra of hydrogen and antihydrogen have been widely studied [13,24–31], while spectral shifts are also known to arise from specialized nonminimal SME interactions with $d = 5$ [32] and from $d = 6$ terms originating in noncommutative quantum field theory [33,34]. The minimal SME also introduces *CPT*-violating effects in positronium decay [35,36].

Here, we investigate the prospects for spectroscopic searches for Lorentz and *CPT* violation using hydrogen, antihydrogen, deuterium, positronium, and hydrogen molecules and molecular ions. We focus on effects that arise from general Lorentz and *CPT* violation in the propagators of electrons, protons, neutrons, and their antiparticles. An analysis of this type has recently become feasible following the detailed classification and enumeration of Lorentz-violating modifications to the Dirac equation at arbitrary d [37], which includes operators of both renormalizable and nonrenormalizable dimensions. Operators of higher d are of crucial interest in several contexts including, for example, foundational perspectives such as causality and

stability [38,39] or the underlying pseudo-Riemann-Finsler geometry [40,41], practical issues such as the mixing of operators of different d through radiative corrections [42], and phenomenological effects arising in certain theories such as supersymmetric Lorentz-violating models [43] or noncommutative quantum electrodynamics [33,34,44]. The spectroscopic experiments proposed here therefore have potential to bear on many aspects of Lorentz and CPT violation.

Dimensional analysis reveals that operators with larger d can be expected to produce signals growing with energy, whereas the spectroscopic experiments of interest here typically involve nonrelativistic species. Remarkably, however, the nonrelativistic observables for Lorentz violation turn out to be combinations of operators of arbitrary d [37], while spectroscopic methods can achieve high sensitivity, so the experiments proposed here are competitive with other techniques. Our treatment disregards possible Lorentz-violating interactions, as these produce suppressed effects. For instance, the dominant contributions to the various spectra obtained below are independent of the internal electromagnetic four-vector potential in Coulomb gauge, while any applied external electromagnetic fields are minuscule compared to the electron and proton masses and so their Lorentz-violating effects are heavily suppressed. This approach is consistent with other studies of both minimal and nonminimal effects in conventional and muonic atoms [45–47]. We also disregard possible flavor-changing effects, which involve simultaneous lepton- or baryon-number violation with Lorentz violation and so can reasonably be taken as smaller than the effects considered here.

Including the present introduction, the main text of the paper is divided into eight sections. In Sec. II, we initiate the explicit discussion of Lorentz and CPT violation in hydrogen by presenting the underlying theoretical calculations required to analyze spectroscopic experiments. Some basic background information about perturbation theory involving operators of arbitrary d is provided in Sec. II A, followed by a discussion in Sec. II B establishing the coefficients for Lorentz violation relevant for hydrogen spectroscopy. Section II C contains the derivation of the matrix elements for the calculation of the perturbative energy shift due to Lorentz and CPT violation, including both general results and analytical expressions for special cases. In Sec. II D, we address the modifications arising from the presence of an external magnetic field, including the key equations underlying the resulting sidereal and annual variations of the Lorentz- and CPT-violating energy-level shifts.

With the theory in hand, the analysis of various experimental scenarios for hydrogen spectroscopy becomes feasible. This is addressed in Sec. III. We first consider the case of free hydrogen in the absence of applied fields. The effects of Lorentz and CPT violation on the transition probabilities and line shapes are discussed in Sec. III A, along with the prospects for measuring signals. We then turn in Sec. III B to the hyperfine Zeeman spectroscopy of hydrogen, presenting the perturbative frequency shift and studying signals from sidereal variations and from changes in the orientation of the applied magnetic field, corrections due to boosts, and the prospects for a space-based mission. This is followed in Secs. III C and III D by an investigation of potentially observable effects in various nL-$n'L'$ transitions for which precision measurement in hydrogen is experimentally feasible. Where possible in all these applications, we use existing data to extract first or improved constraints on nonminimal coefficients and estimate sensitivities attainable in future experiments.

Following the discussion of hydrogen, we turn our attention in Sec. IV to searches for Lorentz and CPT violation using antihydrogen. We begin in Sec. IV A with an overview of the perturbation theory and effects on the spectrum. Signals in hyperfine transitions are the subject of Sec. IV B, while effects on the $1S$-$2S$ and similar transitions are considered in Sec. IV C. We conclude the treatment of antihydrogen in Sec. IV D with a discussion of the prospects for an anomalous gravitational response of antihydrogen.

Three sections are devoted to signals of Lorentz and CPT violation in other related systems. Deuterium spectroscopy is considered in Sec. V. The perturbative approach adopted is presented in Sec. V A, followed in Sec. V B by a discussion of frequency shifts relevant to high-sensitivity spectroscopy. Observable effects from isotropic coefficients are considered in Sec. V C, while Sec. V D contains a discussion of the prospects for hyperfine measurements using a deuterium maser. Positronium spectroscopy is the subject of Sec. VI, while spectroscopy of hydrogen molecules and related species is considered in Sec. VII. We conclude with a summary in Sec. VIII. Throughout this paper we follow the notation of Ref. [37], with a few exceptions noted in the text.

II. THEORY

In this section, we present the general theoretical framework and calculations for determining the perturbative shifts in the hydrogen spectrum arising from Lorentz and CPT violation. The basic framework for the calculation is discussed, and then the symmetries of the system are used to identify the subset of coefficients for Lorentz and CPT violation that can contribute to modifications of the hydrogen spectrum. The general matrix elements of the perturbative Hamiltonian are calculated, and analytical expressions for the resulting energy shifts are presented in simple cases. We finally address generic effects arising in the presence of an applied magnetic field, including in particular the time dependence of the energy-level shift due to sidereal and annual variations.

A. Basics

The dominant Lorentz-violating perturbations to the spectrum of hydrogen arise from corrections to the propagators of the electron e and the proton p. Introducing a flavor index w taking values e and p, the Lagrange density for the quantum fermion field ψ_w of mass m_w including all kinetic effects from Lorentz and *CPT* violation can be written as [37]

$$\mathcal{L} \supset \frac{1}{2}\overline{\psi_w}(\gamma^\mu i\partial_\mu - m_w + \hat{\mathcal{Q}}_w)\psi_w + \text{H.c.}, \tag{1}$$

where $\hat{\mathcal{Q}}_w$ is the sum of all possible terms formed by contracting SME coefficients for Lorentz and *CPT* violation with derivatives $i\partial_\mu$. The operator $\hat{\mathcal{Q}}_w$ is a spinor matrix. It can be expanded in Dirac matrices, converted to momentum space, and decomposed in spherical coordinates, which permits the classification and enumeration of the corresponding effects. At each mass dimension d and for each flavor w, only certain combinations of coefficients for Lorentz violation are observable, due to the freedom to redefine the spinor basis without affecting the physics. Each of these combinations, called effective coefficients, controls a physically distinct Lorentz-violating effect. Spectroscopy of the hydrogenic systems considered in this work offers access in principle to about half of these effective coefficients, including some with sensitivities corresponding to Planck-suppressed signals.

The leading-order perturbation $\delta h_{\rm H}$ to the free Dirac Hamiltonian $h_{\rm H}$ for the hydrogen atom can be obtained from the Lagrange density (1) by adding the Lorentz-violating contributions from the electron and the proton. In the center-of-mass frame, the kinetic energies of the electron and proton are small compared to their masses, so it suffices to consider the Hamiltonian perturbation in the nonrelativistic limit,

$$\delta h_{\rm H}^{\rm NR} = \delta h_e^{\rm NR} + \delta h_p^{\rm NR}. \tag{2}$$

For calculational purposes, the operator $\delta h_e^{\rm NR}$ is understood to represent the tensor product of an operator acting on e states with the identity operator acting on p states, and similarly for $\delta h_p^{\rm NR}$. Note that the operators $\delta h_w^{\rm NR}$ depend on the fermion momentum $\boldsymbol{p}$.

For much of the spectroscopic analysis that follows, it is useful to perform a spherical decomposition of the Hamiltonian perturbation $\delta h_{\rm H}^{\rm NR}$ because tests of rotation symmetry are the predominant focus of many searches for Lorentz violation. The perturbation $\delta h_w^{\rm NR}$ can be decomposed as [37]

$$\delta h_w^{\rm NR} = h_{w0} + h_{wr}\boldsymbol{\sigma}\cdot\hat{\boldsymbol{\epsilon}}_r + h_{w+}\boldsymbol{\sigma}\cdot\hat{\boldsymbol{\epsilon}}_- + h_{w-}\boldsymbol{\sigma}\cdot\hat{\boldsymbol{\epsilon}}_+, \tag{3}$$

where $\boldsymbol{\sigma} = (\sigma^1, \sigma^2, \sigma^3)$ is the vector of Pauli matrices. The unit basis vectors $\hat{\boldsymbol{\epsilon}}_r = \hat{\boldsymbol{p}} \equiv \boldsymbol{p}/|\boldsymbol{p}|$, $\hat{\boldsymbol{\epsilon}}_\pm = (\hat{\boldsymbol{\theta}} \pm i\hat{\boldsymbol{\phi}})/\sqrt{2}$ are defined by introducing the usual unit vectors $\hat{\boldsymbol{\theta}}$ and $\hat{\boldsymbol{\phi}}$ for the polar angle θ and azimuthal angle ϕ in momentum space, so that $\hat{\boldsymbol{p}} = (\sin\theta\cos\phi, \sin\theta\sin\phi, \cos\theta)$. The component Hamiltonians h_{w0}, h_{wr}, $h_{w\pm}$ can be expanded in a series of terms involving products of powers of $|\boldsymbol{p}|$, spin-weighted spherical harmonics ${}_sY_{jm}(\hat{\boldsymbol{p}})$ of spin weight s, and nonrelativistic spherical coefficients for Lorentz violation. This permits a quantitative distinction among physical effects resulting from different magnitudes and orientations of the particle momenta. For the spin-independent term the expansion gives

$$h_{w0} = -\sum_{kjm} |\boldsymbol{p}|^k {}_0Y_{jm}(\hat{\boldsymbol{p}})\mathcal{V}_{wkjm}^{\rm NR}, \tag{4}$$

while for the spin-dependent terms the result is

$$\begin{aligned} h_{wr} &= -\sum_{kjm} |\boldsymbol{p}|^k {}_0Y_{jm}(\hat{\boldsymbol{p}})\mathcal{T}_{wkjm}^{\rm NR(0B)}, \\ h_{w\pm} &= \sum_{kjm} |\boldsymbol{p}|^k {}_{\pm1}Y_{jm}(\hat{\boldsymbol{p}})(i\mathcal{T}_{wkjm}^{\rm NR(1E)} \pm \mathcal{T}_{wkjm}^{\rm NR(1B)}). \end{aligned} \tag{5}$$

The quantities $\mathcal{V}_{wkjm}^{\rm NR}$ and $\mathcal{T}_{wkjm}^{\rm NR(qP)}$, where the superscripts qP take the values $0B$, $1B$, $1E$, are the nonrelativistic spherical coefficients for Lorentz violation, which we denote generically by $\mathcal{K}_{wkjm}^{\rm NR}$. Each of these can be separated into two pieces, controlling either *CPT*-even or *CPT*-odd effects [37],

$$\begin{aligned} \mathcal{V}_{wkjm}^{\rm NR} &= c_{wkjm}^{\rm NR} - a_{wkjm}^{\rm NR}, \\ \mathcal{T}_{wkjm}^{\rm NR(qP)} &= g_{wkjm}^{\rm NR(qP)} - H_{wkjm}^{\rm NR(qP)}, \end{aligned} \tag{6}$$

following the standard convention [8] in which a- and g-type coefficients are associated with *CPT*-odd operators and c- and H-type coefficients with *CPT*-even ones. Expressions involving antiparticles can therefore be obtained by reversing the sign of the a- and g-type coefficients. The reader is cautioned that the a- and H-type coefficients contain contributions only from operators of odd mass dimensions d, while the c- and g-type coefficients contain ones only from operators of even d. Note that the mass dimension of each nonrelativistic coefficient is $1 - k$.

A primary target of spectroscopic experiments is measurements of the nonrelativistic spherical coefficients (6). These coefficients are linear combinations of the complete set of spherical coefficients for Lorentz violation, given in Eqs. (111) and (112) of Ref. [37]. The allowed range of the indices k, j, m and the counting of independent coefficient components are provided in Table IV of Ref. [37]. The subscript index k is used in the present work instead of n to avoid confusion with the principal quantum number of the atom. Note that the indices j, m determine the rotational behavior of the spin-weighted spherical harmonics and

hence of the corresponding operators for Lorentz violation, so these indices are distinct from the angular-momentum quantum numbers J, M associated with the atomic states. The basic properties of the spin-weighted spherical harmonics are presented in Appendix A of Ref. [48]. The usual spherical harmonics are recovered when $s = 0$, so $Y_{jm}(\theta,\phi) \equiv {}_0Y_{jm}(\hat{\boldsymbol{p}})$.

For the special index choices $jm = 00$ the corresponding physical effects are isotropic, and following Eq. (114) of Ref. [37] it is convenient to adopt a ring-diacritic notation for the associated coefficients. For the applications in this work, it suffices to define

$$a^{\rm NR}_{w\,k00} \equiv \sqrt{4\pi}\,\mathring{a}^{\rm NR}_{w,k}, \qquad c^{\rm NR}_{w\,k00} \equiv \sqrt{4\pi}\,\mathring{c}^{\rm NR}_{w,k}. \tag{7}$$

We emphasize that the isotropic nonrelativistic coefficients $\mathring{a}^{\rm NR}_{w,k}$ and $\mathring{c}^{\rm NR}_{w,k}$ contain isotropic spherical coefficients $\mathring{a}^{(d)}_k$ and $\mathring{c}^{(d)}_k$ of arbitrarily large d. For example, using Eqs. (93) and (111) of Ref. [37] gives

$$\begin{aligned}
\mathring{a}^{\rm NR}_{w,0} &= \mathring{a}^{(3)}_0 + m_w^2\mathring{a}^{(5)}_0 + m_w^4\mathring{a}^{(7)}_0 + \cdots,\\
\mathring{a}^{\rm NR}_{w,2} &= \mathring{a}^{(5)}_0 + 2m_w^2\mathring{a}^{(7)}_0 + \cdots + \mathring{a}^{(5)}_2 + m_w^2\mathring{a}^{(7)}_2 + \cdots,
\end{aligned} \tag{8}$$

and

$$\begin{aligned}
\mathring{c}^{\rm NR}_{w,0} &= m_w\mathring{c}^{(4)}_0 + m_w^3\mathring{c}^{(6)}_0 + m_w^5\mathring{c}^{(8)}_0 + \cdots,\\
\mathring{c}^{\rm NR}_{w,2} &= \frac{1}{2m_w}\mathring{c}^{(4)}_0 + \frac{3}{2}m_w\mathring{c}^{(6)}_0 + \frac{5}{2}m_w^3\mathring{c}^{(8)}_0 + \cdots\\
&\quad + \frac{1}{m_w}\mathring{c}^{(4)}_2 + m_w\mathring{c}^{(6)}_2 + m_w^3\mathring{c}^{(8)}_2 + \cdots.
\end{aligned} \tag{9}$$

The dominant Lorentz-violating perturbative shifts in the spectrum of atomic hydrogen are obtained by calculating the matrix elements of the perturbation Hamiltonian (2) with respect to the unperturbed states of the system. Lorentz-violating effects involving transitions between different states appear at higher order in this scheme. We take the unperturbed states to be the Schrödinger-Coulomb eigenstates for a reduced mass $m_{\rm r} \equiv m_e m_p/(m_e + m_p)$, coupled to Pauli spinors for each particle. When the perturbative shifts are smaller than the hyperfine structure, the total angular momentum J of the electron and the total angular momentum F of the atom are good quantum numbers. Other relevant quantities for the system include the principal quantum number n and the orbital angular momentum L.

The scales of the perturbative frequency shifts are controlled by the nonrelativistic coefficients $\mathcal{K}^{\rm NR}_{w\,kjm}$. The latter can be viewed as background fields in the chosen inertial frame, which in the above equations for $\delta h^{\rm NR}_w$ is the zero-momentum frame for the hydrogen atom. However, an Earth-based laboratory for spectroscopic experiments is poorly suited to report coefficient measurements because it represents a noninertial frame due to the Earth's rotation about its axis and its revolution around the Sun. Instead, a specified inertial frame can be used, widely chosen to be the canonical Sun-centered frame [6,49]. This frame adopts coordinates T, X, Y, Z with the origin of the time T chosen as the vernal equinox 2000, the X axis pointing towards the vernal equinox, and the Z axis aligned along the Earth's axis of rotation. The Sun-centered frame is inertial to an excellent approximation on the timescale of laboratory experiments, so it provides a standard and conveniently accessible frame for reporting and comparing experimental results.

The nonrelativistic spherical coefficients $\mathcal{K}^{\rm NR}_{w\,kjm}$ can reasonably be taken as uniform and constant on the scale of the solar system [8,9] and hence are constants when expressed in the Sun-centered frame. The Earth's rotation and revolution therefore introduces variations with sidereal time in many coefficients expressed in the laboratory frame, which implies time variations in physical signals [50]. Since the Earth's orbital speed $\beta_\oplus \simeq 10^{-4}$ is small, the orbital motion can be disregarded for experimental analyses focusing on searches for rotation violations. The transformation between the Sun-centered and laboratory frames then reduces to a simple rotation, so the spherical decomposition summarized above offers definite calculational simplifications. Suppose for convenience the laboratory frame coordinates x, y, z are specified with the z axis pointing towards the zenith and the x axis lying at an angle ϕ measured east of south. Then, the coefficients $\mathcal{K}^{\rm NR,lab}_{w\,kjm}$ in the laboratory frame are related to the coefficients $\mathcal{K}^{\rm NR,Sun}_{w\,kjm}$ in the Sun-centered frame by

$$\mathcal{K}^{\rm NR,lab}_{w\,kjm} = \sum_{m'} e^{im'\omega_\oplus T_\oplus + im\phi} d^j_{mm'}(-\chi)\mathcal{K}^{\rm NR,Sun}_{w\,kjm'}, \tag{10}$$

where $\omega_\oplus \simeq 2\pi/(24\ {\rm h}\,56\ {\rm m})$ is the Earth's sidereal frequency, $T_\oplus$ is the local Earth sidereal time, and χ is the colatitude of the experiment. The little Wigner matrices $d^j_{mm'}$ are defined in Eq. (136) of Ref. [48]. The result (10) reveals that the sidereal dependence of the transition frequencies is controlled by the azimuthal indices on the coefficients contributing to the perturbation.

B. Coefficient selection rules

Before calculating explicitly the matrix elements of $\delta h^{\rm NR}_{\rm H}$ in the unperturbed states, it is useful to study the symmetries of the system. We show here that various symmetries imply vanishing values for many matrix elements of operators in the decomposition (3)–(5). This identifies a subset of effective spherical coefficients that are inaccessible at leading order via spectroscopy.

A first observation is that the unperturbed states are parity eigenstates. It follows that only even-parity perturbations can contribute to the energy shift at first order.

Since all operators in the decomposition (3)–(5) have definite parity [37], it is straightforward to identify the inaccessible coefficients. For the coefficients a^{NR}_{wkjm}, c^{NR}_{wkjm}, which are associated with the usual spherical harmonics, j must be even to contribute, which turns out to imply that k must be even as well. For the coefficients $g^{\mathrm{NR}(qP)}_{wkjm}$, $H^{\mathrm{NR}(qP)}_{wkjm}$, the parity is even if k is even and either $P = E$ with even j or $P = B$ with odd j.

A second observation is that the sums over j in Eqs. (4) and (5) can be truncated according to the angular momenta of the unperturbed state of interest. The key to implementing this truncation is the following proposition: if T_{jm} transforms as a spherical-tensor operator under the transformation generated by an angular-momentum operator $\boldsymbol{K}$ with associated quantum numbers K and m_K, then the matrix element $\langle Km'_K|T_{jm}|Km_K\rangle$ vanishes unless $j \leq 2K$. This result is a direct consequence of the triangular condition $|j_1 - j_2| \leq j_3 \leq j_1 + j_2$ of the Clebsch-Gordan coefficients $\langle j_1 m_1 j_2 m_2|j_3 m_3\rangle$ and the Wigner-Eckart theorem [51].

To illustrate the use of this proposition to truncate the sums over j, consider first the spin-independent terms in Eq. (4). These operators transform as spherical operators with $\boldsymbol{K}$ identified as $\boldsymbol{L}$, $\boldsymbol{J}$, or $\boldsymbol{F}$. Now, if K is a good quantum number, then a matrix element in the unperturbed state can be expressed as a linear combination of matrix elements in the states $|Km_K\rangle$ with K fixed. As a result, if the matrix elements in the states $|Km_K\rangle$ vanish, then so does the matrix element in the unperturbed state. For $K = J$, the proposition then implies that only operators satisfying the inequality $j \leq 2J$ can contribute to the energy shift. Since $2J$ is an odd number and since only even values of j contribute to the energy shift as noted above, we can express the condition on j for the case $K = J$ as $j < 2J$. For $K = L$ or $K = F$, no stronger constraints on the allowed values of j are obtained. For example, if $F = J - 1/2$ then $j \leq 2F = 2J - 1$, which is equivalent to $j < 2J$ because j is an integer. To summarize, among the spin-independent operators only those satisfying the condition $j < 2J$ can contribute to the energy shift of a state with angular momentum J. A similar argument applies to the spin-dependent terms with B-type parity, leading to the conclusion that among this set of terms only those satisfying $j \leq 2F - 1$ can contribute to the energy shift of a state with total angular momentum F.

Invariance under time reversal is another symmetry of the system. This symmetry can be used along with the Wigner-Eckart theorem to show that the spin-dependent terms with E-type parity in Eq. (5) cannot contribute to the energy shift at first order in perturbation theory. To see this, we begin by considering a spin-dependent operator of E-type parity having fixed j and $m = 0$, which takes the schematic form

$$T^E_{j0} = \sqrt{2}\sum_k |\boldsymbol{p}|^k \mathcal{T}^{\mathrm{NR}(1E)}_{kj0\ +1} Y_{j0}(\hat{\boldsymbol{p}})(\sigma^2 \cos\phi - \sigma^1 \sin\phi). \tag{11}$$

Under time reversal $\boldsymbol{p} \to -\boldsymbol{p}$ and $\boldsymbol{\sigma} \to -\boldsymbol{\sigma}$, so the operator transforms as $T^E_{j0} \to (-1)^{j+1} T^E_{j0}$. Also, states transform as $|Fm_F\rangle \to |F(-m_F)\rangle$ up to a phase factor, which implies

$$\langle Fm_F|T^E_{j0}|Fm_F\rangle = (-1)^{j+1}\langle F(-m_F)|T^E_{j0}|F(-m_F)\rangle. \tag{12}$$

The Wigner-Eckart theorem and the properties of the Clebsch-Gordan coefficients permit the replacement $-m_F \to m_F$ on the right-hand side of this equation, accompanied by a phase factor $(-1)^j$. We thus obtain the equality

$$\langle Fm_F|T^E_{j0}|Fm_F\rangle = -\langle Fm_F|T^E_{j0}|Fm_F\rangle, \tag{13}$$

revealing that all the matrix elements of T_{j0} vanish. Using the Wigner-Eckart theorem again, this result can be extended to the general matrix elements $\langle Fm'_F|T^E_{jm}|Fm_F\rangle$ via the identity

$$\langle Fm'_F|T^E_{jm}|Fm_F\rangle = \frac{\langle FF|T^E_{j0}|FF\rangle}{\langle FFj0|FF\rangle}\langle Fm_F jm|Fm'_F\rangle, \tag{14}$$

because the Clebsch-Gordan coefficient $\langle FFj0|FF\rangle$ always differs from zero when $2F \geq j$. We can thus confirm that $\langle Fm'_F|T^E_{jm}|Fm_F\rangle$ vanishes and hence that the spin-dependent terms with E-type parity in Eq. (5) cannot contribute to perturbative energy shifts.

While the various constraints above restrict the sums over j in the decomposition (3)–(5), the sums over k remain unconstrained. Evaluation of the matrix elements of operators $|\boldsymbol{p}|^k$ with $k > 4$ reveals that they diverge when n and L are small. This technical problem might be resolved by a suitable regularization. However, on dimensional grounds the size of the matrix elements is governed by a factor $(\alpha m_r)^k$, where α is the fine-structure constant. This factor heavily suppresses the resulting energy shifts even for sizeable coefficients for Lorentz violation. For instance, a large $k = 6$ coefficient of order 1 GeV^{-5} produces a spectroscopic frequency shift of only about a nanohertz. We therefore limit our attention to $k \leq 4$ in this work. This choice further restricts the allowed values of j [37], with the maximum allowed value j_{max} given as $j_{\mathrm{max}} = k$ for the spin-independent terms and $j_{\mathrm{max}} = k + 1$ for the spin-dependent terms of B-type parity.

Combining all the results in this subsection, we can identify the subset of nonrelativistic spherical coefficients of interest for spectroscopic experiments. Table I summarizes the situation for each type of coefficient. The first column of the table lists coefficients that in principle can

TABLE I. Contributing nonrelativistic spherical coefficients.

$\mathcal{K}^{\mathrm{NR}}_{wkjm}$	kjm	Number	Condition	C	PT	CPT
a^{NR}_{wkjm}	200, $22m$, 400, $42m$, $44m$	21	$j \leq 2J-1$	$-$	$+$	$-$
c^{NR}_{wkjm}	200, $22m$, 400, $42m$, $44m$	21	$j \leq 2J-1$	$+$	$+$	$+$
$g^{\mathrm{NR}(0B)}_{wkjm}$	$01m$, $21m$, $23m$, $41m$, $43m$, $45m$	34	$j \leq 2F-1$	$+$	$-$	$-$
$g^{\mathrm{NR}(1B)}_{wkjm}$	$01m$, $21m$, $23m$, $41m$, $43m$, $45m$	34	$j \leq 2F-1$	$+$	$-$	$-$
$H^{\mathrm{NR}(0B)}_{wkjm}$	$01m$, $21m$, $23m$, $41m$, $43m$, $45m$	34	$j \leq 2F-1$	$-$	$-$	$+$
$H^{\mathrm{NR}(1B)}_{wkjm}$	$01m$, $21m$, $23m$, $41m$, $43m$, $45m$	34	$j \leq 2F-1$	$-$	$-$	$+$

contribute at first order in perturbation theory to a spectral shift of a state with quantum numbers F and J. The second column shows the allowed values of the triplet kjm of indices, where $-j \leq m \leq j$ as usual. The third column gives the total number of independent components for each type of coefficient. Since there are two flavors for each coefficient for hydrogen, $w = e$ and $w = p$, a total of 356 independent nonrelativistic spherical components are measurable in principle via spectroscopic experiments on hydrogen, with each corresponding to a distinct physical effect. The fourth column lists the constraint on j for a measurement involving a state of angular momentum J or F. The final three columns display the C, PT, and CPT handedness of the corresponding operators.

Note that among the listed coefficients only the eight with $jkm = 200$ or $jkm = 400$ govern isotropic effects that are spectroscopically observable. They correspond to the coefficients $\mathring{a}^{\mathrm{NR}}_{w,2}$, $\mathring{a}^{\mathrm{NR}}_{w,4}$, $\mathring{c}^{\mathrm{NR}}_{w,2}$, and $\mathring{c}^{\mathrm{NR}}_{w,4}$ given by the definitions (7). The coefficients with $jkm = 000$, which satisfy all the above criteria, have been omitted from Table I because they produce only constant energy shifts in a given frame and hence are undetectable via spectroscopy. Detecting them might be feasible, for example, by studying anisotropies of the dispersion relation for hydrogen in a boosted frame, but investigating this lies outside our present scope. They also become detectable in principle in the presence of interactions such as gravity [9]. This issue is revisited in the context of studies of the gravitational response of antihydrogen in Sec. IV D below.

C. Matrix elements

In this subsection, we present some explicit results for matrix elements of the perturbation Hamiltonian $\delta h^{\mathrm{NR}}_{\mathrm{H}}$ introduced in Eq. (2). For each nonrelativistic spherical operator in $\delta h^{\mathrm{NR}}_{\mathrm{H}}$, a given matrix element can be decomposed as the product of two pieces, one depending on the principal quantum number n and the other independent of it. In what follows, we provide general expressions for each of these two pieces. For free-atom states with arbitrary total quantum number F, the energy shift cannot be expressed in closed form due to the algebraic complexities of degenerate perturbation theory. However, we can obtain an analytical result for the cases $F = 0$ and $F = 1$. The situation in the presence of an applied magnetic field is discussed in Sec. II D.

1. General case

The piece of the matrix element that depends on the principal quantum number n is given by the expectation value of the operator $|\boldsymbol{p}|^k$ in the unperturbed states. For the cases $k = 0$, 2, and 4 of interest here, we find

$$\begin{aligned}
\langle |\boldsymbol{p}|^0 \rangle_{nL} &= 1, \\
\langle |\boldsymbol{p}|^2 \rangle_{nL} &= \left(\frac{\alpha m_{\mathrm{r}}}{n}\right)^2, \\
\langle |\boldsymbol{p}|^4 \rangle_{nL} &= \left(\frac{\alpha m_{\mathrm{r}}}{n}\right)^4 \left(\frac{8n}{2L+1} - 3\right).
\end{aligned} \tag{15}$$

The first of these equations reflects the normalization of the unperturbed states. Note that only the case $k = 4$ depends on the angular-momentum quantum number L.

The second piece of the matrix element is independent of n. Using the spherical decomposition, it can be expressed in terms of the Clebsch-Gordan coefficients.

To illustrate this fact, we begin by considering the spin-independent term (4). Denoting the unperturbed states by the ket $|nFJLm_F\rangle$, a calculation of the expectation value of the usual spherical harmonics gives

$$\begin{aligned}
&\langle nFJLm_F|_0 Y_{jm}(\hat{\boldsymbol{p}})|nFJLm_F\rangle \\
&\quad = \sqrt{\frac{2j+1}{4\pi}} \sum_{m_L m_J} \sum_{m_1 m_2} \langle L0jm|L0\rangle \langle Lm_L jm|Lm_L\rangle \\
&\qquad \times \left\langle \frac{1}{2} m_1 Lm_L | Jm_J \right\rangle^2 \left\langle Jm_J \frac{1}{2} m_2 | Fm_F \right\rangle^2.
\end{aligned} \tag{16}$$

Note that the result is independent of the flavor w. In this equation, the Clebsch-Gordan coefficients involving J and F arise from the addition of orbital and spin angular momenta. The other Clebsch-Gordan coefficients originate in the triple integral of the spherical harmonics. This result and the Wigner-Eckart theorem in the generic form (14) can be combined to derive the spin-independent matrix elements in the fixed-F subspace. We find

$$\langle nFJLm'_F|h_{e0}+h_{p0}|nFJLm_F\rangle = -\sum_{wkjm}\mathcal{V}^{\rm NR}_{wkjm}\langle|\boldsymbol{p}|^k\rangle_{nL}\langle Fm_Fjm|Fm'_F\rangle \times\frac{\langle FJLF|_0Y_{j0}(\hat{\boldsymbol{p}})|FJLF\rangle}{\langle FFj0|FF\rangle}, \quad (17)$$

which demonstrates that the calculation of the matrix elements for the spin-independent term can be reduced to a determination of Clebsch-Gordan coefficients. A similar result holds for the spin-dependent term.

More generally, the above methods can be used to determine the matrix elements of the full perturbation $\delta h^{\rm NR}_{\rm H}$. Explicitly, after some calculation we find

$$\langle nFJLm'_F|\delta h^{\rm NR}_{\rm H}|nFJLm_F\rangle = \sum_{jm}A_{jm}\langle Fm_Fjm|Fm'_F\rangle, \quad (18)$$

where the weights $A_{jm}(nFJL)$ are given by

$$A_{jm} = -\sum_{wk}\langle|\boldsymbol{p}|^k\rangle_{nL}\left[\Lambda^{(0E)}_j\mathcal{V}^{\rm NR}_{wkjm}+\frac{\Lambda^{(0B)}_j}{2J+1}\mathcal{T}^{\rm NR(0B)}_{wkjm} -\Lambda^{(1B)}_j\left(\frac{\delta_{we}}{2(L-J)}+\frac{\delta_{wP}}{2(J-F)}\right)\mathcal{T}^{\rm NR(1B)}_{wkjm}\right], \quad (19)$$

with $\delta_{ab}=1$ if $a=b$ and $\delta_{ab}=0$ otherwise. In this expression, the factors $\Lambda^{(qP)}_j$ are related to the ratio of the expectation value of the operator and the corresponding Clebsch-Gordan coefficient. This can be verified for the spin-independent term by comparing Eqs. (17) and (19). Note that the weights obey the identity

$$A^*_{jm} = (-1)^mA_{j(-m)}, \quad (20)$$

by virtue of the properties of the coefficients for Lorentz violation [37].

The factors $\Lambda^{(qP)}_j$ can be expressed explicitly in terms of the quantum numbers of the state involved. For the factors $\Lambda^{(0E)}_0(F,J)$ associated with the spin-independent terms, we find

$$\Lambda^{(0E)}_0(F,J) = \frac{1}{\sqrt{4\pi}} \quad (21)$$

when $j=0$, and

$$\Lambda^{(0E)}_j(F,J) = i^j\frac{j-1}{2^{2j}}\left(1-2j\frac{F-J}{2J+1}\right)\frac{(J-j/2)!}{(J+j/2)!} \times\sqrt{\frac{(2j+1)(2F+j+1)!}{\pi(2F+1)(2F-j)!}} \quad (22)$$

when $j=2$ or $j=4$. For the factors $\Lambda^{(1B)}_j(F)$ associated with the spin-dependent terms, we obtain

$$\Lambda^{(1B)}_j(F) = \left(\frac{1}{2}(j-1)\right)!\sqrt{\frac{2^{(1-j)/2}}{j!!}}\Lambda^{(0B)}_j(F) = i^{j-1}\sqrt{\frac{j!!(2j+1)(F+\frac{1}{2}(j+1))!(2F-j)!!}{2^{(j-1)/2}\pi(2F+1)(F-\frac{1}{2}(j+1))!(2F+j)!!}} \quad (23)$$

for $j=1,3,5$. In these expressions, the double-factorial symbol !! is defined as usual by $N!!=N(N-2)\ldots1$ for odd N and $N!!=N(N-2)\ldots2$ for even N.

For convenience, Table II presents the numerical values for some instances of the factors $\Lambda^{(qP)}_j$. The table lists the numerical values of the factors for energy levels with orbital angular momentum $L\le2$. The left-hand side of the table concerns the factors $\Lambda^{(0E)}_j(F,J)$ associated with the spin-independent perturbation, displaying their values for $j=2,4$, $J=\frac{3}{2},\frac{5}{2}$, and $F=1,2,3$. The right-hand side gives values of the factors $\Lambda^{(0B)}_j(F)$ and $\Lambda^{(1B)}_j(F)$ for spin-dependent effects, for the ranges $j=1,3,5$ and $F=1,2,3$.

To illustrate the methods described in this subsection, we construct the matrix element for the perturbative energy shift in the $F=1$ subspace of the ground state $J=1/2$. Inspecting Table I reveals that only the spin-independent terms with $j=0$ and the spin-dependent terms with $j=1$ can contribute, while k can take the values 0, 2, and 4. From the general expression (18), the matrix element $\delta h(m'_F,m_F)$ in the $F=1$ subspace takes the form

$$\delta h(m'_F,m_F) = A_{00}\delta_{m'_Fm_F}+\sum_mA_{1m}\langle1m_F1m|1m'_F\rangle. \quad (24)$$

To determine the weight $A_{00}(11\frac{1}{2}0)$ using Eq. (19), we need the expectation values (15) evaluated at $n=1$ and

TABLE II. Some numerical values of the factors $\Lambda^{(qP)}_j$.

j	J	F	$\Lambda^{(0E)}$	j	F	$\Lambda^{(0B)}$	$\Lambda^{(1B)}$
2	$\frac{3}{2}$	1	$-\frac{1}{2\sqrt{2\pi}}$	1	1	$\sqrt{\frac{2}{3\pi}}$	$\sqrt{\frac{2}{3\pi}}$
		2	$-\frac{1}{2}\sqrt{\frac{7}{10\pi}}$		2	$\frac{3}{5}\sqrt{\frac{2}{\pi}}$	$\frac{3}{5}\sqrt{\frac{2}{\pi}}$
	$\frac{5}{2}$	2	$-2\sqrt{\frac{2}{35\pi}}$		3	$\frac{6}{7\sqrt{\pi}}$	$\frac{6}{7\sqrt{\pi}}$
		3	$-\frac{2}{7}\sqrt{\frac{3}{\pi}}$	3	2	$-\frac{6}{5}\sqrt{\frac{2}{\pi}}$	$-\frac{2}{5}\sqrt{\frac{3}{\pi}}$
4	$\frac{5}{2}$	2	$\frac{1}{\sqrt{14\pi}}$		3	$-2\sqrt{\frac{6}{7\pi}}$	$-\frac{2}{\sqrt{7\pi}}$
		3	$\frac{1}{7}\sqrt{\frac{11}{2\pi}}$	5	3	$\frac{10}{7}\sqrt{\frac{3}{\pi}}$	$\frac{2}{7}\sqrt{\frac{5}{\pi}}$

$L = 0$ and the factor $\Lambda_0^{(0E)}(1, \frac{1}{2})$ obtained from Eq. (21). To calculate the weight $A_{1m}(11\frac{1}{2}0)$ requires the values of $\Lambda_1^{(0B)}(1)$ and $\Lambda_1^{(1B)}(1)$ obtained from Table II. Collecting all the pieces, we find

$$A_{00}\left(11\frac{1}{2}0\right) = \sum_{q=0}^{2} -(\alpha m_{\mathrm{r}})^{2q}(1+4\delta_{q2})\sum_{w}\frac{\mathcal{V}^{\mathrm{NR}}_{w(2q)00}}{\sqrt{4\pi}} \tag{25}$$

for the spin-independent weight, and

$$A_{1m}\left(11\frac{1}{2}0\right) = \frac{1}{\sqrt{6\pi}}\sum_{q=0}^{2} -(\alpha m_{\mathrm{r}})^{2q}(1+4\delta_{q2}) \times \sum_{w}(\mathcal{T}^{\mathrm{NR}(0B)}_{w(2q)1m} + 2\mathcal{T}^{\mathrm{NR}(1B)}_{w(2q)1m}) \tag{26}$$

for the spin-dependent one.

2. Analytical energy shifts for $F = 0$ and $F = 1$

Since the unperturbed hydrogen energy levels are $(2F+1)$-fold degenerate, the perturbative corrections to the energy levels for fixed F are obtained by the eigenvalues of a $(2F+1)\times(2F+1)$ matrix, which is specified by Eq. (18). In general, these eigenvalues are determined by the roots of a polynomial of degree $2F+1$ corresponding to the secular equation of the matrix (18). This implies that a closed-form expression for the energy shifts at arbitrary F is unattainable. However, for the special cases $F = 0$ and $F = 1$ the secular polynomial can be solved in closed form. An analytical expression for the energy shifts can therefore be found, as we demonstrate next. For simplicity, we suppress the arguments $nFJL$ of the weights $A_{jm}(nFJL)$ in what follows.

Consider first the energy shift $\delta\epsilon(n, L)$ for the case $F = 0$. Since this energy state is nondegenerate, the shift can be obtained directly from Eq. (18). The result is

$$\delta\epsilon(n, L) = A_{00} = -\sum_{wk}\langle|\boldsymbol{p}|^k\rangle_{nL}\frac{\mathcal{V}^{\mathrm{NR}}_{wk00}}{\sqrt{4\pi}}. \tag{27}$$

From Eqs. (19) and (21), we can infer that the weight A_{00} depends only on the quantum numbers n and L. In fact, this feature holds for any F and J because the identity $\langle Fm_F00|Fm'_F\rangle = \delta_{m_F m'_F}$ implies that the contribution involving the isotropic coefficients with $jm = 00$ to the matrix element of the perturbation in the fixed-F subspace is given by A_{00} times the identity matrix. The energy shift can therefore always be expressed as the sum of contributions from the isotropic coefficients with ones from the anisotropic coefficients, with the former being given by $A_{00}(nL)$ independent of the values of F and J. One consequence of this observation is that isotropic coefficients can only contribute to frequency shifts for transitions with $\Delta n \neq 0$ or $\Delta L \neq 0$.

The expression for the $F = 1$ case is more involved because it is obtained from the solution of a cubic equation. The energy shift $\delta\epsilon(n, L, J, \xi)$ for this case takes the form

$$\delta\epsilon(n, L, J, \xi) = A_{00} + \frac{1 - i\xi\sqrt{3}}{9\xi^2 - 3}\sqrt[3]{\frac{\Delta_1 - \sqrt{\Delta_1^2 - 4\Delta_0^3}}{2}} + \frac{1 + i\xi\sqrt{3}}{9\xi^2 - 3}\frac{\Delta_0}{\sqrt[3]{\frac{\Delta_1 - \sqrt{\Delta_1^2 - 4\Delta_0^3}}{2}}}, \tag{28}$$

where $\xi = -1, 0, 1$. The quantities Δ_0 and Δ_1 can be written in terms of the weights $A_{jm}(n1JL)$ and Clebsch-Gordan coefficients. The expression for Δ_0,

$$\Delta_0 = \frac{9}{2}\sum_{jm}\frac{A_{jm}A^*_{jm}}{2j+1}, \tag{29}$$

explicitly shows that it is a rotational scalar because A_{jm} transforms dually to A^*_{jm} under observer rotations. Similarly, we can conclude from the structure of Δ_1,

$$\Delta_1 = -\sum_{jm_3}\sum_{m_1m_2}\frac{27\sqrt{(2j+1)(2j+3)}}{2\times 5^{j-1/2}}\langle jm_1jm_2|2m_3\rangle \times \langle 2m_3 2(-m_3)|00\rangle A_{jm_1}A_{jm_2}A_{2(-m_3)}, \tag{30}$$

that it too is a rotational scalar. One way to understand this is to notice that the weights A_{jm} transform under observer rotations like $\langle jm|$, and the equation for Δ_1 can be viewed as the sum of singlets $\langle 00|$ obtained by the angular-momentum coupling of $\langle jm_1|$ with $\langle jm_2|$ and then to $\langle 2m_3|$.

The result (28) holds for both allowed values of J. However, its complexity reduces significantly for $J = 1/2$. As can be seen from Table I, the $j = 2$ coefficients provide no contribution for $J = 1/2$ and so the weight A_{2m} vanishes. This implies that $\Delta_1 = 0$, thereby reducing Eq. (28) to

$$\delta\epsilon\left(n, L, \frac{1}{2}, \xi\right) = A_{00} + \frac{1}{\sqrt{2}}\xi A, \tag{31}$$

where $A \equiv \sqrt{\sum_m A^*_{1m}A_{1m}}$. The contribution from the anisotropic coefficients to the energy shift thus takes the form of a linear Zeeman shift, where ξ can be interpreted as the eigenvalues of the component of the total angular momentum $\boldsymbol{F}$ in the direction of the pseudovector A^*_{1m}. In terms of the unperturbed state $|n1\frac{1}{2}Lm_F\rangle$, the corresponding eigenvectors $|nL\frac{1}{2}\xi\rangle$ take the form

$$\left|nL\frac{1}{2}0\right\rangle = \frac{1}{A}\sum_m A_{1m}\left|n1\frac{1}{2}Lm\right\rangle,$$
$$\left|nL\frac{1}{2}(\pm1)\right\rangle = \frac{1}{N_\pm}\left[A_{11}^*(A_{10}\mp A)^2\left|n1\frac{1}{2}L(-1)\right\rangle + 2(A_{10}\mp A)|A_{11}|^2\left|n1\frac{1}{2}L0\right\rangle + 2A_{11}|A_{11}|^2\left|n1\frac{1}{2}L(+1)\right\rangle\right], \quad (32)$$

where the factors $N_\pm$ are normalizations.

In the expressions (27), (28), and (31) for the energy shifts, the weights A_{jm} containing the nonrelativistic coefficients for Lorentz violation appear only in combinations that are observer rotation scalars. This is a general feature of energy shifts for any F, which can be understood as follows. Recall that an observer transformation amounts merely to changing a basis, without changing the physics [8,9]. However, to specify completely a quantum observer transformation requires also defining its effect on the basis of states in the Hilbert space. The definition can be chosen freely, and it is convenient for the argument here to require quantum observer rotations to leave the basis states $|nFJLm_F\rangle$ invariant. This choice has similarities to the adoption of the Heisenberg picture in quantum mechanics. By construction, the operator $\delta h_{\rm H}^{\rm NR}$ is a scalar under observer rotations. The matrix elements $\langle nFJLm_F'|\delta h_{\rm H}^{\rm NR}|nFJLm_F\rangle$ then explicitly form a rotation scalar, consistent with the notion that the perturbed energy of the atom should be invariant under observer rotations. However, the weights A_{jm} with $jm \neq 00$ transform nontrivially under observer rotations, so in the final expression for the energy shift they can appear only in combinations that are rotational scalars. In fact, the combinations are also scalars under particle rotations, which transform the system while leaving unchanged the coefficients for Lorentz violation. As a result, neither observer nor particle rotations affect the expressions for the energy shifts. The physical manifestation of Lorentz violation appears as the lifting of the degeneracy of the unperturbed energy levels of the free atom, reflected in the appearance of the parameter ξ, with the size of the splitting determined by the magnitude of the coefficients for Lorentz violation.

D. Applied magnetic field

The complications in calculating the spectral shifts for free hydrogen arise in part from the rotational symmetry of the unperturbed states. Applying an additional known perturbation to the system can break this symmetry and can thereby considerably simplify the analysis. As an example with crucial relevance to many experimental situations, we study here some consequences of applying a constant uniform magnetic field. We assume the associated energy shift is small compared to the scale of the hyperfine structure but large compared to any Lorentz-violating shifts. In this scenario, the applied magnetic field lifts the $(2F+1)$-fold degeneracy, so nondegenerate perturbation theory can be used to determine the overall energy shifts.

Choosing for convenience the laboratory frame so that the applied magnetic field is aligned with the z axis, the energy shifts $\delta\epsilon(nFJLm_F)$ of the Zeeman levels are determined by the diagonal components of the matrix elements (18), which have $m_F' = m_F$. This gives

$$\delta\epsilon(nFJLm_F) = \sum_j A_{j0}(nFJL)\langle Fm_F j0|Fm_F\rangle, \quad (33)$$

where the weights A_{j0} are defined in Eq. (19). Only weights with $m = 0$ contribute, as the Clebsch-Gordan coefficients $\langle Fm_F jm|Fm_F\rangle$ vanish unless $m = 0$.

The Clebsch-Gordan coefficients $\langle Fm_F j0|Fm_F\rangle$ are even functions of m_F for even j and are odd functions of m_F for odd j. This implies that $\langle F0j0|F0\rangle = 0$ for odd values of j. However, a glance at Table I shows that the only Lorentz-violating operators with even j producing spectroscopic contributions are spin independent. As a result, spin-dependent Lorentz-violating terms cannot contribute at leading order to the shift of any energy level with $m_F = 0$. This means, for example, that the transition frequency for any two levels with $m_F = 0$ can at most depend on spin-independent terms.

A key feature of an applied magnetic field is that it sets a definite orientation for the experimental system. Since nonzero coefficients for Lorentz violation imply a fixed orientation in the background, generic changes of direction of the magnetic field alter its alignment with the coefficients and so can produce corresponding changes in the perturbative energy shifts. Possible origins of a changing magnetic-field orientation relative to the coefficients include the rotation of the Earth, the revolution of the Earth around the Sun, and any effects in the laboratory due, for example, to placing the apparatus on a turntable. In the laboratory frame, these appear as a consequence of time-dependent coefficients for Lorentz violation, as outlined in Sec. II A. The motion of the Earth thus naturally produces sidereal and annual variations in some energy levels and hence in certain spectroscopic frequencies. Next, we present some general considerations for these variations. More explicit experimental applications are presented in Sec. III.

1. Sidereal variations

First, consider effects arising from the Earth's rotation about its axis. In the laboratory frame with the magnetic field along the z direction as above, the relevant nonrelativistic spherical coefficients $\mathcal{K}_{wkjm}^{\rm NR,lab}$ have $m = 0$ and vary with sidereal time due to the rotation. The relationship between the coefficients $\mathcal{K}_{wkjm}^{\rm NR,Sun}$ in the Sun-centered

frame and the coefficients $\mathcal{K}_{wkj0}^{\mathrm{NR,lab}}$ in the laboratory frame is given by

$$\mathcal{K}_{wkj0}^{\mathrm{NR,lab}} = \sum_m e^{im\omega_\oplus T_\oplus} d^j_{0m}(-\vartheta)\mathcal{K}_{wkjm}^{\mathrm{NR,Sun}}. \tag{34}$$

This differs from Eq. (10) due to the choice of the laboratory frame coordinates. In particular, the angle ϑ is now the relative angle between the applied magnetic field and the Earth's axis of rotation. A possible constant phase factor shifting $\omega_\oplus T_\oplus$ has been chosen by setting the orientation of the magnetic field in the XZ plane of the Sun-centered frame at $T_\oplus = 0$.

Combining Eqs. (33) and (34) yields the energy shift $\delta\epsilon(nFJLm_F)$ in the presence of an applied magnetic field expressed in the Sun-centered frame. We find

$$\begin{aligned}\delta\epsilon(nFJLm_F) = \sum_{jm} d^{(j)}_{0|m|}(-\vartheta)\langle Fm_F j0|Fm_F\rangle \\ \times [\mathrm{Re}A^{\mathrm{Sun}}_{j|m|}\cos(|m|\omega_\oplus T_\oplus) \\ - \mathrm{Im}A^{\mathrm{Sun}}_{j|m|}\sin(|m|\omega_\oplus T_\oplus)],\end{aligned} \tag{35}$$

where the weights $A^{\mathrm{Sun}}_{jm}(nFJL)$ are defined in the Sun-centered frame by an expression of the same form as the weights (19).

The sidereal variations (35) induce oscillations of the spectroscopic lines as a function of sidereal time. The frequencies of these oscillations are harmonics $m\omega_\oplus$ of the Earth's sidereal frequency $\omega_\oplus$, where $-j_{\max} \le m \le j_{\max}$ and $j_{\max}$ is the maximum j value for the two energy levels involved in the transition. As shown in Sec. II B, $j_{\max}$ is determined by the quantum numbers J and F. Denoting by $K_{\max}$ the maximum among F and J for both energy levels, the harmonics that appear are given by $-2K_{\max}+1 \le m \le 2K_{\max}-1$.

The above result for the harmonic frequencies of spectroscopic lines holds for general Lorentz violation. However, as discussed in Sec. II B, we are limiting our attention in the present work to terms with $k \le 4$. This corresponds to the restriction $j \le 5$, as can be confirmed from Table I, and hence involves only harmonic frequencies $\omega \le 5\omega_\oplus$. An example generating fifth-harmonic oscillations is the transition $2S_{1/2} - 3D^{F=3}_{J=5/2}$, which is one of a family of transitions considered in Sec. III D below. Higher harmonics are also signals of Lorentz violation and could be sought experimentally, but they involve more suppressed effects.

2. Annual variations

The transformation (34) between the Sun-centered frame and the laboratory frame holds at zeroth order in the laboratory speed. However, the orbital motion of the Earth around the Sun offers another source of variations for tests of Lorentz and CPT symmetry, which to date has been used to extract constraints on SME coefficients in comparatively few analyses [18,49,52]. Next, we consider some leading-order boost effects.

The instantaneous Lorentz transformation from the Sun-centered frame to the laboratory frame can be viewed as the combination of a boost from the Sun-centered frame to a frame comoving with the instantaneous laboratory frame, followed by a rotation to align the latter two frames [49]. The required boost velocity $\boldsymbol{\beta}$ is the vector sum $\boldsymbol{\beta} = \boldsymbol{\beta}_\oplus + \boldsymbol{\beta}_L$ of the instantaneous Earth orbital velocity $\boldsymbol{\beta}_\oplus$ in the Sun-centered frame and the instantaneous velocity $\boldsymbol{\beta}_L$ of the laboratory frame relative to the Earth's rotation axis. The Earth's orbital speed $\beta_\oplus \simeq 10^{-4}$ is much greater than the typical rotation speed $\beta_L \approx r_\oplus\omega_\oplus \sin\chi \simeq 10^{-6}$ for a laboratory at colatitude $\chi \simeq 45°$, but both motions are considered here as they yield distinct phenomenological effects. To a sufficient approximation the Earth's orbit can be taken as circular, so the velocity $\boldsymbol{\beta}_\oplus$ can be written as

$$\boldsymbol{\beta}_\oplus = \beta_\oplus \sin\Omega_\oplus T\hat{X} - \beta_\oplus\cos\Omega_\oplus T(\cos\eta\hat{Y} + \sin\eta\hat{Z}), \tag{36}$$

where $\Omega_\oplus \simeq 2\pi/(365.26\ \mathrm{d})$ is the Earth's orbital frequency, T is the time in the Sun-centered frame, and $\eta \simeq 23.4°$ is the angle between the XY plane and the Earth's orbital plane. Similarly, the velocity $\boldsymbol{\beta}_L$ takes the form

$$\boldsymbol{\beta}_L = -\beta_L \sin\omega_\oplus T_\oplus \hat{X} + \beta_L\cos\omega_\oplus T_\oplus \hat{Y}, \tag{37}$$

where $T_\oplus$ is the local Earth sidereal time. Note that the difference $T - T_\oplus$ is merely a phase that physically represents a convenient choice of local time zero for a specified tangential velocity.

One advantage to considering boost effects arises because the boost and parity operators fail to commute, implying that parity-even operators in the laboratory frame incorporate parity-odd ones in the Sun-centered frame. The connection between the two sets of operators is provided by the boost velocity, which changes sign under parity. The experimental sensitivity to parity-odd Lorentz violation is therefore suppressed by at least a factor of 10^{-4}, but as shown below the observable signals are distinct. Another advantage arises because in addition to mixing operators of different parity, the transformation between the two frames also mixes the irreducible rotation representations. This can enrich the expected signals for Lorentz violation. For example, laboratory measurements of an isotropic Lorentz-violating effect can also test anisotropic effects in the Sun-centered frame, which then appear combined with the boost velocity. The mixing of irreducible rotation representations does, however, imply a significant calculational issue for boost effects because performing the spherical decomposition is no longer natural, yielding cumbersome transformation rules for the spherical

operators. To avoid this issue, we work here with the Cartesian basis, for which calculations are more direct.

In the context of the applications discussed in Sec. III below, two types of parity-even laboratory observables are of particular interest: scalars and axial 3-vectors. For example, the former is relevant for the $1S$-$2S$ transition, while the latter is relevant to hyperfine Zeeman transitions. Consider first the simplest case involving the laboratory-frame measurement of a parity-even observer rotational scalar S^{lab} such as the weight $A_{00}(nL)$ in Eq. (33). The scalar S^{lab} can be expressed in the Sun-centered frame as

$$S^{\text{lab}} = S^{\text{Sun}} + V^J \beta^J, \tag{38}$$

where V^J is defined in the Sun-centered frame and transforms as a vector under observer rotations. Note that V^J can receive only contributions from anisotropic parity-odd Lorentz-violating operators in the Sun-centered frame. Substituting for β^J using Eq. (36) then reveals that in the laboratory frame the measurement of S exhibits annual variations. Similarly, Eq. (37) predicts sidereal variations of S. The two effects have distinct experimental signatures and are sensitive to different combinations of the components of V^J in the Sun-centered frame. As a result, experiments performing a boost analysis on a scalar observable can achieve interesting and distinctive sensitivities to coefficients for Lorentz violation.

Next, we consider a measurement of the z component A^z of an observer axial 3-vector A^J in the laboratory frame, such as the weight $A_{10}(nFJL)$ in Eq. (33). At first order in β^J and in terms of quantities in the Sun-centered frame, A^z can be written as

$$A^z = R^{zJ} A^{\text{Sun},J} + R^{zJ} \beta^K T^{JK}, \tag{39}$$

where T^{JK} is defined in the Sun-centered frame and transforms as a rank-2 pseudotensor under spatial rotations. The quantity R^{zJ} is the zth row of the rotation matrix R^{jJ} between the boosted frame and the laboratory frame, with entries given by

$$\begin{aligned} R^{zX} &= \sin\vartheta \cos(\omega_\oplus T_\oplus + \varphi), \\ R^{zY} &= \sin\vartheta \sin(\omega_\oplus T_\oplus + \varphi), \\ R^{zZ} &= \cos\vartheta, \end{aligned} \tag{40}$$

where as before ϑ is the angle between the magnetic field and the Earth's rotation axis. The phase φ is the angle between the X axis and the projection of the magnetic field on the XY plane at $T_\oplus = 0$. A useful perspective is to view R^{zJ} as a unitary vector pointing in the direction of the applied magnetic field.

The first term in Eq. (39) is just the $j = 1$ component of the right-hand side of Eq. (35), expressed in the Cartesian basis. This produces sidereal signals as discussed in Sec. II D 1, so it suffices here to consider the second term $R^{zJ}\beta^K T^{JK}$ in Eq. (39). To compare the pseudotensor T^{JK} to the spherical decomposition, it is convenient to decompose T^{JK} into irreducible rotation representations. This decomposition gives

$$\begin{aligned} R^{zJ}\beta^K T^{JK} = \frac{1}{3} R^{zJ}\beta^J T^{KK} + R^{zJ}\beta^K T^{[JK]} \\ + R^{zJ}\beta^K \left(T^{(JK)} - \frac{1}{3}\delta^{JK} T^{LL} \right), \end{aligned} \tag{41}$$

where indices in brackets and parentheses indicate antisymmetrization and symmetrization, respectively, both with a factor of $1/2$.

The first term in Eq. (41) contains the trace T^{KK}, which in the spherical basis corresponds to combinations of nonrelativistic coefficients of B-type parity with $jm = 00$. Its contribution is proportional to $R^{zJ}\beta^J$, so the corresponding signals can be altered significantly by manipulating the direction of the magnetic field. For example, if the magnetic field is chosen orthogonal to $\boldsymbol{\beta}_L$, then $R^{zJ}\beta_L^J = 0$ and only annual variations arise from this term. If instead the magnetic field is parallel to $\boldsymbol{\beta}_L$, then $R^{zJ}\beta^J = \beta_L + R^{zJ}\beta_\oplus^J$. For more generic orientations the signal can be complicated, with coupled sidereal and annual variations.

The contribution in Eq. (41) involving the antisymmetric representation $T^{[JK]}$ contains nonrelativistic spherical coefficients of E-type parity with $j = 1$. This term can be viewed as being contracted with a factor $R^{z[J}\beta^{K]}$, which represents the components of the cross product of the vector R^{zJ} with the velocity β^K. If the magnetic field is parallel to $\boldsymbol{\beta}_L$, then the contributions from $SR^{zJ}\beta^K T^{[JK]}$ vary only at the annual frequency $\Omega\oplus$. If the magnetic field is parallel to the Earth's rotation axis, then the configuration is insensitive to the combination of coefficients contained in $\epsilon^{ZJK}T^{JK}$. Generic orientations of the magnetic field again lead to coupled sidereal and annual variations.

The final term in Eq. (41) involves the traceless symmetric part of the pseudotensor, which corresponds to nonrelativistic spherical coefficients of B-type parity with $j = 2$. If the magnetic field is chosen along the Earth's rotation axis, the term of order $\beta_\oplus$ exhibits only annual variations and the experiment is sensitive to the combinations of coefficients contained in $T^{(ZJ)}$ and T^{JJ}. In this configuration, the term of order β_L involves only the fundamental frequency $\omega_\oplus$. For other orientations of the magnetic field, the signal also incorporates variations at the second harmonic $2\omega_\oplus$.

III. APPLICATIONS

This section discusses observable experimental signals for Lorentz and *CPT* violation that could appear in spectroscopic studies of hydrogen. We begin by addressing the case of free hydrogen in the absence of applied fields, characterizing the resulting level splitting and possible

experimental signals. Experiments with hyperfine Zeeman transitions are treated next. We obtain the energy-level and frequency shifts due to Lorentz and CPT violation and study several types of time variations in experimental signals, including sidereal and annual modulations together with turntable and orbital effects. Existing experimental data are used to place constraints on nonrelativistic coefficients. Two subsections treat spectroscopy involving the transitions nL-$n'L'$, including in particular the $1S$-$2S$ transition. We obtain the associated frequency shifts and discuss new constraints and the future reach available via a self-consistent analysis or via sidereal and annual variations.

A. Signals without background fields

In the absence of applied fields, the physical manifestation of Lorentz violation in free atomic hydrogen is a splitting of otherwise degenerate energy levels. In the Sun-centered frame, the perturbed states can be constructed by diagonalizing the Lorentz violation in the degenerate subspace. For example, as discussed in Sec. II C 2, Lorentz violation causes the ground state of free hydrogen to split into four sublevels in a pattern analogous to hyperfine Zeeman splitting, despite the absence of a magnetic field. At leading order, the ground states are eigenstates of the operator $\boldsymbol{A}\cdot\boldsymbol{F}$ restricted to the corresponding subspace, where $\boldsymbol{A}$ is the vector formed from the A_{1m} coefficients in Eq. (31) and $\boldsymbol{F}$ is the total angular momentum. In this subsection, we consider prospects for experimental investigations of this degeneracy lifting.

1. Transition probabilities

In the Sun-centered frame, the splitting of the energy levels in free hydrogen is time independent because the coefficients for Lorentz and CPT violation can be taken as constant in this frame. Suppose an experiment is designed to excite transitions between these states using a laser with a fixed polarization in the laboratory frame. In the Sun-centered frame, the laboratory is rotating due to the Earth's spin and the laser polarization rotates with it. The relative orientation between the polarization of the laser and the split hydrogenic states therefore changes as a function of sidereal time, affecting the transition probabilities. This represents a unique signal of Lorentz violation.

To see more explicitly the effect, we restrict our attention to the comparatively simple case with $J=1/2$. Suppose the laser has linear polarization aligned along the laboratory z axis, and suppose we want to excite the transition between the eigenstates $F=0$ and $F=1$, $\xi=0$ with energies fixed by Eq. (31). Using the dipole approximation, the transition probability is proportional to the squared magnitude of the dipole matrix element $\mathcal{T}_{fi}$ between the initial state $|i\rangle$ and the final state $|f\rangle$, $|\mathcal{T}_{fi}|^2 \propto |\langle i|z|f\rangle|^2$. In terms of the basis states $|nFJLm_F\rangle$ and the weights (26) introduced in Sec. II C, we have

$$|i\rangle = \left|n0\frac{1}{2}L0\right\rangle, \qquad |f\rangle = \frac{1}{A}\sum_m A_{1m}\left|n'1\frac{1}{2}L'm\right\rangle. \quad (42)$$

These expressions are valid in any frame. The basis $|nL\tfrac{1}{2}Fm_F\rangle$ can be taken as quantum observer invariant under frame transformations, as discussed in Sec. II C 2, but the weights A_{1m} transform under rotations. In the laboratory frame, the squared magnitude of the dipole matrix element becomes

$$|\mathcal{T}_{fi}|^2 \propto |\langle i|z|f\rangle|^2 = \frac{|A_{10}^{\rm lab}|^2}{A^2}\left|\left\langle nL\frac{1}{2}00|z|n'L'\frac{1}{2}10\right\rangle\right|^2. \quad (43)$$

We assume here an adiabatic rotation so that the perturbation method is valid. This is reasonable as the Earth's sidereal period is much greater than the timescale for photon absorption. Finally, converting this result to the Sun-centered frame using Eq. (10) reveals the time variation of the transition probabilities at harmonics of the sidereal frequency $\omega_\oplus$.

An interesting insight obtained from Eq. (43) is that the sidereal variation of the transition probability can be an unsuppressed effect, as it depends only on the ratio of coefficients for Lorentz and CPT violation rather than their absolute values. This distinctive feature has no parallel in typical experiments performed in applied fields, such as the observations of Zeeman hyperfine transitions discussed in Sec. III B below. The catch here is that an experiment measuring the unsuppressed transition probabilities must be able to resolve the energy splitting due to the Lorentz and CPT violation, which itself is a suppressed effect.

2. Line shapes

Since the transition probabilities vary with sidereal time, so do the observed line shapes. To illustrate this, we assume that the Lorentz-violating splitting is detectable and that an ensemble of particles in the state $F=1$, $\xi=0$ can be produced. If this system is exposed to an oscillating magnetic field $\boldsymbol{B}=\boldsymbol{B}_0\cos\omega t$, the time-dependent perturbation can be taken as

$$\Delta h(t) = \mu_B(g_e\boldsymbol{S_e}\cdot\boldsymbol{B}_0 + g_p\boldsymbol{S_p}\cdot\boldsymbol{B}_0)\cos\omega t, \quad (44)$$

where μ_B is the Bohr magneton and g_w is to the gyromagnetic ratio of the particle of flavor w. The time t coincides with the local Earth sidereal time $T_\oplus$ up to a phase. Note that the frequency for the transition $\Delta F=-1$, $\Delta\xi=0$ is unaffected by Lorentz violation, so it coincides with the ground-state hyperfine-splitting frequency ω_0.

Suppose now the oscillation frequency ω of the magnetic field is tuned near resonance, $\omega=\omega_0+\Delta\omega$, where $\Delta\omega \ll \omega_0$. For generic orientations of the field, the setup can then be approximated as a two-state system. Using the

rotating-field approximation [53], the transition probability is given by

$$\mathcal{P}(t) = \frac{\gamma^2}{\gamma^2 + \Delta\omega^2} \sin^2\left(\frac{1}{2}\sqrt{\gamma^2 + \Delta\omega^2}\, t\right), \tag{45}$$

where $\gamma = (g_e - g_p)(\boldsymbol{B}\cdot\hat{\boldsymbol{A}})$. The magnetic field rotates with the laboratory and the Earth at angular frequency $\omega_\oplus$, so in the Sun-centered frame the product $\boldsymbol{B}\cdot\hat{\boldsymbol{A}}$ and hence γ depends on sidereal time. The explicit dependence is

$$\begin{aligned}\hat{\boldsymbol{B}}\cdot\hat{\boldsymbol{A}} = {} & A_{10}\cos\vartheta - \sqrt{2}\sin\vartheta \mathrm{Re}A_{11}\cos(\omega_\oplus T_\oplus + \phi_0) \\ & + \sqrt{2}\sin\vartheta \mathrm{Im}A_{11}\sin(\omega_\oplus T_\oplus + \phi_0),\end{aligned} \tag{46}$$

where ϑ is the angle between the magnetic field and the rotation axis of the Earth. The phase ϕ_0 is the azimuthal angle of the magnetic field in the Sun-centered frame at time $T_\oplus = 0$. Substituting this expression into Eq. (45) determines the line shape for the transition, including its variation with sidereal time.

The two-state approximation used above fails for configurations with orthogonal or near-orthogonal $\boldsymbol{B}$ and $\boldsymbol{A}$ because the probability of the stimulated transition with $\Delta\xi = 0$ then becomes smaller and comparable to other allowed transitions. None of the transitions are on resonance in this scenario, so the probability for a stimulated transition can be disregarded. For example, if $A_{10}\cos\vartheta$ is negligible compared to the other terms in Eq. (46), then $\hat{\boldsymbol{B}}\cdot\hat{\boldsymbol{A}}$ fluctuates to zero and back, implying that the signal for Lorentz violation includes peaks and valleys in the transition probability as a function of the sidereal time.

3. Prospects

The vector $\boldsymbol{A}$ is determined by the coefficients for Lorentz and *CPT* violation. Assuming this vector is nonzero and known, the amusing possibility arises that a hydrogen maser could be created based on the Lorentz-violating level splitting. Constructing the oscillating magnetic field $\boldsymbol{B}$ to be aligned with $\boldsymbol{A}$ would generate an approximate two-state system without the need for the usual applied external field to break the system degeneracy. The necessary population inversion could be produced, for example, by overlapping the Lorentz-violating background field with an inhomogeneous magnetic field to select the states seeking low field. A possible advantage of a Lorentz-violation maser is that the vector $\boldsymbol{A}$ is expected to be highly homogeneous because the coefficients for Lorentz violation can be assumed uniform and constant in the Sun-centered frame [8], so the issues for conventional masers arising from the inhomogeneity of the applied magnetic field would be irrelevant. However, realizing a Lorentz-violation maser in an Earth-based laboratory would face the challenge of overcoming the effective sidereal oscillation of $\boldsymbol{A}$ in the laboratory due to the Earth's rotation. This tends to skew its alignment with $\boldsymbol{B}$ and hence would permit the excitation of transitions between the ground state and the levels $F = 1$, $\xi = \pm 1$, destroying the two-state approximation and reducing the emission of coherent microwaves.

More generally, the similarities between the Lorentz-violating splittings and conventional linear Zeeman shifts provide an intuitive guide to prospective experimental options. For example, transitions between the different $F = 1$ sublevels could be investigated using tools like those adopted for studies of $F = 1$ Zeeman transitions in the presence of a uniform magnetic field. Current sensitivities to the $F = 1$ Lorentz-violating splittings have attained about 1 mHz using measurements of hyperfine Zeeman transitions [14–16], so we can assume the resonance frequency between the $F = 1$ levels lies below this value. One option to improve the sensitivity might be to prepare an ensemble of atoms in the $F = 1$ state and probe them with a magnetic field oscillating at a frequency below 1 mHz. Assuming a mechanism to monitor induced transitions can be implemented, then sweeping over decreasing frequencies could lead to better sensitivities to the coefficients for Lorentz violation. Note, however, that for $J > 1/2$ the Lorentz-violating splitting lacks a Zeeman-type structure, so studies of the various associated transitions would require developing the corresponding phenomenology.

Another possibility is to search for line separation or broadening arising from the Lorentz-violating level splittings. Suppose a transition between two states with $J = 1/2$ is studied. Ideally, the Lorentz-violating splitting would be detected in the form of multiple resonance peaks. Even if individual peaks cannot be resolved, the modified line shapes could be calculated and the minimum value of the effect leading to resolvable peaks within the particular experimental scenario could be determined. This would correspond to a constraint on the coefficients for Lorentz violation. Note that the parallel to the Zeeman hyperfine splitting implies that the putative signal for Lorentz violation can be approximated experimentally by applying to the ensemble of hydrogen atoms a uniform external magnetic field rotating with sidereal frequency. Moreover, the Lorentz violation also produces line broadening, which could be studied directly. Consider, for example, the transitions $F = 0$ to $F = 1$ under the assumption that levels with all values of ξ are excited with equal probability. An estimate of the Lorentz-violating line broadening ΔE can be found by calculating the statistical deviation arising from the availability of levels of different ξ. Ignoring the natural linewidth, this gives

$$(\Delta E)^2 = \frac{1}{3}|\boldsymbol{A}|^2. \tag{47}$$

The result indicates that the Lorentz-violating broadening is related to the magnitude of the vector $\boldsymbol{A}$.

B. Hyperfine Zeeman transitions

In this subsection, we consider effects of Lorentz and *CPT* violation on the hyperfine levels of hydrogen in the presence of a weak magnetic field. The $1S_{1/2}$ level in hydrogen is split into two sublevels, a ground state with total atomic angular momentum $F = 0$ and an excited state with $F = 1$. Applying a weak magnetic field further splits the $F = 1$ hyperfine level into three Zeeman sublevels with energies determined by the eigenvalue m_F of the component of $\boldsymbol{F}$ along the magnetic field. We determine the frequency shifts from Lorentz and *CPT* violation, and we discuss some signals involving sidereal variations, changes of the orientation of the magnetic field, and boosts. Signals in space-based missions and in other hydrogenic systems are also described.

1. Frequency shift

The Lorentz-violating energy shifts of the hyperfine Zeeman sublevels for $J = 1/2$, $L = 0$ or 1, and any n can be obtained from Eq. (33) along with the expression (19) for the weights $A_{00}(n1\frac{1}{2}L)$. The result is

$$\delta\epsilon(m_F) = -\sum_{q=0}^{2}\left(\frac{\alpha m_{\rm r}}{n}\right)^{2q}\left(1+\left(\frac{8n}{2L+1}-4\right)\delta_{q2}\right) \times\sum_{w}\left[\frac{\mathcal{V}^{\rm NR}_{w(2q)00}}{\sqrt{4\pi}}+\frac{m_F}{2\sqrt{3\pi}}(\mathcal{T}^{\rm NR(0B)}_{w(2q)10}+2\mathcal{T}^{\rm NR(1B)}_{w(2q)10})\right], \tag{48}$$

where the quantities $\mathcal{V}^{\rm NR}_{w(2q)00}$, $\mathcal{T}^{\rm NR(0B)}_{w(2q)10}$, $\mathcal{T}^{\rm NR(1B)}_{w(2q)10}$ are expressed in terms of nonrelativistic spherical coefficients by Eq. (6). Note that this extends the known result for the minimal SME [13] to include contributions from the $d = 4$ coefficients $g_{\lambda\mu\nu}$ along with ones involving operators of arbitrary d.

The frequency shifts for the hyperfine Zeeman transitions of the ground state follow from this result. Denoting by Δm_F the difference between the values of m_F for the initial sublevel and the final one, we obtain

$$2\pi\delta\nu = -\frac{\Delta m_F}{2\sqrt{3\pi}}\sum_{q=0}^{2}(\alpha m_{\rm r})^{2q}(1+4\delta_{q2}) \times\sum_{w}[g^{\rm NR(0B)}_{w(2q)10}-H^{\rm NR(0B)}_{w(2q)10}+2g^{\rm NR(1B)}_{w(2q)10} -2H^{\rm NR(1B)}_{w(2q)10}]. \tag{49}$$

Note that the isotropic coefficients, which are contained in $\mathcal{V}^{\rm NR}_{k00}$ and modify the energies according to Eq. (48), are absent from this frequency shift. This agrees with the result obtained in Sec. II C 2 that isotropic coefficients only contribute to transitions with $\Delta n \neq 0$ or $\Delta L \neq 0$. Note also that the result (49) contains the minimal-SME limit via the restriction

$$g^{\rm NR(0B)}_{w010}+2g^{\rm NR(1B)}_{w010}-H^{\rm NR(0B)}_{w010}-2H^{\rm NR(1B)}_{w010} \to 2\sqrt{3\pi}[b^w_3-m_w d^w_{30}-H^w_{12}-m_w g^{w(A)}_3+m_w g^{w(M)}_{120}], \tag{50}$$

where the superscripts (A) and (M) indicate the irreducible axial and irreducible mixed-symmetry combinations of the minimal-SME coefficients $g^w_{\kappa\lambda\nu}$, respectively [81,82]. The frequency shift (49) thereby matches the result reported in Ref. [13] with only b^w_μ, $d^w_{\mu\nu}$, and $H^w_{\mu\nu}$ contributing at leading order, which neglects the g-type minimal-SME coefficients as suppressed by the necessary accompanying breaking of the electroweak $\mathrm{SU}(2)\times\mathrm{U}(1)$ symmetry [8].

The expression (49) reveals that only transitions with $\Delta m_F \neq 0$ are sensitive to Lorentz violation at leading order, independent of the operator mass dimension d. One implication of this observation is that the standard transition used in hydrogen masers, $F = 0 \to F = 1$ with $\Delta m_F = 0$, is insensitive to Lorentz violation. The Lorentz violation considered in this work involves only propagator effects, which cannot shift the standard transition frequency because the reduced density matrices for the spin singlet and entangled triplet are identical and so yield identical expectation values for any operator that acts on only one subsystem.

2. Sidereal variations

At zeroth order in the boost, the nonrelativistic spherical coefficients in the laboratory frame can be expressed in terms of coefficients in the canonical Sun-centered frame as

$$\mathcal{K}^{\rm NR,lab}_{wk10} = \mathcal{K}^{\rm NR,Sun}_{wk10}\cos\vartheta - \sqrt{2}{\rm Re}\mathcal{K}^{\rm NR,Sun}_{wk11}\sin\vartheta\cos\omega_\oplus T_\oplus + \sqrt{2}{\rm Im}\mathcal{K}^{\rm NR,Sun}_{wk11}\sin\vartheta\sin\omega_\oplus T_\oplus, \tag{51}$$

which is a special case of Eq. (34). As before, $\omega_\oplus$ is the Earth's sidereal rotation frequency, $T_\oplus$ is the sidereal time, and ϑ is the angle between the applied magnetic field and the Earth's rotation axis. Together with the expression (49) for the frequency shift, the above relation predicts that the hyperfine Zeeman transition frequencies oscillate with frequency $\omega_\oplus$ in the presence of Lorentz violation. This result is in agreement with the discussion in Sec. II D 1, with the identification $K_{\rm max} = F = 1$ and hence obtaining $|m_{\rm max}| = 2K_{\rm max} - 1 = 1$.

An experiment performed with a maser located at the Harvard-Smithsonian Center for Astrophysics searched for sidereal variations of the hyperfine Zeeman transitions with $F = 1$ and $\Delta m_F = \pm 1$, finding no signal to within ± 0.37 mHz at one standard deviation [14–16]. Using the

frequency shift (49) for colatitude $\chi \simeq 48°$, this implies the bound

$$\left| \sum_{q=0}^{2} (\alpha m_r)^{2q} (1 + 4\delta_{q2}) \sum_w [g^{\mathrm{NR}(0B)}_{w(2q)10} - H^{\mathrm{NR}(0B)}_{w(2q)10} + 2g^{\mathrm{NR}(1B)}_{w(2q)10} - 2H^{\mathrm{NR}(1B)}_{w(2q)10}] \right| < 9 \times 10^{-27}\ \mathrm{GeV}, \tag{52}$$

which constrains a subset of the nonrelativistic spherical coefficients in the Sun-centered frame.

Intuition about the implications of this constraint can be gained by adopting the assumption that only one coefficient is nonzero at a time and extracting the resulting limits. Table III presents the constraints on individual nonrelativistic spherical coefficients obtained in this way. The results hold equally for electron and proton coefficients. Note that several of these lie well below the level at which Planck-scale signals might be expected to arise in some models.

We emphasize that this type of measurement bounds the effects of certain Lorentz-violating operators at arbitrary d, even though only the subset of nonrelativistic spherical coefficients with $k \leq 4$ and $j = 1$ is accessible. This is because a nonrelativistic spherical coefficient with $j = 1$ is a linear combination of an infinite subset of the basic spherical coefficients with $d \geq 3$ [37]. Note also that in terms of the basic spherical coefficients the experiment has greater reach for protons than for electrons due to the mass factors that enter the relevant linear combinations. For example, the sensitivity to the basic spherical coefficient at mass dimension d and with $k = 0$ is numerically that of the corresponding nonrelativistic spherical coefficient suppressed by a factor of $(0.94)^{3-d}/3$ for the proton and a factor of $(5.1 \times 10^{-4})^{3-d}/3$ for the electron.

3. Changes of magnetic-field orientation

The bound (52) is insensitive to nonrelativistic spherical coefficients with $m = 0$ in the Sun-centered frame because these coefficients enter the frequency (51) without the dependence on $T_\oplus$ necessary for the experimental signal. However, Eq. (51) predicts that these coefficients do change with the angle ϑ between the magnetic field and the Earth's rotation axis. An experiment involving a changing magnetic-field orientation is therefore of interest. One possibility along these lines would be to place the apparatus on a rotating turntable.

For simplicity, suppose the rotation axis of the turntable points towards the zenith and the magnetic field is perpendicular to it. Defining the laboratory-frame z axis to lie along the magnetic field, the laboratory-frame coefficients are given in terms of Sun-frame coefficients by

$$\begin{aligned} \mathcal{K}^{\mathrm{NR,lab}}_{wk10} = & -\mathcal{K}^{\mathrm{NR,Sun}}_{wk10} \sin\chi \cos T_r \omega_r \\ & - \sqrt{2}\mathrm{Re}\mathcal{K}^{\mathrm{NR,Sun}}_{wk11} \cos\chi \cos\omega_r T_r \cos\omega_\oplus T_\oplus \\ & + \sqrt{2}\mathrm{Im}\mathcal{K}^{\mathrm{NR,Sun}}_{wk11} \cos\chi \cos\omega_r T_r \sin\omega_\oplus T_\oplus \\ & + \sqrt{2}\mathrm{Re}\mathcal{K}^{\mathrm{NR,Sun}}_{wk11} \sin\omega_r T_r \sin\omega_\oplus T_\oplus \\ & + \sqrt{2}\mathrm{Im}\mathcal{K}^{\mathrm{NR,Sun}}_{wk11} \sin\omega_r T_r \cos\omega_\oplus T_\oplus, \end{aligned} \tag{53}$$

where χ is the colatitude of the experiment and ω_r is the angular rotation frequency of the turntable. For convenience, we have introduced a time T_r shifted relative to $T_\oplus$, with the origin $T_r = 0$ chosen to be the time when the magnetic field points south. In this scenario, the coefficients with $m = 0$ in the Sun-centered frame are independent of the sidereal frequency, producing variations at the turntable angular frequency ω_r of the coefficients in the laboratory frame and hence of the measured transition frequencies. The attainable sensitivity to $m = 0$ coefficients in an experiment of this type is expected to be similar to the sensitivities presented in Table III for the corresponding $m = 1$ coefficients.

TABLE III. Constraints on the moduli of the real and imaginary parts of electron and proton nonrelativistic coefficients determined from hyperfine Zeeman transitions in hydrogen using Eq. (52).

Coefficient $\mathcal{K}$	Constraint on $\lvert\mathrm{Re}\mathcal{K}\rvert$, $\lvert\mathrm{Im}\mathcal{K}\rvert$
$H^{\mathrm{NR}(0B)}_{011}$, $g^{\mathrm{NR}(0B)}_{011}$	$<9 \times 10^{-27}$ GeV
$H^{\mathrm{NR}(1B)}_{011}$, $g^{\mathrm{NR}(1B)}_{011}$	$<5 \times 10^{-27}$ GeV
$H^{\mathrm{NR}(0B)}_{211}$, $g^{\mathrm{NR}(0B)}_{211}$	$<7 \times 10^{-16}$ GeV^{-1}
$H^{\mathrm{NR}(1B)}_{211}$, $g^{\mathrm{NR}(1B)}_{211}$	$<4 \times 10^{-16}$ GeV^{-1}
$H^{\mathrm{NR}(0B)}_{411}$, $g^{\mathrm{NR}(0B)}_{411}$	$<9 \times 10^{-6}$ GeV^{-3}
$H^{\mathrm{NR}(1B)}_{411}$, $g^{\mathrm{NR}(1B)}_{411}$	$<5 \times 10^{-6}$ GeV^{-3}

4. Annual variations

As described in Sec. II D 2, the inclusion of boosts in the analysis implies the appearance of contributions from parity-odd operators. The frequency shift in the laboratory frame transforms as the z component of a vector, so for present purposes we denote it as $\delta\nu^z$. Its expression in the Sun-centered frame takes the generic form (39) at first order in the boost velocity $\boldsymbol{\beta}$,

$$2\pi\delta\nu^z = 2\pi R^{zJ}\delta\nu^{\mathrm{Sun},J} + \Delta m_F \sum_{df} R^{zJ} T^{(d)JK}_w (\beta^K{}_\oplus + \beta^K_L), \tag{54}$$

where $\boldsymbol{\beta}_\oplus$, $\boldsymbol{\beta}_L$, and R^{zJ} are defined in Eqs. (36), (37), and (40), respectively. The form of the pseudotensor $T^{(d)JK}_w$ depends on the operator mass dimension d and the particle flavor w.

TABLE IV. Values of the pseudotensors $T_w^{(d)JK}$ in Eq. (54) for the electron and proton in atomic hydrogen for $3 \leq d \leq 8$.

d	$V_w^{(d)J}$
3	$\tilde{H}_{w,\mathrm{eff}}^{JK}$
4	$-2m_w\tilde{g}_{w,\mathrm{eff}}^{K(TJ)}$
5	$3m_w^2\tilde{H}_{w,\mathrm{eff}}^{J(TKT)} + (\alpha m_\mathrm{r})^2\tilde{H}_{w,\mathrm{eff}}^{J(KLL)}$
6	$-4m_w^3\tilde{g}_{w,\mathrm{eff}}^{J(TTTK)} - 4(\alpha m_\mathrm{r})^2 m_w\tilde{g}_{w,\mathrm{eff}}^{J(TLLK)}$
7	$5m_w^4\tilde{H}_{w,\mathrm{eff}}^{J(TTTTK)} + 10(\alpha m_\mathrm{r})^2 m_w^2\tilde{H}_{w,\mathrm{eff}}^{J(TTLLK)} + 5(\alpha m_\mathrm{r})^4\tilde{H}_{w,\mathrm{eff}}^{J(KLLMM)}$
8	$-6m_w^5\tilde{g}_{w,\mathrm{eff}}^{J(TTTTTK)} - 20(\alpha m_\mathrm{r})^2 m_w^3\tilde{g}_{w,\mathrm{eff}}^{J(TTTLLK)} - 30(\alpha m_\mathrm{r})^4 m_w\tilde{g}_{w,\mathrm{eff}}^{J(KTLLMM)}$

Table IV provides explicit expressions for $T_w^{(d)JK}$ with $3 \leq d \leq 8$ in terms of the particle rest masses m_w, the fine-structure constant α, the reduced mass m_r of the system, and the effective Cartesian coefficients for Lorentz violation defined in Eqs. (27) and (28) of Ref. [37]. Only leading-order nonrelativistic contributions from each coefficient are included. In the table, parentheses around sets of n indices indicate total symmetrization with respect to all indices enclosed, including a factor of $1/n!$.

Examining Eq. (54) and Table IV reveals that only the first index of each effective Cartesian coefficient is contracted with the rotation matrix. This feature arises because only the first two indices of the g- and H-type effective Cartesian coefficients are coupled to the particle spin via contraction in the original Lagrange density [37]. The applied magnetic field interacts with the magnetic dipole moment of the particle and so fixes the particle's spin orientation in the laboratory frame. The spin follows any adiabatic rotation of the magnetic field, which thereby changes the value of the contraction between the coefficients and the spin. However, the g- and H-type effective Cartesian coefficients are antisymmetric on the first two indices, so the result can always be interpreted as a rotation associated with the first index on any coefficient.

The Cartesian basis is convenient for boost corrections. However, as outlined in Sec. II D 2, we can decompose $T_w^{(d)JK}$ in terms of irreducible representations of the rotation group. These irreducible representations are associated with spherical coefficients. For example, for mass dimensions $d = 3$ and $d = 4$, we obtain

$$\begin{aligned}
\epsilon_{zJK}T_w^{(3)JK} &= \sqrt{\frac{3}{\pi}}H_w{}_{110}^{(3)(1E)},\\
\epsilon_{zJK}T_w^{(4)JK} &= -m_w\sqrt{\frac{3}{\pi}}g_w{}_{110}^{(4)(1E)},\\
T_w^{(4)JJ} &= -m_w\sqrt{\frac{9}{\pi}}g_w{}_{100}^{(4)(0B)},\\
T_w^{(4)zz} - \frac{1}{3}T_w^{(4)JJ} &= -m_w\sqrt{\frac{5}{\pi}}g_w{}_{120}^{(4)(0B)}.
\end{aligned} \tag{55}$$

These and similar expressions for $d > 4$ can be used to relate results in the Cartesian and spherical bases.

As discussed in Sec. II D 2, orienting the magnetic field parallel to the Earth's rotation axis decouples the sidereal and annual variations of the measured frequency, with sidereal variations associated to terms of order β_L and annual variations to terms of order $\beta_\oplus$. At first order in the boost parameter, the frequency shift for this orientation of the magnetic field is given in the Sun-centered frame by

$$\begin{aligned}
\delta\nu^z = \delta\nu^{\mathrm{Sun},Z} - \frac{\Delta m_F}{2\pi}\sum_{wd}[&T_w^{(d)ZZ}\beta_\oplus\sin\eta\cos\Omega_\oplus T\\
&+ T_w^{(d)ZY}(\beta_\oplus\cos\eta\cos\Omega_\oplus T - \beta_L\cos\omega_\oplus T_\oplus)\\
&+ T_w^{(d)ZX}(\beta_L\sin\omega_\oplus T_\oplus - \beta_\oplus\sin\Omega_\oplus T)],
\end{aligned} \tag{56}$$

where $\Omega_\oplus \simeq 2\pi/(365.26\ \mathrm{d})$ is the Earth orbital frequency, $\eta \simeq 23.5°$ is the Earth's orbital tilt, and χ is the colatitude of the experiment.

As an illustration of the expected sensitivity of an experiment in this configuration, suppose a search finds no signal for the annual variations $\delta\nu^z$ at the level of ± 1 mHz. Then, constraints of order 10^{-23} GeV would be implied on $T_w^{(d)JK}$. For minimal coefficients, this corresponds to limits of order 10^{-23} GeV on H^{TX} and H^{TY} in the electron and proton sectors, limits of order 10^{-19} on g^{XYZ}, g^{YXX}, g^{XYY}, g^{XTT} and g^{YTT} in the electron sector, and limits of order 10^{-23} on the corresponding coefficients in the proton sector. For the nonminimal sector, the disparity between the electron and proton masses implies that the experiment is more sensitive to proton coefficients. For example, limits on the $d = 8$ coefficients proportional to m_w^5 would be about 10^{-23} GeV^{-4} in the proton sector and about 10^{-6} GeV^{-4} in the electron sector.

For other orientations of the magnetic field, one readily isolated signal of Lorentz violation associated with the boost correction is the twice-sidereal variation of the frequency, which decouples from other variations. We can express this term as

$$\delta\nu_{2\omega_\oplus} = \frac{1}{4\pi}\beta_L \Delta m_F \sin\vartheta \times \sum_{wd}[\cos 2\omega_\oplus T_\oplus (T_w^{(d)XY} + T_w^{(d)YX}) + \sin 2\omega_\oplus T_\oplus (T_w^{(d)YY} - T_w^{(d)XX})], \quad (57)$$

where ϑ is the angle between the magnetic field and the Earth's rotation axis. For simplicity, the direction of the magnetic field at $T_\oplus = 0$ is taken to lie in the XZ plane in the Sun-centered frame, which eliminates a phase shift. Assuming an experimental search establishes no signal for the second-harmonic sidereal variations $\delta\nu_{2\omega_\oplus}$ at the level of ± 1 mHz, then constraints of order 10^{-21} GeV would be implied for $T_w^{(d)JK}$. For minimal coefficients, this corresponds to sensitivities of order 10^{-18} to g^{ZXY}, g^{YZX}, g^{ZXX} and g^{ZYY} in the electron sector and of order 10^{-21} for the same coefficients in the proton sector.

5. Space-based experiments

Laboratory measurements of boost effects provide no control over the orbital and rotational motion of the Earth. As a result, space-based experiments offer broader options for studies of the full range of possible boost effects due to the choice and variability of orbital and rotational motions for various space platforms. Here, we consider some prospects for measurements with a space-based hydrogen maser. For example, the Atomic Clock Ensemble in Space (ACES) mission [54] incorporates a hydrogen maser in the payload to be delivered and operated on the International Space Station (ISS). As discussed in Sec. III B 1, conventional maser transitions with $\Delta m_F = 0$ provide no leading-order sensitivity to effects from Lorentz violation. We therefore assume the maser is configured instead to achieve sensitivity to transitions with $\Delta m_F \neq 0$, perhaps using a double-resonance technique [55] similar to that already successfully implemented in the laboratory for tests of Lorentz and *CPT* invariance [14–16].

In the context of the minimal SME, specifics for analyzing data from space missions studying Lorentz violation are discussed in Ref. [56]. In the presence of nonminimal operators, the expected experimental signals have the same generic behavior because they too are governed by the form (39). As a result, using the information in Table IV permits the measurement of nonminimal coefficients as well. Satellite experiments offer a particular advantage for this purpose because the boost of the space platform differs from the boost of laboratory experiments on the Earth. More explicitly, consider the term $R^{zJ}\beta^K T^{JK}$ in Eq. (39). The rotation matrix can be altered by changing the orientation of the magnetic field in both Earth- and space-based experiments, producing sensitivity to the combinations $\beta^K T^{JK}$. However, space-based experiments can vary the boost β^K more broadly as well, which offers the potential to disentangle more components of T^{JK}.

For space-based experiments, the frequency shift takes the same form as Eq. (54) but with modified expressions for the rotation matrix and boost parameter. For simplicity, suppose the applied magnetic field is oriented parallel to the direction of propagation of the satellite relative to the center of mass of the Earth, and approximate the orbit as circular. This configuration could in principle be realized in an experiment on the ISS, for example. We can then view the instantaneous components R_{zK} of the rotation matrix as forming a unitary vector parallel to the satellite velocity $\boldsymbol{\beta}_s$. It follows that $R^{zJ}\beta_s^J = \beta_s$, where β_s is the average satellite speed, and also that $\epsilon_{JKL}R^{zJ}\beta_s^K = 0$. Comparing these results with Eq. (41) reveals that only the symmetric piece of T^{JK} varies with the direction of the boost relative to the Earth. Note that other orientations of the magnetic field relative to the direction of motion would introduce variations involving the trace and antisymmetric pieces of T^{JK}.

For the parallel configuration, an explicit calculation reveals that the term in the frequency that depends on $\boldsymbol{\beta}_s$ varies only at the second harmonic $2\omega_s$ of the mean satellite orbital angular frequency ω_s. The form of this term is

$$\delta\nu_{2\omega_s} = \frac{\Delta m_F}{16\pi}\sum_{wd}\beta_s(A_{sw}^{(d)}\sin 2\omega_s T_s + A_{cw}^{(d)}\cos 2\omega_s T_s), \quad (58)$$

where T_s is a reference time in the Sun-centered frame chosen such that $T_s = 0$ when the satellite crosses the equatorial plane on an ascending orbit. The amplitudes A_s and A_c are given by

$$\begin{aligned} A_{sw}^{(d)} &= 4\cos\zeta\sin 2\alpha(T_w^{(d)XX} - T_w^{(d)YY}) \\ &\quad - 8\cos\zeta\cos 2\alpha T_w^{(d)(XY)} - 8\sin\zeta\cos\alpha T_w^{(d)(ZX)} \\ &\quad + 8\sin\zeta\sin\alpha T_w^{(d)(YZ)}, \\ A_{cw}^{(d)} &= -2\sin^2\zeta(T_w^{(d)XX} + T_w^{(d)YY} - 2T_w^{(d)ZZ}) \\ &\quad - 2(3+\cos 2\zeta)\sin 2\alpha T_w^{(d)(XY)} \\ &\quad - (3+\cos 2\zeta)\cos 2\alpha(T_w^{(d)XX} - T_w^{(d)YY}) \\ &\quad + 4\sin 2\zeta\cos\alpha T_w^{(d)(YZ)} \\ &\quad - 4\sin 2\zeta\sin\alpha T_w^{(d)(XZ)}, \end{aligned} \quad (59)$$

where ζ is the angle between the satellite orbital axis and the Earth's rotation axis, and α is the azimuthal angle between the satellite's orbital plane and the X axis in the Sun-centered frame.

Direct inspection of the result (58) for the satellite experiment demonstrates that distinct combinations of coefficients appear relative to the frequency shift (57) involving the second harmonic of the sidereal frequency for an Earth-based experiment. Note that for a ground-based experiment at colatitude χ the frequency is

proportional to $\beta_L \sin\chi$, which is the tangential speed of the laboratory relative to the Earth's axis of rotation. This speed is an order of magnitude smaller than the speed β_s of a satellite such as the ISS relative to the Earth. This shows that an experiment realized on a space platform is more sensitive to this type of variation as well as offering access to more coefficient components that a ground-based counterpart.

C. $nS_{1/2}$-$n'S_{1/2}$ and $nS_{1/2}$-$n'P_{1/2}$ transitions

We next turn our attention to the effects of Lorentz and *CPT* violation on high-precision studies of the hydrogen transitions with $J = 1/2$ and $\Delta J = 0$, and in particular the transitions $nS_{1/2}$-$n'S_{1/2}$ and $nS_{1/2}$-$n'P_{1/2}$. The most prominent of these is perhaps the $1S$-$2S$ transition, which has recently been measured to a relative uncertainty of 4.2×10^{-15} [57]. Other transitions of this type that are measured to high precision include [58] the classical $2S_{1/2} - 2P_{1/2}$ Lamb shift [59], the $1S_{1/2}$-$3S_{1/2}$ transition [60], several $2S_{1/2}$-$nS_{1/2}$ transitions [61–63], and the $2S_{1/2}$-$4P_{1/2}$ transition [64]. In this subsection, we first present a general expression for the frequency shifts due to Lorentz and *CPT* violation. We then outline the extraction of constraints by matching theoretical expectations to experimental results and by studying sidereal and annual variations involving boosts.

1. Frequency shift

In searching for most effects of Lorentz and *CPT* violation, the absolute sensitivity of an experiment is of more significance than its relative precision because all nonrelativistic coefficients for Lorentz and *CPT* violation carry mass dimensions. It is therefore reasonable to neglect the contribution from the spin-dependent coefficients to Eq. (49) for any of the hydrogen transitions of interest here, as the attainable absolute sensitivity is significantly below that accessible to the hyperfine Zeeman transitions. For example, the long lifetime of the $2S_{1/2}$ state and the impressive relative precision achieved on the $1S$-$2S$ transition [57] yields the lowest absolute uncertainty of about 10 Hz among the optical transitions in hydrogen, but this remains 4 or more orders of magnitude below the absolute sensitivity reached in hyperfine measurements. Studies of optical transitions involving variations with sidereal time and colatitude at zeroth order in the boost are therefore of lesser interest.

In contrast, the $nS_{1/2}$-$n'S_{1/2}$ and $nS_{1/2}$-$n'P_{1/2}$ transitions offer sensitivity to isotropic coefficients for Lorentz and *CPT* violation that cannot be accessed via Zeeman hyperfine transitions. For example, Table I reveals that only coefficients with $j = 0$ and $j = 1$ contribute to the $1S$-$2S$ transition. Effects involving the coefficients with $j = 1$ can be neglected as above, but those involving the isotropic components with $j = 0$ are of definite interest. We therefore proceed in this subsection under the assumption that any transition with $\Delta J = 0$ and $J = 1/2$ is sensitive only to isotropic coefficients in the laboratory frame.

Within this scenario, we find that in the laboratory frame the frequency shift of any hydrogen transition n, L-n', L' with $J = 1/2$, $\Delta J = 0$ due to Lorentz and *CPT* violation can be written as

$$2\pi\delta\nu = 2m_r(\varepsilon_n - \varepsilon_{n'})\sum_w (\mathring{c}^{\rm NR}_{w,2} - \mathring{a}^{\rm NR}_{w,2}) - 4m_r^2\left[\varepsilon_n^2\left(\frac{8n}{2L+1} - 3\right) - \varepsilon_{n'}^2\left(\frac{8n'}{2L'+1} - 3\right)\right] \times \sum_w (\mathring{c}^{\rm NR}_{w,4} - \mathring{a}^{\rm NR}_{w,4}), \tag{60}$$

where $\varepsilon_n \equiv -\alpha^2 m_r/2n^2$. Note that the quantities $\mathcal{V}^{\rm NR}_{wk00}$ contain only isotropic coefficients, all of which are absent in the analogous expression (49) for the frequency shift of the hyperfine Zeeman levels. Also, only contributions from coefficients with $k \geq 2$ occur, a result consistent with previous conclusions that minimal coefficients have no effect on the $1S$-$2S$ transition at leading order in Lorentz and *CPT* violation [13,29]. We remark in passing that contributions to the $1S$-$2S$ transition are known to appear when higher-order corrections in minimal coefficients are included [17,29].

2. Self-consistent analysis

At leading order in $\beta_\oplus$, the transformation of isotropic coefficients from the laboratory frame to the Sun-centered frame is the identity map, $\mathcal{K}^{\rm lab}_{k00} \to \mathcal{K}^{\rm Sun}_{k00}$. The expression (60) for the frequency shift of any hydrogen transition $n, L \to n', L'$ with $J = 1/2$, $\Delta J = 0$ therefore also holds in the Sun-centered frame. At zeroth order in the boost, the result represents a constant shift in the transition frequency. However, a tiny constant frequency shift is challenging to measure experimentally.

One approach to studying the shift (60) is to compare the experimental data to the theoretical prediction for conventional Lorentz-invariant physics. To date, the available experimental data all appear consistent with theoretical expectations within the 10 Hz absolute uncertainty. However, making a definitive theoretical prediction requires knowledge of constants such as the Rydberg constant and the proton radius, which at present are also determined via hydrogen spectroscopy. For example, the contribution due to the coefficients $\mathcal{V}^{\rm NR}_{w200}$ acts to produce a shift δR_∞ in the Rydberg constant, given by

$$\delta R_\infty = \frac{4\pi m_r^2}{m_e} R_\infty \sum_w (\mathring{c}^{\rm NR}_{w,2} - \mathring{a}^{\rm NR}_{w,2}). \tag{61}$$

Analogously, the contribution due to the coefficients $\mathcal{V}^{\rm NR}_{w400}$ produces a change $\delta\nu_{\rm Lamb}$ in the classical Lamb shift, given by

$$2\pi\delta\nu_{\rm Lamb} = -\frac{2}{3}(\alpha m_{\rm r})^4 \sum_w (\overset{\circ}{c}{}^{\rm NR}_{w,4} - \overset{\circ}{a}{}^{\rm NR}_{w,4}), \qquad (62)$$

which could change the proton radius determined by hydrogen spectroscopy. This presents a self-consistency issue for direct comparison of experiment with theory, as the theoretical prediction based on Lorentz-invariant physics cannot be immediately disentangled from Lorentz-violating effects on the hydrogen spectrum.

Techniques to avoid this issue are possible, at least in principle. One option could be to measure the coefficients for Lorentz and *CPT* violation by comparing several transitions. For example, a best fit to the shift (60) could be performed. A related option is to perform a careful self-consistent comparison. In practice, the present limiting absolute uncertainty of order 10 kHz on the various transitions is likely to lead to maximal attainable sensitivities of about 10^{-7} GeV^{-1} on coefficients with $k = 2$ and of about 10^5 GeV^{-3} on ones with $k = 4$. Performing an analysis of this type remains an interesting open possibility to set first or improved constraints on several coefficients. Moreover, the efforts underway to improve the data from hydrogen spectroscopy with an eye to a more precise determination of the Rydberg constant and the proton radius [65–69] offer the potential for substantially improved future sensitivities on Lorentz and *CPT* violation.

3. Sidereal and annual variations due to boost corrections

As described in Sec. II D 2, isotropic terms in the laboratory frame can be used to study anisotropies in the Sun-centered frame by incorporating boost corrections in the analysis. Consider, for example, the $1S$-$2S$ transition. Using the expression (38), the frequency shift $\delta\nu$ due to Lorentz and *CPT* violation in the laboratory frame can be converted to the Sun-centered frame, giving

$$2\pi\delta\nu = 2\pi\delta\nu^{\rm Sun} + \sum_{wd} V_w^{(d)J} (\boldsymbol{\beta}_\oplus + \boldsymbol{\beta}_{\boldsymbol{L}})^J. \qquad (63)$$

The first term on the right-hand side is the constant shift discussed in Sec. III C 2. The second term is suppressed by boost factors but offers interesting prospects for measuring anisotropic coefficients in the Sun-centered frame. Analogous results for other transitions can also be obtained.

The boost factors in Eq. (63) generate time variations in the $1S$-$2S$ frequency. The dependence of $\delta\nu$ on the Earth's velocity $\boldsymbol{\beta}_\oplus$ introduces annual variations given by

$$V_w^{(d)J}\beta_\oplus^J = \beta_\oplus[\sin\Omega_\oplus T V_w^{(d)X} - \cos\Omega_\oplus T(\cos\eta V_w^{(d)Y} + \sin\eta V_w^{(d)Z})], \qquad (64)$$

where $\Omega_\oplus$ is the Earth orbital frequency. The dependence on the laboratory velocity $\boldsymbol{\beta}_{\boldsymbol{L}}$ produces sidereal variations, given by

$$V_w^{(d)J}\beta_L^J = \beta_L(\cos\omega_\oplus T_\oplus V_w^{(d)Y} - \sin\omega_\oplus T_\oplus V_w^{(d)X}), \qquad (65)$$

where $\omega_\oplus$ is the Earth sidereal frequency.

Table V provides explicit expressions for $V_w^{(d)J}$ with $5 \le d \le 8$ in terms of the rest masses m_w of the particles of flavor $w = e$ and $w = p$, the fine-structure constant α, the reduced mass $m_{\rm r}$ of the system, and the effective Cartesian coefficients for Lorentz violation defined in Eq. (27) of Ref. [37]. Only leading-order contributions from each coefficient are included. Note that all the spin-independent minimal coefficients leave unaffected the $1S$-$2S$ frequency at leading order in the nonrelativistic limit [13,29], so both $V_w^{(3)J}$ and $V_w^{(4)J}$ vanish at this order.

Studies at subleading nonrelativistic order are also of interest. For example, an experimental search for annual variations of the $1S$-$2S$ transition frequency has been used to measure the coefficients $c_e^{(TJ)}$ in the minimal SME to parts in 10^{11} [18]. We can reinterpret the results in terms of the nonrelativistic coefficients and thereby extract first measurements of a variety of nonminimal coefficients. At this order, the restriction of $V_w^{(4)J}$ to the coefficients $c_e^{(TJ)}$ in the electron sector of the minimal SME gives

$$\sum_{wd} V_w^{(d)J} = \frac{5}{4}\alpha^2 m_e c_e^{(TJ)}. \qquad (66)$$

Adopting this relation, the results in Eq. (4) of Ref. [18] generalize to

$$\sum_{wd} V_w^{(d)X} = -(5.3 \pm 3.2) \times 10^{-19}\ \text{GeV} \qquad (67)$$

and

TABLE V. Values of the vectors $V_w^{(d)J}$ in Eq. (63) for the electron and proton in atomic hydrogen with $5 \le d \le 8$.

d	$V_w^{(d)J}$
5	$\frac{3}{4}(\alpha m_{\rm r})^2(2a_{w\rm eff}^{(5)TTJ} + a_{w\rm eff}^{(5)KKJ})$
6	$-3(\alpha m_{\rm r})^2 m_w(c_{w\rm eff}^{(6)TTTJ} + c_{w\rm eff}^{(6)TKKJ})$
7	$\frac{5}{2}(\alpha m_{\rm r})^2 m_w^2(2a_{w\rm eff}^{(7)TTTTJ} + 3a_{w\rm eff}^{(7)TTKKJ}) + \frac{67}{16}(\alpha m_{\rm r})^4 a_{w\rm eff}^{(7)KKLLJ}$
8	$-\frac{15}{2}(\alpha m_{\rm r})^2 m_w^3(c_{w\rm eff}^{(8)TTTTTJ} + 2c_{w\rm eff}^{(8)TTTKKJ}) - \frac{201}{8}(\alpha m_{\rm r})^4 m_w c_{w\rm eff}^{(8)TKKLLJ}$

TABLE VI. Sensitivities to the absolute value of nonminimal cartesian coefficients for $5 \leq d \leq 8$ from Eqs. (67) and (68).

Coefficient $\mathcal{K}_{\text{eff}}^{(d)\nu\mu_1\ldots\mu_{d-3}}$	J	Electron (GeV^{4-d})	Proton (GeV^{4-d})
$a_{\text{eff}}^{(5)TTJ}$	X	$<3.4 \times 10^{-8}$	$<3.4 \times 10^{-8}$
	Y	$<5.6 \times 10^{-8}$	$<5.6 \times 10^{-8}$
	Z	$<1.3 \times 10^{-7}$	$<1.3 \times 10^{-7}$
$a_{\text{eff}}^{(5)KKJ}$	X	$<6.7 \times 10^{-8}$	$<6.7 \times 10^{-8}$
	Y	$<1.1 \times 10^{-7}$	$<1.1 \times 10^{-7}$
	Z	$<2.5 \times 10^{-7}$	$<2.5 \times 10^{-7}$
$c_{\text{eff}}^{(6)TTTJ}$	X	$<3.3 \times 10^{-5}$	$<1.8 \times 10^{-8}$
	Y	$<5.5 \times 10^{-5}$	$<3.0 \times 10^{-8}$
	Z	$<1.3 \times 10^{-4}$	$<6.9 \times 10^{-8}$
$c_{\text{eff}}^{(6)TKKJ}$	X	$<3.3 \times 10^{-5}$	$<1.8 \times 10^{-8}$
	Y	$<5.5 \times 10^{-5}$	$<3.0 \times 10^{-8}$
	Z	$<1.3 \times 10^{-4}$	$<6.9 \times 10^{-8}$
$a_{\text{eff}}^{(7)TTTTJ}$	X	$<3.9 \times 10^{-2}$	$<1.1 \times 10^{-8}$
	Y	$<6.5 \times 10^{-2}$	$<1.9 \times 10^{-8}$
	Z	<0.15	$<4.4 \times 10^{-8}$
$a_{\text{eff}}^{(7)TTKKJ}$	X	$<2.6 \times 10^{-2}$	$<7.6 \times 10^{-9}$
	Y	$<4.3 \times 10^{-2}$	$<1.3 \times 10^{-8}$
	Z	<0.1	$<2.9 \times 10^{-8}$
$a_{\text{eff}}^{(7)KKLLJ}$	X	$<8.7 \times 10^{2}$	$<8.7 \times 10^{2}$
	Y	$<1.5 \times 10^{3}$	$<1.5 \times 10^{3}$
	Z	$<3.4 \times 10^{3}$	$<3.4 \times 10^{3}$
$c_{\text{eff}}^{(8)TTTTTJ}$	X	<51	$<8.1 \times 10^{-9}$
	Y	<85	$<1.4 \times 10^{-8}$
	Z	$<2.0 \times 10^{2}$	$<3.1 \times 10^{-8}$
$c_{\text{eff}}^{(8)TTTKKJ}$	X	<25	$<4.1 \times 10^{-9}$
	Y	<43	$<6.8 \times 10^{-9}$
	Z	<98	$<1.6 \times 10^{-8}$
$c_{\text{eff}}^{(8)TKKLLJ}$	X	$<2.8 \times 10^{5}$	$<1.5 \times 10^{2}$
	Y	$<4.7 \times 10^{5}$	$<2.6 \times 10^{2}$
	Z	$<1.1 \times 10^{6}$	$<6.0 \times 10^{2}$

$$\sum_{wd}(2.3V_w^{(d)Y} + V_w^{(d)Z}) = -(1.1 \pm 2.3) \times 10^{-18}\ \text{GeV}. \tag{68}$$

We can now use the results in Table V to extract attained sensitivities to nonminimal Cartesian coefficients in the electron and proton sectors. Table VI displays the resulting sensitivities to the absolute values of Cartesian a- and c-type coefficients for $5 \leq d \leq 8$. As before, we adopt the standard assumption that only one coefficient is nonzero at a time. The first column of this table lists the Cartesian coefficient and the second column its component. The third and fourth columns contain the resulting constraints in the electron and proton sectors, respectively.

In contrast to tests using annual variations, sidereal-variation studies of the $1S$-$2S$ transition remain unexplored to date. While this type of experiment is expected to be about 2 orders of magnitude less sensitive to the vectors $V_w^{(d)J}$, different combinations of coefficients for Lorentz and CPT violation are involved. Pursuing this possibility remains an interesting open avenue for future research.

D. $nS_{1/2}$-$n'P_{3/2}$ and $nS_{1/2}$-$n'D$ transitions

The interest in improving the experimental values of the Rydberg constant and the proton radius has spurred the development of high-precision spectroscopy with atomic hydrogen. Experiments have measured or plan to study the transitions $2S_{1/2}$-$nP_{3/2}$ [64–67], $1S_{1/2}$-$3D$ [68], and $2S_{1/2}$-nD [61–63,69]. The absolute uncertainties achieved for the corresponding frequencies are typically in the 10 kHz range, reaching values as low as about 1 kHz in some cases [58].

In the context of searching for Lorentz and CPT violation, the sensitivities of these measurements to the nonrelativistic spherical coefficients with $j = 0$ and $j = 1$ are weaker than those from hyperfine Zeeman and $1S$-$2S$ transitions. However, a glance at Table I reveals that the involvement in a transition of a level with $J \geq 3/2$ or $F \geq 3/2$ means that nonrelativistic spherical coefficients with $j \geq 2$ can be measured. For example, a transition to a state nD with $F = 3$ could be sensitive to all the coefficients with $k \leq 4$ contributing to the matrix element (18). The $nS_{1/2}$-$n'P_{3/2}$ and $nS_{1/2}$-$n'D$ transitions therefore offer excellent prospects for studying certain effects from Lorentz and CPT violation that otherwise are difficult to observe.

The Lorentz-violating perturbative corrections to a specific frequency of interest depend on the particular details of the experiment. For example, the magnitudes of applied fields and the nature of the measurement need to be considered to obtain expressions for the corrections. For an experiment sensitive to the hyperfine structure with the hyperfine energy dominating all perturbations, the Lorentz-violating corrections may be obtained from the matrix elements (18). Comparatively simple expressions can be obtained in some cases, as illustrated for a weak applied magnetic field in Sec. II D. In this scenario, the signals for Lorentz and CPT violation are similar to those discussed in previous sections of this work, including sidereal and annual variations of the measured frequency.

For definiteness and simplicity, we limit our attention here to the scenario with a weak applied magnetic field. The analysis of experiments with more involved configurations, which can often include large applied Zeeman or Stark fields, is of substantial interest but lies outside our present scope. Nonetheless, the discussion here demonstrates the potential for discovery in these types of experiments and serves to motivate future investigations of Lorentz- and CPT-violating signals using other experimental configurations.

High-precision spectroscopy of atomic hydrogen typically concerns transitions involving the $1S$ ground state or the metastable $2S$ state. The Lorentz- and *CPT*-violating corrections to these levels have been discussed in previous subsections, so the discussion here focuses on the energy corrections to the $nP_{3/2}$ and nD states. The nonrelativistic spherical coefficients that can contribute to the corrections are displayed in Table I. In the Sun-centered frame and at zeroth order in the boost, the explicit form of the energy corrections in the presence of a weak magnetic field is given by Eq. (35). The weights $A^{\mathrm{Sun}}_{jm}(nFJL)$ are specified by the result (19) with the factors $\Lambda^{(qP)}_{j}$ given for $J \leq 5/2$ in Table II, while the expectation values $\langle |\boldsymbol{p}|^k \rangle_{nL}$ are provided in Eq. (15).

The expression (35) displays the sidereal variations in the energy shifts. Any nonrelativistic spherical coefficient $\mathcal{K}^{\mathrm{NR}}_{kjm}$ contributing to the shift introduces oscillations at the mth harmonic of the sidereal frequency $\omega_\oplus$. The allowed harmonics are determined by J and F, as described in Sec. II D 1. As an explicit example, consider a transition to a state $nD^{F=2}_{5/2}$. Table I shows that contributions arise from spin-independent terms with $j = 0, 2, 4$ and spin-dependent ones with $j = 1, 3$. We therefore can expect variations up to the fourth harmonic of the sidereal frequency. The first harmonic receives contributions from coefficients with $1 \leq j \leq 4$, the second from $2 \leq j \leq 4$, the third from $3 \leq j \leq 4$, and the fourth only from $j = 4$. Table I also shows the relation between the k and j indices. For example, only coefficients with $k \geq 4$ can contribute to the fourth harmonic.

Using this information, we can form estimates of the potential sensitivities to nonrelativistic coefficients from searches for sidereal variations in $nS_{1/2}$-$n'P_{3/2}$ and $nS_{1/2}$-$n'D$ transitions. Table VII provides the results obtained under the assumption that the absolute experimental uncertainty for these variations is 10 kHz. The first column of the table displays the relevant nonrelativistics spherical coefficients, generically denoted as $\mathcal{K}^{\mathrm{NR}}_{kjm}$. The second column shows the range of $K \equiv J, F$ for the relevant transitions. The third column presents the values of nL^F_J for the excited energy levels used in obtaining the specific estimates. The smallest value of n producing contributions is chosen for these levels, as an experiment with fixed absolute uncertainty is less sensitive to coefficients with $k \neq 0$ and larger n. The final column lists the potential sensitivities to the moduli of the real and imaginary parts of the coefficients taken one at a time, derived with values of m_F and χ chosen to maximize the sensitivity. Note that the coefficients shown in Table VII remain unmeasured in any experiments to date. Note also that sensitivity to both electron and proton coefficients is achieved despite the mass difference between the particles, which can be traced to their equal but opposite angular momenta.

TABLE VII. Potential sensitivities from sidereal variations to the moduli of the real and imaginary parts of electron and proton nonrelativistic coefficients in Table I.

$\mathcal{K}^{\mathrm{NR}}_{kjm}$	K values	nL^F_J	Sensitivity
a^{NR}_{22m}, c^{NR}_{22m}	$J \geq 3/2$	$2P^2_{3/2}$	6×10^{-8} GeV^{-1}
$H^{\mathrm{NR}(0B)}_{23m}$, $g^{\mathrm{NR}(0B)}_{23m}$	$F \geq 2$	$2P^2_{3/2}$	2×10^{-7} GeV^{-1}
$H^{\mathrm{NR}(1B)}_{23m}$, $g^{\mathrm{NR}(1B)}_{23m}$	$F \geq 2$	$2P^2_{3/2}$	1×10^{-7} GeV^{-1}
a^{NR}_{42m}, c^{NR}_{42m}	$J \geq 3/2$	$2P^2_{3/2}$	7×10^{3} GeV^{-3}
$H^{\mathrm{NR}(0B)}_{43m}$, $g^{\mathrm{NR}(0B)}_{43m}$	$F \geq 2$	$2P^2_{3/2}$	2×10^{4} GeV^{-3}
$H^{\mathrm{NR}(1B)}_{43m}$, $g^{\mathrm{NR}(1B)}_{43m}$	$F \geq 2$	$2P^2_{3/2}$	1×10^{4} GeV^{-3}
a^{NR}_{44m}, c^{NR}_{44m}	$J \geq 5/2$	$3D^3_{5/2}$	7×10^{4} GeV^{-3}
$H^{\mathrm{NR}(0B)}_{45m}$, $g^{\mathrm{NR}(0B)}_{45m}$	$F \geq 3$	$3D^3_{5/2}$	7×10^{4} GeV^{-3}
$H^{\mathrm{NR}(1B)}_{45m}$, $g^{\mathrm{NR}(1B)}_{45m}$	$F \geq 3$	$3D^3_{5/2}$	3×10^{4} GeV^{-3}

IV. ANTIHYDROGEN

The techniques developed in the previous sections to search for Lorentz and *CPT* violation using spectroscopy of atomic hydrogen can also be applied to other hydrogenic systems. In this section, we turn our attention to the emerging field of antihydrogen spectroscopy. A number of collaborations have as goal the precision spectroscopy of antihydrogen, including the Antihydrogen Laser Physics Apparatus (ALPHA) Collaboration [19], the Atomic Spectroscopy and Collisions Using Slow Antiprotons (ASACUSA) Collaboration [20], and the Antihydrogen Trap (ATRAP) Collaboration [21]. Several studies of the gravitational response of antihydrogen are under development, including ones by the Antihydrogen Experiment: Gravity, Interferometry, Spectroscopy (AEGIS) Collaboration [70], the ALPHA Collaboration [71], and the Gravitational Behavior of Antihydrogen at Rest (GBAR) Collaboration [72]. A proposal for an antimatter gravity experiment (AGE) also exists [73].

Since *CPT* violation in realistic effective field theory necessarily comes with Lorentz violation [8,10], which implies the breaking of rotation and boost symmetry, a natural question to ask is whether experiments with antihydrogen spectroscopy can attain sensitivities to new physics that is inaccessible or impractical to access with experiments using rotated or boosted ordinary matter. The answer is affirmative, as might intuitively be expected. Indeed, the form of Eq. (6) already reveals that coefficients for Lorentz violation for a given species always appear in summed pairs, one controlling *CPT*-odd and one *CPT*-even operators, and this feature holds in the full relativistic theory as well [37]. As a result, experiments with strictly nonrelativistic electrons or protons in any combination cannot explore the full parameter space for the coefficients and hence cannot study the full range of possible physical effects. For example, although the individual nonrelativistic spherical coefficients modifying the antihydrogen spectrum

are the same as those for hydrogen listed in Table I, the nonrelativistic spectral modifications involve disparate coefficient combinations and so experiments on both are necessary to discern the relevant CPT-violating physics. Situations can even be envisaged in which no effect exists in nonrelativistic hydrogen but a large signal occurs in antihydrogen, such as the isotropic invisible model discussed in Sec. IX B of Ref. [86], which allows comparatively large effects in the antihydrogen hyperfine structure while damping those in hydrogen.

In principle, high-precision experiments with heavily boosted electrons and protons offer additional options for a complete coverage of possible effects because the combinations $\mathcal{V}^{\mathrm{NR}}_{wkjm}$ and $\mathcal{T}^{\mathrm{NR}(qP)}_{wkjm}$ in Eq. (6) involve coefficients of different dimensions accompanied by distinct momentum dependences. However, precision measurements involving significant boosts come with additional experimental challenges. Typical analyses take advantage of the comparatively small boost $\sim 10^{-4}$ due to the Earth's orbital motion [18,49,52]. In this scenario, for example, the dominant sensitivities to nonminimal coefficients available to antihydrogen spectroscopy are enhanced by about 8 orders of magnitude relative to those of hydrogen spectroscopy using annual variations due to the parity selection rules described in Sec. II D 2. In practice, a comprehensive search for Lorentz and CPT violation therefore requires performing experiments with positrons and antiprotons in various combinations as well.

Among studies of Lorentz and CPT symmetry using positrons and antiprotons, antihydrogen has distinctive sensitivity due to its intrinsic spherical symmetry and flavor content. The symmetries of other experiments, such as the cylindrical symmetry of ones trapping and studying individual positrons or antiprotons in Penning traps [74–78], make them sensitive to different sets of coefficients and thus different physical effects [79]. Positronium and protonium do have spherical symmetry but involve C-invariant particle-antiparticle combinations of only one flavor and hence also have distinct physical sensitivities. Moreover, other intrinsic factors can enhance the difference between various types of experiments. For example, certain coefficients for Lorentz and CPT violation are accompanied by factors of the particle momentum, which is about $m_e\alpha \simeq 3.7$ keV for antihydrogen but differs in other types of experiments. In short, spectroscopy of antihydrogen represents a unique tool to probe Lorentz and CPT violation, and one that is essential for the definitive and unambiguous detection of CPT violation involving the nonrelativistic spherical coefficients considered in this work.

In this section, we begin with a description of the implementation of the CPT transformation on the hydrogen spectrum. We then address the effects of nonminimal coefficients on hyperfine and $1S$-$2S$ transitions. Finally, we offer some comments on experiments testing the gravitational response of antihydrogen.

A. Basics

The form of the leading-order Lorentz- and CPT-violating perturbation $\delta h^{\mathrm{NR}}_{\bar{\mathrm{H}}}$ to the nonrelativistic Hamiltonian for free antihydrogen is similar to that for hydrogen,

$$\delta h^{\mathrm{NR}}_{\bar{\mathrm{H}}} = \delta h^{\mathrm{NR}}_{\bar{e}} + \delta h^{\mathrm{NR}}_{\bar{p}}, \tag{69}$$

involving the sum of perturbative contributions from the positron $\bar{e} \equiv e^+$ and the antiproton $\bar{p}$. The individual perturbations are given by expressions similar to Eqs. (3)–(5) for hydrogen,

$$\delta h^{\mathrm{NR}}_{\bar{w}} = h_{\bar{w}0} + h_{\bar{w}r}\boldsymbol{\sigma}\cdot\hat{\boldsymbol{\epsilon}}_r + h_{\bar{w}+}\boldsymbol{\sigma}\cdot\hat{\boldsymbol{\epsilon}}_- + h_{\bar{w}-}\boldsymbol{\sigma}\cdot\hat{\boldsymbol{\epsilon}}_+, \tag{70}$$

where $\bar{w}$ represents either $\bar{e}$ or $\bar{p}$. The spin-independent term is

$$h_{\bar{w}0} = -\sum_{kjm} |\boldsymbol{p}|^k {}_0Y_{jm}(\hat{\boldsymbol{p}})\mathcal{V}^{\mathrm{NR}}_{\bar{w}kjm}, \tag{71}$$

while the spin-dependent ones are

$$\begin{aligned} h_{\bar{w}r} &= -\sum_{kjm} |\boldsymbol{p}|^k {}_0Y_{jm}(\hat{\boldsymbol{p}})\mathcal{T}^{\mathrm{NR}(0B)}_{\bar{w}kjm}, \\ h_{\bar{w}\pm} &= \sum_{kjm} |\boldsymbol{p}|^k {}_{\pm1}Y_{jm}(\hat{\boldsymbol{p}})(i\mathcal{T}^{\mathrm{NR}(1E)}_{\bar{w}kjm} \pm \mathcal{T}^{\mathrm{NR}(1B)}_{\bar{w}kjm}). \end{aligned} \tag{72}$$

In these equations, the quantities $\mathcal{V}^{\mathrm{NR}}_{\bar{w}kjm}$ and $\mathcal{T}^{\mathrm{NR}(qP)}_{\bar{w}kjm}$ are CPT-transformed versions of those given for hydrogen in Eq. (6),

$$\begin{aligned} \mathcal{V}^{\mathrm{NR}}_{\bar{w}kjm} &= c^{\mathrm{NR}}_{wkjm} + a^{\mathrm{NR}}_{wkjm}, \\ \mathcal{T}^{\mathrm{NR}(qP)}_{\bar{w}kjm} &= -g^{\mathrm{NR}(qP)}_{wkjm} - H^{\mathrm{NR}(qP)}_{wkjm}. \end{aligned} \tag{73}$$

These expressions include operators of arbitrary mass dimension d. When restricted to the minimal-SME coefficients, the above equations reduce to those used in the previous literature on CPT violation in antihydrogen [13].

The physical effects of Lorentz and CPT violation in antihydrogen are determined by the matrix elements of $\delta h^{\mathrm{NR}}_{\bar{\mathrm{H}}}$ in the unperturbed states. The coefficient selection rules for hydrogen presented in Sec. II B are valid for antihydrogen, and in particular the nonrelativistic spherical coefficients contributing to modify the antihydrogen spectrum are those listed in Table I. The methods used in Sec. II C to derive the matrix elements for hydrogen can also be applied, but the corrections to the antihydrogen spectrum must be obtained by performing a CPT transformation on the hydrogen matrix elements. This involves both using the antihydrogen perturbative Hamiltonian $\delta h^{\mathrm{NR}}_{\bar{\mathrm{H}}}$ and the antihydrogen states, which are CPT transformations of the hydrogen ones. Specifically, the CPT counterpart of an energy state $|nFJLm_F\rangle$ in hydrogen is the state

$|nFJL(-m_F)\rangle$ in antihydrogen, as the net result of the *CPT* transformation is to replace the atom with the antiatom and to invert the direction of the total angular momentum F.

To illustrate the idea, consider the antihydrogen energy shift $\delta\bar{\epsilon}(nFJLm_F)$ in the presence of a weak uniform magnetic field. For hydrogen, the energy shift $\delta\epsilon(nFJLm_F)$ of the Zeeman levels is provided by Eq. (33). For antihydrogen, noting that the uniform magnetic field and the magnetic dipole moment are both invariant under *CPT*, we find instead

$$\begin{aligned}\delta\bar{\epsilon}(nFJLm_F) &= \sum_j \bar{A}_{j0}(nFJL)\langle F(-m_F)j0|F(-m_F)\rangle \\ &= \sum_j (-1)^j \bar{A}_{j0}(nFJL)\langle Fm_F j0|Fm_F\rangle, \quad (74)\end{aligned}$$

where the weights $\bar{A}_{j0}$ are given by Eq. (19) with the replacement $w \to \bar{w}$ throughout. In the second line, we have used the Wigner-Eckart theorem and the properties of the Clebsch-Gordan coefficients. As shown in Sec. II B, the weights A_{jm} can acquire contributions for even j only from coefficients associated with spin-independent operators and for odd j only from coefficients associated with spin-dependent operators. This reveals a simple relationship between the shifts of the hydrogen and antihydrogen spectra: given the expression for the shift in a hydrogen energy level, the shift of the corresponding antihydrogen level is obtained by implementing the replacements

$$a_{wkjm}^{\mathrm{NR}} \to -a_{wkjm}^{\mathrm{NR}}, \qquad H_{wkjm}^{\mathrm{NR}(qP)} \to -H_{wkjm}^{\mathrm{NR}(qP)}. \quad (75)$$

Comparing this rule to the operator transformations listed in Table I, we infer that the antihydrogen spectral shifts can be obtained by charge conjugation of the hydrogen ones. This result extends the minimal-SME result obtained in Ref. [13].

The reader is cautioned that the spectral map (75) is a formal statement of correspondence between energy levels, which depends on the labeling of the states. In the above example, the spectra are described using the orientation of the total angular momentum relative to the applied magnetic field, which is a C-invariant notion. If instead the spectra are described using the orientation of the magnetic moment relative to the magnetic field, which is a *CPT*-invariant notion, then the two spectra would be related by a *CPT* transformation. Moreover, the spectral map is distinct from observable quantities such as frequency differences, which in practical scenarios may depend on other factors. For instance, magnetically trapped states in hydrogen have opposite values of m_F from those in antihydrogen, so frequency comparisons of trapped atoms and antiatoms amount to measuring the effect of the *CPT* replacements

$$a_{wkjm}^{\mathrm{NR}} \to -a_{wkjm}^{\mathrm{NR}}, \qquad g_{wkjm}^{\mathrm{NR}(qP)} \to -g_{wkjm}^{\mathrm{NR}(qP)} \quad (76)$$

instead of the C replacements (75). This is intuitively reasonable for tests of the *CPT* theorem, which specifically concerns invariance under *CPT* transformations but makes no statement about invariance under C transformations.

B. Hyperfine transitions

The application of a comparatively weak external magnetic field to antihydrogen splits the two $1S_{1/2}$ levels into four distinct hyperfine Zeeman sublevels, one with $F = 0$ and three with $F = 1$. These splittings can be in principle be studied experimentally. For example, the ASACUSA collaboration plans to measure the corresponding hyperfine transitions using an ultracold beam of antihydrogen atoms [80]. For simplicity, we neglect any boost effects in what follows, and we work in the strict Zeeman or Paschen-Back regimes so that the magnetic mixing of states in intermediate regimes can be neglected. Extensions of the results below to include these more general cases are possible and may be of interest for some future applications but lie beyond our present scope.

The Lorentz- and *CPT*-violating shifts in the antihydrogen energies can be found from the expression (48) for hydrogen by implementing the coefficient map (75). The resulting hyperfine frequency shifts $2\pi\delta\bar{\nu}$ for transitions with a given Δm_F take the form

$$\begin{aligned}2\pi\delta\bar{\nu} = &-\frac{\Delta m_F}{2\sqrt{3\pi}}\sum_{q=0}^{2}(\alpha m_r)^{2q}(1+4\delta_{q2}) \\ &\times \sum_w [g_{w(2q)10}^{\mathrm{NR}(0B)} + H_{w(2q)10}^{\mathrm{NR}(0B)} + 2g_{w(2q)10}^{\mathrm{NR}(1B)} \\ &+ 2H_{w(2q)10}^{\mathrm{NR}(1B)}] \quad (77)\end{aligned}$$

in the laboratory frame. In the minimal-SME limit, the combination of nonrelativistic spherical coefficients appearing in this expression reduces to minimal Cartesian coefficients according to

$$\begin{aligned}&g_{w010}^{\mathrm{NR}(0B)} + 2g_{w010}^{\mathrm{NR}(1B)} + H_{w010}^{\mathrm{NR}(0B)} + 2H_{w010}^{\mathrm{NR}(1B)} \\ &\quad \to 2\sqrt{3\pi}[b_3^w + m_w d_{30}^w + H_{12}^w - m_w g_3^{w(A)} + m_w g_{120}^{w(M)}], \quad (78)\end{aligned}$$

where the superscripts (A) and (M) denote the irreducible axial and irreducible mixed-symmetry combinations of the coefficients $g_{\kappa\lambda\nu}^w$, respectively [81,82]. The result (77) therefore reproduces and extends the minimal-SME expression obtained in Ref. [13] under the assumption that only the Cartesian coefficients b_μ^w, $d_{\mu\nu}^w$, and $H_{\mu\nu}^w$ are nonzero, with the g-type coefficients set to zero in accordance with their expected additional suppression due to the breaking of the electroweak $\mathrm{SU}(2) \times \mathrm{U}(1)$ symmetry [8].

The laboratory-frame coefficients appearing in Eq. (77) are time dependent by virtue of the rotation of the Earth and

its revolution about the Sun. As a result, all the signals for Lorentz and CPT violation discussed for hydrogen in Sec. III B have counterparts in antihydrogen experiments. The measured hyperfine Zeeman frequencies in antihydrogen can exhibit sidereal and annual time variations and can be sensitive to the orientation of the magnetic field and the colatitude of the laboratory. For example, at zeroth boost order, the relation between the coefficients in the laboratory and Sun-centered frames is given by Eq. (51), revealing that the frequency shifts $\delta\bar{\nu}$ undergo sidereal variations at the Earth's rotation frequency $\omega_\oplus$.

In addition to searching for the above hyperfine Zeeman signals of Lorentz and CPT violation in antihydrogen alone, interesting prospects for focusing specifically on CPT violation are offered by direct comparisons of measurements with hydrogen and antihydrogen. Note that some caution is required in performing these comparisons, as differences between hydrogen and antihydrogen involving only CPT-even effects can appear unless the assorted time variations and orientation and colatitude dependences are carefully incorporated in the analysis.

As an illustration of a direct comparison, consider the hyperfine Zeeman frequency difference between hydrogen and antihydrogen for transitions with $\Delta m_F = 1$, which in the presence of CPT violation is given by

$$2\pi\Delta\nu \equiv 2\pi\delta\nu - 2\pi\delta\bar{\nu} = -\frac{1}{\sqrt{3\pi}}\sum_{q=0}^{2}(\alpha m_{\rm r})^{2q}(1+4\delta_{q2}) \times \sum_w (g_{w(2q)10}^{\rm NR(0B)} + 2g_{w(2q)10}^{\rm NR(1B)}). \tag{79}$$

This expression depends only on coefficients controlling CPT-odd operators in the perturbation Hamiltonians for hydrogen and antihydrogen. In the minimal-SME limit, this result reduces to

$$\Delta\nu \to -\frac{1}{\pi}(b_3^e - m_e g_3^{e(A)} + m_e g_{120}^{e(M)} + b_3^p - m_p g_3^{p(A)} + m_p g_{120}^{p(M)}), \tag{80}$$

which extends the result presented in Ref. [13] to include g-type coefficients. Note that the result (79) is expressed in the laboratory frame and therefore still generically depends on time. For example, time variations at the Earth's sidereal frequency are given by converting the coefficients to the Sun-centered frame using Eq. (51). This reveals that only the g-type components involving Sun-frame coefficients with $kjm = 010$, 210, and 410 are associated with signals independent of sidereal time.

Studies of the antihydrogen spectrum in the presence of a strong external magnetic field are also of experimental interest. For example, the ALPHA and ATRAP collaborations plan to perform spectroscopy on antihydrogen trapped in the Paschen-Back limit of strong fields [83,84].

For the Paschen-Back splitting of the $1S_{1/2}$ levels, the total angular momentum F is no longer a good quantum number. Instead, the states can be labeled by the spins $S_{\bar{e}} = \pm 1/2$ and $S_{\bar{p}} = \pm 1/2$ of the positron and antiproton, respectively. Incorporating perturbative Lorentz and CPT violation as before, the hyperfine Paschen-Back frequency shifts $\delta\bar{\nu}$ for given ΔS_w in antihydrogen are found to be

$$2\pi\delta\bar{\nu} = -\frac{1}{\sqrt{3\pi}}\sum_{q=0}^{2}(\alpha m_{\rm r})^{2q}(1+4\delta_{q2}) \times \sum_w \Delta S_w [g_{w(2q)10}^{\rm NR(0B)} + H_{w(2q)10}^{\rm NR(0B)} + 2g_{w(2q)10}^{\rm NR(1B)} + 2H_{w(2q)10}^{\rm NR(1B)}] \tag{81}$$

in the laboratory frame. This agrees with the minimal-SME result in Ref. [13] in the appropriate limit.

Converting the coefficients to the Sun-centered frame leads to antihydrogen frequency signals similar to those in the Zeeman limit, including sidereal and annual time variations and dependences on the magnetic-field orientation and laboratory colatitude. A significant difference between the Zeeman shift (77) and the Paschen-Back shift (81) is the lack of sensitivity of the latter to coefficients of one flavor in certain transitions, depending on the specific values of $S_{\bar{e}}$ and $S_{\bar{p}}$. For example, the frequency difference $\Delta\nu_{c\to d} \equiv \delta\nu_{c\to d} - \delta\bar{\nu}_{c\to d}$ for the transition $|c\rangle \to |d\rangle$ essentially involves a proton spin flip because $|c\rangle$ contains highly polarized electron and proton spins with $m_{S_e} = 1/2$ and $m_{S_p} = -1/2$. We find

$$\Delta\nu_{c\to d} = -\frac{1}{\sqrt{3\pi}}\sum_{q=0}^{2}(\alpha m_{\rm r})^{2q}(1+4\delta_{q2}) \times (g_{p(2q)10}^{\rm NR(0B)} + 2g_{p(2q)10}^{\rm NR(1B)}). \tag{82}$$

This reduces in the minimal-SME limit to

$$\Delta\nu_{c\to d} \to -\frac{2}{\pi}(b_3^p - m_p g^{p(A)}{}_3 + m_p g^{p(M)}{}_{120}), \tag{83}$$

in agreement with and extending the result found in Ref. [13].

C. $1S$-$2S$ and $nL_{1/2}$-$n'L'_{1/2}$ transitions

In searching for CPT violation in the minimal SME, hyperfine spectroscopy of antihydrogen has a theoretical advantage over optical spectroscopy because the $1S$-$2S$ transition is insensitive to minimal-SME coefficients in free antihydrogen and exhibits only suppressed sensitivity in magnetically trapped antihydrogen [13]. Here, we show this situation changes for nonminimal operators: optical

spectroscopy offers access to nonminimal SME coefficients with unsuppressed sensitivity. Moreover, some of these coefficients are inaccessible to hyperfine spectroscopy.

The derivation of the relevant spectral shifts for free antihydrogen parallels the one for free hydrogen outlined in Sec. III C. Restricting our attention to isotropic effects as in the hydrogen case, we find that any antihydrogen transition $nL\text{-}n'L'$ with $J = 1/2$, $\Delta J = 0$ experiences a frequency shift $\delta\bar{\nu}$ due to Lorentz and *CPT* violation given in the laboratory frame by

$$2\pi\delta\bar{\nu} = 2m_r(\varepsilon_n - \varepsilon_{n'})\sum_w (\overset{\circ}{a}{}^{\rm NR}_{w,2} + \overset{\circ}{c}{}^{\rm NR}_{w,2}) - 4m_r^2\left[\varepsilon_n^2\left(\frac{8n}{2L+1} - 3\right) - \varepsilon_{n'}^2\left(\frac{8n'}{2L'+1} - 3\right)\right] \times \sum_w (\overset{\circ}{a}{}^{\rm NR}_{w,4} + \overset{\circ}{c}{}^{\rm NR}_{w,4}), \quad (84)$$

where $\varepsilon_n \equiv -\alpha^2 m_r/2n^2$. Note that this result contains only contributions with $k \geq 2$, confirming the absence of unsuppressed effects from the minimal SME [13]. In contrast, the nonminimal coefficients carry negative mass dimensions and so appear accompanied by powers of the relativistic energy of the states. For frequencies, this involves the relativistic energy difference between two levels and hence at leading order a nonzero contribution proportional to powers of the particle masses.

Converting this expression to the Sun-centered frame introduces sidereal and annual variations along with dependences on the orientation of the magnetic field and the laboratory colatitude. In principle, all the types of searches for Lorentz and *CPT* violation discussed in the hydrogen context in Secs. III C and III D are of interest in the antihydrogen context as well. In addition, direct comparisons of results for hydrogen and antihydrogen could permit the extraction of clean constraints on coefficients for *CPT* violation. This includes not only coefficients entering the $1S\text{-}2S$ transition but also coefficients involved with high-J levels, thereby providing access to coefficients with large values of j that are inaccessible to hyperfine spectroscopy.

As an example of a direct comparison between hydrogen and antihydrogen, consider the isotropic coefficients generating frequency shifts for the $1S\text{-}2S$ transition. The shift for antihydrogen is given by

$$2\pi\delta\bar{\nu}_{1S2S} = \frac{3}{4}(\alpha m_r)^2\sum_w (\overset{\circ}{a}{}^{\rm NR}_{w,2} + \overset{\circ}{c}{}^{\rm NR}_{w,2}) + \frac{67}{16}(\alpha m_r)^4\sum_w (\overset{\circ}{a}{}^{\rm NR}_{w,4} + \overset{\circ}{c}{}^{\rm NR}_{w,4}). \quad (85)$$

The frequency difference $\Delta\bar{\nu}_{1S2S} \equiv \delta\nu_{1S2S} - \delta\bar{\nu}_{1S2S}$ between the $1S\text{-}2S$ transitions in hydrogen and antihydrogen is therefore

$$\Delta\bar{\nu}_{1S2S} = -\frac{1}{8\pi}\sum_w [12(\alpha m_r)^2 \overset{\circ}{a}{}^{\rm NR}_{w,2} + 67(\alpha m_r)^4 \overset{\circ}{a}{}^{\rm NR}_{w,4}]. \quad (86)$$

This permits a clean measurement of isotropic *CPT*-violating effects with unsuppressed signals in the comparison between trapped atoms and antiatoms. If attained, an absolute uncertainty of 1 Hz in the $1S\text{-}2S$ transition for both hydrogen and antihydrogen would yield constraints of order 10^{-12} GeV^{-1} on the coefficients $\overset{\circ}{a}{}^{\rm NR}_{w,2}$ and of order 10^{-2} GeV^{-3} on the coefficients $\overset{\circ}{a}{}^{\rm NR}_{w,4}$ in the electron and proton sectors.

Note that in principle the anisotropic coefficients in the general result (84) also contribute to $\delta\bar{\nu}_{1S2S}$. In the weak-field regime, the spin-dependent contributions for $\Delta m_F = 0$ are

$$2\pi\delta\bar{\nu}_{1S2S} \supset \frac{m_F}{8}\sqrt{\frac{3}{\pi}}\sum_{q=1}^{2}(\alpha m_r)^{2q}\left(1 + \frac{67}{12}\delta_{2q}\right) + \sum_w (g_{w(2q)10}^{\rm NR(0B)} + H_{w(2q)10}^{\rm NR(0B)} + 2g_{w(2q)10}^{\rm NR(1B)} + 2H_{w(2q)10}^{\rm NR(1B)}). \quad (87)$$

Note these are nonvanishing only for $m_F \neq 0$. In the strong-field regime and for $\Delta S_w = 0$, the spin-dependent contributions are

$$2\pi\delta\bar{\nu}_{1S2S} \supset \sqrt{\frac{3}{16\pi}}\sum_{q=1}^{2}(\alpha m_r)^{2q}\left(1 + \frac{67}{12}\delta_{2q}\right) + \sum_w S_w(g_{w(2q)10}^{\rm NR(0B)} + H_{w(2q)10}^{\rm NR(0B)} + 2g_{w(2q)10}^{\rm NR(1B)} + 2H_{w(2q)10}^{\rm NR(1B)}). \quad (88)$$

However, at present the planned ASACUSA measurement, which is sensitive to the anisotropic coefficients, is expected to reach an absolute uncertainty of about 100 Hz or better, while measurements of the $1S\text{-}2S$ transition in antihydrogen appear unlikely to approach this benchmark in the near future. It is therefore reasonable at present to disregard contributions from the anisotropic coefficients to the $1S\text{-}2S$ transition. Nonetheless, as antihydrogen is intrinsically a stable antiatom and the natural linewidth of the $2S$ state is about 1 Hz, the $1S\text{-}2S$ transition may offer the most interesting long-term prospects for sub-Hz sensitivities.

In parallel with the hydrogen case discussed in Sec. III C 2, the presence of Lorentz and *CPT* violation can also cause apparent shifts in various fundamental constants measured in antihydrogen experiments. For instance, the apparent shift $\delta\bar{R}_\infty$ of the Rydberg constant in antihydrogen due to Lorentz and *CPT* violation is given by

$$\delta\bar{R}_\infty = \frac{4\pi m_r^2}{m_e} R_\infty \sum_w (\overset{\circ}{a}{}^{\rm NR}_{w,2} + \overset{\circ}{c}{}^{\rm NR}_{w,2}). \tag{89}$$

A direct comparison of a measurement of the Rydberg constant (61) performed using hydrogen with one using antihydrogen therefore can be expected to reveal a discrepancy ΔR_∞ given by

$$\Delta R_\infty \equiv R_\infty - \bar{R}_\infty = -\frac{8\pi m_r^2}{m_e} R_\infty \sum_w \overset{\circ}{a}{}^{\rm NR}_{w,2}. \tag{90}$$

This difference depends purely on CPT-odd effects. Other fundamental constants may similarly be affected. For example, if future experiments can perform high-precision spectroscopy of the $2S$-$2P$ transition to determine the classical Lamb shift in antihydrogen,

$$2\pi\delta\bar{\nu}_{\rm Lamb} = -\frac{2}{3}(\alpha m_r)^4 \sum_w (\overset{\circ}{a}{}^{\rm NR}_{w,4} + \overset{\circ}{c}{}^{\rm NR}_{w,4}), \tag{91}$$

or of the two-photon transitions $2S$-nD in antihydrogen, then the radius of the antiproton could be determined. Since Lorentz and CPT violation produces an apparent shift in these transitions, a discrepancy between the proton and antiproton radii could emerge.

D. Antihydrogen and gravity

A long-standing question is whether antiparticles and particles interact identically with gravity [85]. Several experiments have been proposed to test this idea directly using antihydrogen, including AEGIS [70], GBAR [72], ALPHA [71], and AGE [73]. While the present work is focused on the spectroscopic effects of nonminimal operators for Lorentz and CPT violation in flat spacetime, we offer in this subsection a few comments about the role of nonminimal operators in the gravitational couplings of antihydrogen.

A theoretical model in which the gravitational response of antihydrogen differs from that of hydrogen is presented in Sec. IX B of Ref. [86]. The model, called the isotropic parachute model (IPM), is an effective quantum field theory, constructed as a subset of the gravitationally coupled minimal SME [9]. The IPM overcomes various objections to theories with different antimatter and matter couplings to gravity, demonstrating explicitly that energy can be conserved, that the binding-energy content can be largely irrelevant to the gravitational response, and that restrictions from other systems such as neutral kaons can be evaded.

In the IPM, the anomalous gravitational response of antimatter compared to matter is a consequence of CPT violation and hence of Lorentz violation in the underlying effective field theory. The IPM is an isotropic theory, formulated in an asymptotically Minkowski spacetime with a weak gravitational field and designed to produce a predominantly null effect in matter by cancellation of CPT-even and CPT-odd effects in the minimal SME. The physical Lorentz and CPT violation in hydrogen is therefore countershaded from detection [87]. The anomalous response in antihydrogen arises because for antimatter the signs of the CPT-odd contributions change, disrupting the cancellation. Explicitly, in the IPM the uniform constant background pieces $\bar{a}_T^w$ and $\bar{c}_{TT}^w$ of the isotropic minimal-SME Cartesian coefficients a_T^w and c_{TT}^w are related by

$$\alpha\bar{a}_T^w = \frac{1}{3} m \bar{c}_{TT}^w, \tag{92}$$

for particles of flavor w, where α is a model-dependent quantity determined by the gravitational coupling for Lorentz-violating effects.

In the context of hydrogen and antihydrogen, the conditions (92) for $w = e$ and $w = p$ represent two constraints on four independent coefficients, so the IPM is a two-parameter model. The resulting inertial and gravitational masses of hydrogen are equal while those of antihydrogen differ,

$$m_i^H = m_g^H, \qquad m_i^{\bar{H}} \neq m_g^{\bar{H}}. \tag{93}$$

However, the strength of the anomalous gravitational response of antimatter in the IPM has recently been constrained to parts in 10^7 by an analysis combining data from torsion-balance tests, matter-wave interferometry, and microwave, optical, and Mössbauer clock-comparison experiments, and by taking advantage of the differing bound kinetic energies of nuclei [88]. Any IPM effects in antihydrogen are therefore beyond the reach of the currently proposed antihydrogen experiments.

The IPM uses only isotropic minimal operators in the SME. However, the gravitational sector of the SME includes not only minimal pure-gravity and matter-gravity couplings, but also nonminimal couplings [9] that have definite experimental signatures [89]. These nonminimal couplings are also of potential relevance in the present context, and in particular we expect them to enhance substantially the prospects for a strong anomalous gravitational response of antihydrogen. A detailed study of nonminimal effects in this context is challenging and lies well outside our present scope, although it is likely to offer interesting insights. Nonetheless, we can provide some intuition by following the conceptual path presented in Ref. [86] in the special limit where only isotropic nonminimal coefficients in the matter-gravity sector contribute, keeping only zeroth-order nonrelativistic effects and first-order gravitational couplings.

In this comparatively simple limit, starting with the generalized Dirac equation incorporating both operators for Lorentz and CPT violation of arbitrary mass dimension and gravitational couplings, the corresponding perturbative

Hamiltonian contains no momentum-dependent Lorentz violation and the Lorentz-violating energy dependence involves only the particle mass. The calculation therefore proceeds with the minimal-SME background coefficients $\bar{a}_T^w$ and $\bar{c}_{TT}^w$ now accompanied by a series of terms involving nonminimal background coefficients and the particle mass. Since these quantities are all constants, the derivation has the same algebraic structure as that presented in Ref. [86], up to possible numerical factors due to the increased multiplicity of indices on nonminimal coefficients.

Noting that only the nonminimal isotropic coefficients with $k = 0$ contain the minimal-SME isotropic coefficients and using Eqs. (93), (111), (129), and (130) of Ref. [37], we can deduce that the net result of the calculation involves the replacements

$$\begin{aligned}\bar{a}_T^w &\to \overset{\circ}{\bar{a}}{}^{\mathrm{NR}}_{w,0} = \bar{a}_T^w + \sum_{\text{odd } d\geq 5} N_{a,w}^d m_w^{d-3} \overset{\circ}{\bar{a}}{}_0^{(d)}, \\ \bar{c}_{TT}^w &\to \overset{\circ}{\bar{c}}{}^{\mathrm{NR}}_{w,0} = \bar{c}_{TT}^w + \sum_{\text{even } d\geq 6} N_{c,w}^d m_w^{d-4} \overset{\circ}{\bar{c}}{}_0^{(d)}, \end{aligned} \tag{94}$$

where $N_{a,w}^d$ and $N_{c,w}^d$ are numerical factors. We can then make these replacements in the discussion in Sec. IX B of Ref. [86] and conclude that the vertical acceleration a of an antihydrogen atom of inertial mass $m_i^{\bar{H}}$ and gravitational mass $m_g^{\bar{H}}$ obeys

$$a = \frac{m_g^{\bar{H}}}{m_i^{\bar{H}}} g \equiv \left(1 + \left.\frac{\delta g}{g}\right|_{\bar{H}}\right) g, \tag{95}$$

with

$$\left.\frac{\delta g}{g}\right|_{\bar{H}} = \frac{2}{m_{\bar{H}}} \sum_w \left(\alpha \overset{\circ}{\bar{a}}{}^{\mathrm{NR}}_{w,0} + \frac{1}{3} m_w \overset{\circ}{\bar{c}}{}^{\mathrm{NR}}_{w,0}\right), \tag{96}$$

where w takes the values e and p and $m_{\bar{H}}$ is a constant equal to the inertial mass of an antihydrogen atom in the absence of Lorentz and *CPT* violation.

The above derivation suggests introducing a generalized IPM via the definition

$$\alpha \overset{\circ}{\bar{a}}{}^{\mathrm{NR}}_{w,0} - \frac{1}{3} m_w \overset{\circ}{\bar{c}}{}^{\mathrm{NR}}_{w,0} = 0. \tag{97}$$

The corresponding vertical acceleration for hydrogen is then unaffected,

$$\left.\frac{\delta g}{g}\right|_{H} = \frac{2}{m_H} \sum_w \left(\alpha \overset{\circ}{\bar{a}}{}^{\mathrm{NR}}_{w,0} - \frac{1}{3} m_w \overset{\circ}{\bar{c}}{}^{\mathrm{NR}}_{w,0}\right) = 0, \tag{98}$$

while the gravitational response (95) of antihydrogen is anomalous. Note that the presence of the nonminimal coefficients implies two new degrees of freedom at each dimension d. This provides intuition about the connection between nonminimal coefficients and renewed prospects for a comparatively large anomalous gravitational response in antihydrogen. Note also that a complete derivation can be expected to generate a tensor relation between the acceleration of a test body and the acceleration due to gravity, with horizontal components of the acceleration affected. The relation involves spatial components of nonminimal coefficients, along with momentum factors as well. In general, the motion of a freely falling antihydrogen atom in the presence of Lorentz and *CPT* violation is expected to follow a geodesic in a pseudo-Finsler geometry determined by the Riemann metric and the SME coefficients, while its motion in the IPM follows a geodesic in pseudo-Randers spacetime [40].

On the experimental side, the above discussion reveals that studies of the gravitational couplings of antihydrogen probe distinct effects from the spectroscopic tests discussed in this work, as none of the latter can detect isotropic spherical coefficients with $k = 0$ for reasons discussed in Sec. II B. Also, we can use simple dimensional analysis to provide an estimate of the sensitivity of gravitational experiments with antihydrogen to nonminimal coefficients for *CPT* violation. A generic nonrelativistic spherical coefficient $\mathcal{K}_{wkjm}^{\mathrm{NR}}$ has mass dimension $1 - k$, so taking one coefficient nonzero at a time as before and neglecting momentum effects yields expected constraints of order

$$|\mathcal{K}_{wkjm}^{\mathrm{NR}}| \lesssim m_w^{1-k} \left.\frac{\delta g}{g}\right|_{\bar{H}}. \tag{99}$$

For an experiment with 10% uncertainty, this gives constraints of order 10^{-4-3k} GeV^{1-k} on nonrelativistic coefficients in the electron sector and of order 10^{-1} GeV^{1-k} on ones in the proton sector.

V. DEUTERIUM

The differing nuclear and spin structures of the various hydrogen isotopes imply these systems have distinct sensitivities to Lorentz and *CPT* violation. We focus here on deuterium, a stable fermionic system that has been widely studied since its discovery in the early 1930s [90]. Tritium and the higher hydrogen isotopes are unstable and challenging to handle experimentally, although an investigation of the spectroscopic properties of these systems could be worthwhile as well. Note that tritium decays are of interest in the context of precision measurements of the neutrino mass [91] and the associated searches for Lorentz and *CPT* violation in the neutrino sector [92].

The isotope shift for the $1S$-$2S$ transition between deuterium and hydrogen has been measured with a potentially competitive absolute uncertainty of about 15 Hz [93], while the presence of the neutron in the deuteron core changes the angular-momentum couplings and opens opportunities for additional sensitivities to coefficients in the neutron sector of the SME. Moreover, a deuterium

maser [94] could in principle be used to study the deuterium hyperfine structure at mHz sensitivity or better. In this section, we consider these possibilities in turn. We outline an approach to the perturbative Hamiltonian, obtain relevant frequency shifts, and summarize some implications for experimental studies.

Note that our analysis here disregards the gravitational couplings of deuterium. Although antideuterons were first created in the laboratory about 50 years ago [95], antideuterium remains only a theoretical possibility at present. It is expected to be stable, and comparisons of its gravitational response with that of deuterium could conceivably be of interest for at least two theoretical reasons. Both deuterium and antideuterium incorporate neutron coefficients for Lorentz and *CPT* violation and therefore a comparison of their gravitational properties would further extend tests of models such as the generalized IPM discussed in Sec. IV D. Also, deuterium and antideuterium are fermions, and as such their behavior in weak gravitational fields involves a different set of spin-dependent coefficients for Lorentz and *CPT* violation [9,86,96]. However, the production, trapping, and experimental manipulation of antideuterium remains at present a futuristic challenge, so detailed theoretical considerations of the free fall of antideuterium lie outside our present scope.

A. Isotropic Lorentz-violating perturbations

Since the deuteron is a bound state of two hadrons, for which exact expressions for the energy levels are lacking, the perturbative methods developed above for atomic hydrogen cannot be applied directly. Nonetheless, the dominant contributions from isotropic Lorentz and *CPT* violation can be obtained within plausible assumptions. These are of interest in the context of $1S$-$2S$ and similar transitions in deuterium.

As a reasonable first approximation to the Hamiltonian $H_{\rm D}$ governing the dominant deuterium physics of relevance here, we can write the three-body expression

$$H_{\rm D} \approx \frac{\boldsymbol{p}_e^2}{2m_e} + \frac{\boldsymbol{p}_p^2}{2m_p} + \frac{\boldsymbol{p}_n^2}{2m_n} + V(\boldsymbol{r}_{ep}) + U(\boldsymbol{r}_{pd}), \qquad (100)$$

where $\boldsymbol{p}_w$ is the three-momentum of the particle of flavor $w = e,\ p,\ n$, m_w is the corresponding mass, $\boldsymbol{r}_{ep}$ is the relative position of the electron and proton, and $\boldsymbol{r}_{pd}$ is the relative position of the proton and neutron. The potential V accounts for the electromagnetic interaction between the proton and electron, while U describes the nuclear interactions between the proton and neutron. For simplicity, we work in the zero-momentum inertial frame of the deuterium atom.

To separate the Hamiltonian while keeping the dominant Lorentz-invariant physics, we can reinterpret the dynamics of the proton and neutron in terms of the motion of the deuteron and the motion of the proton and neutron relative to the deuteron center of mass. It is therefore convenient to define $\boldsymbol{p} \equiv \boldsymbol{p}_p + \boldsymbol{p}_n = -\boldsymbol{p}_e$ and $\boldsymbol{p}_{pd} \equiv (\boldsymbol{p}_p - \boldsymbol{p}_n)/2$, with the latter being the momentum of the proton relative to the center of mass of the deuteron. It is also a sufficient approximation for present purposes to take $m_n \approx m_p$ and $\boldsymbol{r}_{ep} \approx \boldsymbol{r}_d \equiv \boldsymbol{r}_{ep} + \boldsymbol{r}_{pd}/2$. The vector $\boldsymbol{r}_d$ can be viewed as the approximate position of the deuteron center of mass with respect to the electron. It follows that $V(\boldsymbol{r}_{ep}) \approx V(\boldsymbol{r}_d)$. With these definitions and approximations, the Hamiltonian $H_{\rm D}$ takes the form

$$H_{\rm D} \approx \frac{\boldsymbol{p}^2}{2m_{\rm r}} + V(\boldsymbol{r}_d) + \frac{\boldsymbol{p}_{pd}^2}{m_p} + U(\boldsymbol{r}_{pd}), \qquad (101)$$

where $m_{\rm r} \approx 2m_p m_e/(2m_p + m_e)$ is the reduced mass of deuterium. This expression is separable, so its solution is the tensor product of the solutions of the two individual systems.

The next step is to express the Lorentz-violating perturbation in terms of these variables. Following the scenario introduced in Sec. II A, we can suppose that each of the three particles e, p, n experiences a perturbation $\delta h_w^{\rm NR}$ of the form (3). As discussed in Sec. III C 1, the $1S$-$2S$ and similar transitions are of interest primarily in the context of measuring isotropic coefficients for Lorentz violation, so we restrict our attention here to the quantities $\mathcal{V}_{wkjm}^{\rm NR} \equiv c_{wkjm}^{\rm NR} - a_{wkjm}^{\rm NR}$ defined in Eq. (6), but now with $w = e, p, n$.

Under these assumptions, we find that the isotropic part of the perturbation Hamiltonian $\delta h_{\rm D}^{\rm NR}$ can be written in the form

$$\delta h_{\rm D}^{\rm NR} = -\frac{1}{\sqrt{4\pi}} \sum_{k=2,4} \left(\mathcal{V}_{ek00}^{\rm NR} |\boldsymbol{p}|^k + \mathcal{V}_{pk00}^{\rm NR} \left| \frac{1}{2}\boldsymbol{p} + \boldsymbol{p}_{pd} \right|^k + \mathcal{V}_{nk00}^{\rm NR} \left| \frac{1}{2}\boldsymbol{p} - \boldsymbol{p}_{pd} \right|^k \right). \qquad (102)$$

This operator expression describes the leading-order perturbative effects arising from isotropic Lorentz and *CPT* violation.

B. $1S$-$2S$ transition

The deuterium energy-level shifts are given by expectation values of the perturbation Hamiltonian $\delta h_{\rm D}^{\rm NR}$ in the Lorentz-invariant states. In performing the calculations, only the cross terms $\boldsymbol{p} \cdot \boldsymbol{p}_{pd}$ and $(\boldsymbol{p} \cdot \boldsymbol{p}_{pd})^2$ that couple both systems could in principle be challenging to handle. However, the former is odd under a parity transformation of either momentum and hence yields zero contribution at leading order. To treat the quadratic term, we can plausibly assume the two systems are sufficiently decoupled so that $\langle (\boldsymbol{p} \cdot \boldsymbol{p}_{pd})^2 \rangle \approx \langle \boldsymbol{p}^2 \rangle \langle \boldsymbol{p}_{pd}^2 \rangle / 2$. Also, the contribution to the $1S$-$2S$ and other nL-$n'L'$ transitions can be expected to depend on a nonzero power of $\boldsymbol{p}$. Moreover, the magnitude

of $\boldsymbol{p}_{pd}$ is roughly 100 MeV while that of $\boldsymbol{p}$ is about 1 keV, so $\langle \boldsymbol{p}^2\rangle\langle \boldsymbol{p}_{pd}^2\rangle \gg \langle \boldsymbol{p}^4\rangle$.

Combining these considerations and using the expectation values (15), we find that the frequency shift $\delta\nu_{\rm D}$ of the nL-$n'L'$ transition in deuterium due to isotropic Lorentz and *CPT* violation is given by

$$2\pi\delta\nu_{\rm D} = \frac{m_{\rm r}}{\sqrt{\pi}}(\varepsilon_{n'}-\varepsilon_n)\left[\mathcal{V}_{e200}^{\rm NR}+\frac{1}{4}(\mathcal{V}_{p200}^{\rm NR}+\mathcal{V}_{n200}^{\rm NR}) + \langle \boldsymbol{p}_{pd}^2\rangle(\mathcal{V}_{p400}^{\rm NR}+\mathcal{V}_{n400}^{\rm NR})\right] - \frac{2m_{\rm r}^2}{\sqrt{\pi}}\left[\varepsilon_{n'}^2\left(\frac{8n'}{2L'+1}-3\right)-\varepsilon_n^2\left(\frac{8n}{2L+1}-3\right)\right] \times\left(\mathcal{V}_{e400}^{\rm NR}+\frac{1}{16}(\mathcal{V}_{p400}^{\rm NR}+\mathcal{V}_{n400}^{\rm NR})\right), \tag{103}$$

where $\varepsilon_n \equiv -\alpha^2 m_{\rm r}/2n^2$ and $\langle \boldsymbol{p}_{pd}^2\rangle \simeq 10^4$ MeV^2. This expression generalizes the result (60) for hydrogen and reduces to it in the limit where the proton and neutron are taken to have identical momenta, each of magnitude half that of the electron momentum.

The $1S$-$2S$ transition in deuterium provides interesting sensitivity to anisotropic coefficients in the Sun-centered frame via boost corrections that produce sidereal and annual variations. At leading order in the boost parameter, the deuterium $1S$-$2S$ transition frequency takes the same form (63) as its hydrogen counterpart, except that the sum over flavors now includes also the neutron. The leading-order contributions for the electron vectors $V_e^{(d)J}$ have the same form as for hydrogen and so can be found in Table V. The leading-order contributions for the proton and neutron vectors $V_p^{(d)J}$ and $V_n^{(d)J}$ with $5 \le d \le 8$ can be obtained from Table VIII. In this table, m_w represents the rest masses of the proton $w = p$ and neutron $w = n$. As before, α is the fine-structure constant, $m_{\rm r}$ is the reduced mass of the system, and the effective Cartesian coefficients for Lorentz violation are defined in Eq. (27) of Ref. [37]. The minimal-SME spin-independent coefficients $V_w^{(3)J}$ and $V_w^{(4)J}$ vanish at leading order in the nonrelativistic limit and so have no effect on the $1S$-$2S$ frequency, in parallel with the hydrogen case [13,29].

The time variations in the deuterium $1S$-$2S$ transition are determined by the same expressions as for hydrogen, namely, Eq. (64) for the annual frequency $\Omega_\oplus$ and Eq. (65) for the sidereal frequency $\omega_\oplus$. However, the deuterium transition offers some advantages over its hydrogen counterpart. One is the sensitivity of deuterium to neutron coefficients. A more subtle advantage is that the motion of the proton in the nucleus makes the deuterium experiment substantially more sensitive to some of the proton coefficients. The point is that in hydrogen the proton is a comparatively placid object with momentum opposite that of the electron, with magnitude $\sim\alpha m_e$ of a few keV. In contrast, the proton and neutron in deuterium together have total momentum opposite that of the electron, but each nucleon has momentum of over 100 MeV, producing an expectation value $\langle \boldsymbol{p}_{pd}^2\rangle \sim 10^4$ MeV^2. As a result, measurements of the deuterium $1S$-$2S$ transition offer about a billionfold greater sensitivity than hydrogen to the proton coefficients $a_{p\,\rm eff}^{KKLLJ}$ and $c_{p\,\rm eff}^{TKKLLJ}$, as can be deduced from the entries for $d = 7, 8$ in Table VIII.

We remark in passing that a study of subleading effects in the deuterium $1S$-$2S$ frequency along the lines of the experiment with hydrogen performed in Ref. [18] could also be used to constrain minimal SME coefficients in the neutron sector. The analogue of the minimal-SME match (66) for deuterium involves both proton and neutron coefficients,

$$\sum_{wd} V_w^{(d)J} = \frac{5}{4}\alpha^2 m_{\rm r}\left[c_e^{(TJ)}+\frac{1}{4}(c_p^{(TJ)}+c_n^{(TJ)})\right], \tag{104}$$

and this expression could be used to determine sensitivities to nonminimal coefficients in all three sectors $w = e, p, n$ as for the hydrogen case.

C. Comparative analyses

In atomic hydrogen, the isotropic coefficients produce an effective shift of the Rydberg constant given by Eq. (61). An analogous effect occurs in deuterium, but the shift is instead given by

$$\delta R_{\infty,\rm D} = \frac{2\sqrt{\pi}m_{\rm r}^2}{m_e}R_\infty\left[\mathcal{V}_{e200}^{\rm NR}+\frac{1}{4}(\mathcal{V}_{p200}^{\rm NR}+\mathcal{V}_{n200}^{\rm NR}) + \langle \boldsymbol{p}_{pd}^2\rangle(\mathcal{V}_{p400}^{\rm NR}+\mathcal{V}_{n400}^{\rm NR})\right]. \tag{105}$$

TABLE VIII. Values of the vectors $V_w^{(d)J}$ in Eq. (63) for the proton and neutron in deuterium with $5 \le d \le 8$.

d	$V_w^{(d)J}$
5	$\frac{3}{16}(\alpha m_{\rm r})^2(2a_{w\,\rm eff}^{(5)TTJ}+a_{w\,\rm eff}^{(5)KKJ})$
6	$-\frac{3}{4}(\alpha m_{\rm r})^2 m_w(c_{w\,\rm eff}^{(6)TTTJ}+c_{w\,\rm eff}^{(6)TKKJ})$
7	$\frac{5}{8}(\alpha m_{\rm r})^2 m_w^2(2a_{w\,\rm eff}^{(7)TTTTJ}+3a_{w\,\rm eff}^{(7)TTKKJ})+\frac{3}{4}(\alpha m_{\rm r})^2\langle \boldsymbol{p}_{pd}^2\rangle a_{w\,\rm eff}^{(7)KKLLJ}$
8	$-\frac{15}{8}(\alpha m_{\rm r})^2 m_w^3(c_{w\,\rm eff}^{(8)TTTTTJ}+2c_{w\,\rm eff}^{(8)TTKKJ})-\frac{9}{2}(\alpha m_{\rm r})^2 m_w\langle \boldsymbol{p}_{pd}^2\rangle c_{w\,\rm eff}^{(8)TKKLLJ}$

Since the shift δR_∞ in hydrogen and the shift $\delta R_{\infty,\mathrm{D}}$ in deuterium are distinct, any difference between the values obtained for the Rydberg constant in experiments with hydrogen and with deuterium could be a signal for Lorentz and CPT violation. Similarly, the change $\delta\nu_{\mathrm{Lamb,D}}$ in the classical Lamb shift ($2S_{J=1}$-$2P_{J=1}$) in deuterium,

$$2\pi\delta\nu_{\mathrm{Lamb,D}} = -\frac{(\alpha m_{\mathrm{r}})^4}{3\sqrt{\pi}}\left[\mathcal{V}_{e400}^{\mathrm{NR}} + \frac{1}{16}(\mathcal{V}_{p400}^{\mathrm{NR}} + \mathcal{V}_{n400}^{\mathrm{NR}})\right], \tag{106}$$

differs from the change $\delta\nu_{\mathrm{Lamb}}$ in the hydrogen Lamb shift given by Eq. (62). A signal for Lorentz and CPT violation would therefore be an observed discrepancy between experimental values obtained in the two systems.

The above comparative analyses can also be extended to physical effects in other transitions. These could include, for example, the transitions $2S$-$4D$, $2S$-$8D$, and $2S$-$12D$, all of which have been measured in deuterium [61,63,69]. To illustrate the extraction of constraints on coefficients for Lorentz violation via this method, we consider here a comparative analysis of the two experimental values of the difference between the proton and deuteron radii obtained in Refs. [61] and [98]. As before, only the contributions from isotropic coefficients for Lorentz and CPT violation are included, as other types of searches are more sensitive to anisotropic coefficients.

Consider first the weighted difference

$$\Delta = \nu_{2S4S} - \frac{1}{4}\nu_{1S2S} \tag{107}$$

between the $2S$-$4S$ frequency ν_{2S4S} and the $1S$-$2S$ frequency ν_{1S2S}, measured for hydrogen and deuterium in Ref. [61]. The change in the isotope shift $\delta\nu_{\mathrm{shift}}$ between the two measurements is governed by the difference $\delta(r_d^2 - r_p^2)$ between the square of the charge radii of the proton and deuteron,

$$2\pi\delta\nu_{\mathrm{shift}} = -\frac{7\pi\alpha^4 R_\infty}{24 r_e^2}\delta(r_d^2 - r_p^2), \tag{108}$$

where r_e is the classical electron radius. The frequency shift $\delta\nu_{\mathrm{LV}}$ of Δ due to Lorentz and CPT violation is given by

$$2\pi\delta\nu_{\mathrm{LV}} = -\frac{89(\alpha m_{\mathrm{r}})^4}{4096\sqrt{4\pi}}(15\mathcal{V}_{p400}^{\mathrm{NR}} - \mathcal{V}_{n400}^{\mathrm{NR}}). \tag{109}$$

Assuming the observed value of $\delta\nu_{\mathrm{shift}}$ arises entirely from $\delta\nu_{\mathrm{LV}}$, we find that the difference between the square of the charge radii determined in Ref. [61] is approximately given by

$$\delta(r_d^2 - r_p^2) \approx (2\times 10^{-6})(15\mathcal{V}_{p400}^{\mathrm{NR}} - \mathcal{V}_{n400}^{\mathrm{NR}})\ \mathrm{GeV}^3\,\mathrm{fm}^2, \tag{110}$$

where the coefficients for Lorentz and CPT violation have units of GeV^{-3}.

Next, consider the difference between the square of the charge radii obtained in Ref. [98] from measurements of the $1S$-$2S$ frequency ν_{1S2S} in hydrogen and deuterium. In this case, the change in the isotope shift $\delta\nu_{\mathrm{shift}}$ is given by

$$2\pi\delta\nu_{\mathrm{shift}} = \frac{7\pi\alpha^4 R_\infty}{3 r_e^2}\delta(r_d^2 - r_p^2), \tag{111}$$

while the Lorentz-violating shift $\delta\nu_{\mathrm{LV}}$ is

$$2\pi\delta\nu_{\mathrm{LV}} = \frac{3(\alpha m_{\mathrm{r}})^2}{16\sqrt{4\pi}}[3\mathcal{V}_{p200}^{\mathrm{NR}} - \mathcal{V}_{n200}^{\mathrm{NR}} - 4\langle \boldsymbol{p}_{pd}^2\rangle(\mathcal{V}_{p400}^{\mathrm{NR}} + \mathcal{V}_{n400}^{\mathrm{NR}})]. \tag{112}$$

The assumption that the observed frequency shift originates from Lorentz violation now gives the difference between the square of the charge radii as approximately

$$\delta(r_d^2 - r_p^2) \approx (2\times 10^5)[3\mathcal{V}_{p200}^{\mathrm{NR}} - \mathcal{V}_{n200}^{\mathrm{NR}} - 4\langle \boldsymbol{p}_{pd}^2\rangle(\mathcal{V}_{p400}^{\mathrm{NR}} + \mathcal{V}_{n400}^{\mathrm{NR}})]\ \mathrm{GeV}^3\,\mathrm{fm}^2. \tag{113}$$

We see that this expression and the result (110) provide two distinct measures of $\delta(r_d^2 - r_p^2)$ in terms of coefficients for Lorentz and CPT violation.

The two reported experimental values are essentially in agreement. Note that the above results make use of values of the Rydberg constant and the mass ratios of the electron to the proton and to the deuteron. In principle, these quantities could be shifted by Lorentz and CPT violation, so we take a conservative value of less than $0.02\ \mathrm{fm}^2$ for the uncertainty in $|\delta(r_d^2 - r_p^2)|$. Disregarding coefficients in the electron sector, which give contributions proportional to the difference of powers of the reduced masses of deuterium and hydrogen and so are suppressed by 4 or more orders of magnitude relative to coefficients in the proton and neutron sectors, we can finally extract the constraint

$$|3\mathring{a}_{p,2}^{\mathrm{NR}} - \mathring{a}_{n,2}^{\mathrm{NR}} - 4\langle \boldsymbol{p}_{pd}^2\rangle(\mathring{a}_{p,4}^{\mathrm{NR}} + \mathring{a}_{n,4}^{\mathrm{NR}}) - 3\mathring{c}_{p,2}^{\mathrm{NR}} + \mathring{c}_{n,2}^{\mathrm{NR}} - 4\langle \boldsymbol{p}_{pd}^2\rangle(\mathring{c}_{p,4}^{\mathrm{NR}} + \mathring{c}_{n,4}^{\mathrm{NR}})| < 2\times 10^{-7}\ \mathrm{GeV}^{-1} \tag{114}$$

on coefficients for Lorentz and CPT violation.

Similar comparative analyses can be performed in other systems. An example discussed in Ref. [46] is a comparison of radii using the isotope shift between muonic hydrogen and muonic deuterium. A complete analysis of this system would place constraints on muon coefficients for Lorentz and CPT violation as well as proton and neutron coefficients.

D. Deuterium maser

The successful construction and operation of a deuterium maser with absolute frequency uncertainty around 1 mHz [94] implies that high-precision spectroscopy of the hyperfine structure of deuterium is a realistic possibility. The high momenta of the proton and neutron in the deuteron core, which as described in Sec. V B leads to a billionfold gain in sensitivity to certain coefficients for Lorentz and *CPT* violation in $1S$-$2S$ spectroscopy, can similarly be expected to enhance the sensitivity to coefficients affecting the hyperfine transitions of the deuterium maser relative to the hydrogen one. Moreover, the deuteron core exists in an admixture of orbital angular momentum 0 and 2, so the deuterium maser also provides access to coefficients with larger values of j.

To study the corrections to the hyperfine structure in deuterium, a reasonable description of the unperturbed ground state is required. The angular part of this state can be obtained by coupling the spin S_d of the deuteron to the spin S_e of the electron. The deuteron component involves the coupling of the triplet state of the proton and the neutron with a superposition of $L=0$ and $L=2$ orbital states of the nuclear motion [97]. As a result, the unperturbed wave function for the ground state can be expressed as

$$\langle \boldsymbol{p}, \boldsymbol{p}_{pd} | F m_F \rangle = \psi_{10}(p) \sum_{S_e S_d} \langle \frac{1}{2} S_e 1 S_d | F m_F \rangle | S_e \rangle \langle \boldsymbol{p_{pd}} | S_d \rangle, \tag{115}$$

where ψ_{10} is the spin-independent piece, S_e is the electron spin, and S_d is the deuteron spin. The deuteron spin wave function takes the form

$$\langle \boldsymbol{p}_{pd} | S_d \rangle = \sum_{l=0}^{1} \Psi_{2l}(p_{pd}) \sum_{qm} \langle 1 q (2l) m | 1 S_d \rangle Y_{(2l)m}(\hat{\boldsymbol{p}}_{pd}) \chi_q, \tag{116}$$

where Ψ_{2l} contains the radial piece and χ_m is the spin-triplet wave function constructed from the proton and neutron spin states.

Using this wave function, we can determine the perturbative shifts by calculating the expectation values of the full perturbative Hamiltonian $\delta h_{\mathrm{D}}^{\mathrm{NR}}$ obtained following the discussion in Sec. II A, assuming each particle e, p, n experiences a perturbation of the form (3). In the hyperfine Zeeman regime, the effects from isotropic coefficients cancel as usual. Neglecting these coefficients, we find the energy-level shifts are

$$\delta\varepsilon(F, m_F) = -\frac{m_F}{3\sqrt{3\pi}} \sum_{q=0}^{2} \frac{(\alpha m_{\mathrm{r}})^{2q}}{2(F-1)} (1 + 4\delta_{q2}) \times (\mathcal{T}_{e(2q)10}^{\mathrm{NR}(0B)} + 2\mathcal{T}_{e(2q)10}^{\mathrm{NR}(1B)}). \tag{117}$$

Comparison of this expression with the energy-level shifts (48) and frequency shifts (49) for the hydrogen maser shows that both types of maser are sensitive to the same combination of electron coefficients. The deuterium maser therefore has no particular advantage over the hydrogen maser in this regard. Note also that the two deuterium-maser transitions $F=3/2 \to F=1/2$ with $m_F = \mp 1/2 \to m_F = \pm 1/2$, which are the most independent of fluctuations in the applied magnetic field, are insensitive to Lorentz and *CPT* violation at leading order. This parallels the result for $F=1 \to F=0$ with $m_F=0$ for the hydrogen maser.

The calculation of the perturbative shifts due to the proton and neutron coefficients is more involved. Since the deuteron spin is a good quantum number, the coefficient selection rules discussed in Sec. II B imply that only proton and neutron coefficients with $j \le 2$ can contribute, so only the cases $j=1$ and $j=2$ need be considered. Some identities are useful to evaluate the factors involving the momentum and spin-weighted spherical harmonics. Writing $\boldsymbol{p} \equiv \boldsymbol{p}_a + \boldsymbol{p}_b$, we find for $j=1$ the identities

$$\begin{aligned} |\boldsymbol{p}|_s Y_{1m}(\hat{\boldsymbol{p}}) &= |\boldsymbol{p}_a|_s Y_{1m}(\hat{\boldsymbol{p}}_a) + |\boldsymbol{p}_b|_s Y_{1m}(\hat{\boldsymbol{p}}_b), \\ |\boldsymbol{p}|\sigma^s(\hat{\boldsymbol{p}}) &= |\boldsymbol{p}_a|\sigma^s(\hat{\boldsymbol{p}}_a) + |\boldsymbol{p}_b|\sigma^s(\hat{\boldsymbol{p}}_b). \end{aligned} \tag{118}$$

For $j=2$, we obtain

$$\begin{aligned} |\boldsymbol{p}|^2 Y_{20}(\hat{\boldsymbol{p}}) &= |\boldsymbol{p}_a|^2 Y_{20}(\hat{\boldsymbol{p}}_a) + |\boldsymbol{p}_b|^2 Y_{20}(\hat{\boldsymbol{p}}_b) \\ &\quad + \frac{1}{2} |\boldsymbol{p}_a||\boldsymbol{p}_b| \sqrt{\frac{5}{\pi}} (3\cos\theta_a \cos\theta_b - \cos\gamma), \end{aligned} \tag{119}$$

where $\cos\gamma \equiv \hat{\boldsymbol{p}}_a \cdot \hat{\boldsymbol{p}}_b$.

Armed with these identities, we can determine the perturbative level shifts. Consider first the expectation value of the spin-dependent terms with $j=1$. Choosing as before the applied magnetic field to be aligned with the laboratory z axis, we require the expectation value of Eq. (3) for $jm=10$. We find

$$\delta\varepsilon(F, m_F) = -\frac{1}{3\sqrt{6\pi}} \frac{m_F}{2^{F-2}} \sum_k \langle \boldsymbol{p}_{pd}^{2k} \rangle \times \sum_w (\mathcal{T}_{w(2q)10}^{\mathrm{NR}(0B)} + 2\mathcal{T}_{w(2q)10}^{\mathrm{NR}(1B)}), \tag{120}$$

where w takes the values p and n.

For states with $F=1/2$, only proton and neutron coefficients with $j=1$ contribute to the hyperfine Zeeman frequencies. However, when $F=3/2$, contributions from coefficients with $j=2$ can appear. In this case, we find the contribution to the energy-level shift is approximately

$$\delta\epsilon(F,m_F)=\frac{1}{\sqrt{5\pi}}\frac{2F-1}{(8m_F^2-10)}\sum_{q=0}^{2}\langle \boldsymbol{p}_{pd}^{2q}\rangle'\sum_w \mathcal{V}_{w(2q)20}^{\rm NR}, \tag{121}$$

where

$$\langle \boldsymbol{p}_{pd}^{2q}\rangle' \equiv \langle\Psi_2|\boldsymbol{p}_{pd}^{2q}|\Psi_2\rangle-\sqrt{8}\mathrm{Re}\langle\Psi_2|\boldsymbol{p}_{pd}^{2q}|\Psi_0\rangle. \tag{122}$$

This depends on the specific model used for the radial deuteron wave functions Ψ_0, Ψ_2.

Combining the above results for electron, proton, and neutron coefficients, we find that the anisotropic shifts in the deuterium hyperfine Zeeman levels are given by

$$\begin{aligned}\delta\epsilon(F,m_F)=&\frac{1}{\sqrt{5\pi}}\frac{2F-1}{(8m_F^2-10)}\sum_{q=0}^{2}\langle \boldsymbol{p}_{pd}^{2q}\rangle'\sum_w \mathcal{V}_{w(2q)20}^{\rm NR}\\&-\frac{1}{3\sqrt{6\pi}}\frac{m_F}{2^{F-2}}\sum_{q=0}^{2}\langle \boldsymbol{p}_{pd}^{2q}\rangle\\&\times\sum_w(\mathcal{T}_{w(2q)10}^{\rm NR(0B)}+2\mathcal{T}_{w(2q)10}^{\rm NR(1B)})\\&-\frac{m_F}{3\sqrt{3\pi}}\sum_{q=0}^{2}\frac{(\alpha m_r)^{2q}}{2(F-1)}(1+4\delta_{q2})\\&\times(\mathcal{T}_{e(2q)10}^{\rm NR(0B)}+2\mathcal{T}_{e(2q)10}^{\rm NR(1B)}),\end{aligned} \tag{123}$$

where the sum over w spans the values p and n. In this expression, the quantities $\mathcal{V}_{w(2q)20}^{\rm NR}$, $\mathcal{T}_{w(2q)10}^{\rm NR(0B)}$, and $2\mathcal{T}_{w(2q)10}^{\rm NR(1B)}$ are given in terms of the coefficients for Lorentz and CPT violation by Eq. (6). Note that the proton and neutron coefficients contribute to all possible hyperfine Zeeman transitions, including the ones that are the most independent of fluctuations in the external magnetic field. Another key feature of this result is the appearance of coefficients with $j=2$, which implies experimental signals at the second harmonic $2\omega_\oplus$ of the sidereal frequency that can be measured in hyperfine Zeeman transitions with $\Delta F\neq 0$. Moreover, the dependence on the expectation values $\langle \boldsymbol{p}_{pd}^{2q}\rangle$ acts to enhance the sensitivity to the coefficients for Lorentz and CPT violation by factors of a billionfold for coefficients with $k=2$ and by 10^{18}-fold for coefficients with $k=4$. Generically, this suggests attainable sensitivities to nonrelativistic coefficients $\mathcal{K}_{kjm}$ with even $k=2,4$ at the level of $|\mathcal{K}|\lesssim 10^{-27+k}$ GeV^{1-k}, representing an impressive potential improvement over the results in Table III as well as sensitivity to numerous coefficients unmeasurable using a hydrogen maser.

This remarkable potential reach naturally suggests investigating the possibility of additional constraints from an analysis of the deuterium hyperfine Zeeman transitions that incorporates the boost relative to the Sun-centered frame, in analogy to the discussion for hydrogen in Sec. III B 4. Adopting a similar notation, we find that the first-order shifts $\delta\epsilon^{(1)}(F,m_F)$ of the energies due to the boost correction take the form

$$\begin{aligned}\delta\epsilon^{(1)}(F,m_F)=&\frac{m_F}{3(F-1)}\sum_d T_e^{(d)JK}R^{zJ}(\beta_\oplus^K+\beta_L^K)\\&+\frac{(2F-1)}{5-4m_F^2}\sum_{wd}T_w^{(d)JKL}M^{JK}(\beta_\oplus^L+\beta_L^L)\\&+\frac{\sqrt{2}}{3}\frac{m_F}{2^{F-2}}\sum_{wd}\bar{T}_w^{(d)JK}R^{zJ}(\beta_\oplus^K+\beta_L^K),\end{aligned} \tag{124}$$

where the sums over w are over the flavors p and n. In this expression, the quantities M^{IJ} represent combinations of rotations given by

$$M^{JK}=2R^{zJ}R^{zK}-R^{xJ}R^{xK}-R^{yJ}R^{yK}. \tag{125}$$

The pseudotensors $T_e^{(d)JK}$ in the electron sector are given by Table IV with $w=e$, while the pseudotensors $\bar{T}_w^{(d)JK}$ in the proton and neutron sectors are also obtained from this table with the substitutions $(\alpha m_{\rm r})^2\to\langle \boldsymbol{p}_{pd}^2\rangle$ and $(\alpha m_{\rm r})^4\to\langle \boldsymbol{p}_{pd}^4\rangle/5$. The explicit forms of the pseudotensors $T_w^{(d)JKL}$ are listed in Table IX in terms of the expectation values $\langle \boldsymbol{p}_{pd}^{2q}\rangle$, the rest masses m_w, the fine-structure constant α, the deuterium reduced mass $m_{\rm r}$, and the effective Cartesian coefficients for Lorentz violation defined in Eqs. (27) and (28) of Ref. [37]. For each coefficient, only the leading-order nonrelativistic contributions are provided.

In parallel with the results for the boost-independent terms, the expectation values $\langle \boldsymbol{p}_{pd}^{k}\rangle$ enhance the attainable sensitivity to spin-dependent coefficients relative to the

TABLE IX. Values of the pseudotensor $T_w^{(d)JKL}$ in Eq. (54) for the proton and neutron in deuterium for $5\le d\le 8$.

d	$T_w^{(d)JKL}$
5	$-\frac{1}{5}\langle \boldsymbol{p}_{pd}^2\rangle(2a_{w\rm eff}^{(5)TTJ}\delta^{KL}+a_{w\rm eff}^{(5)JKL})$
6	$\frac{4}{5}\langle \boldsymbol{p}_{pd}^2\rangle m_w(c_{w\rm eff}^{(6)TTTJ}\delta^{KL}+c_{w\rm eff}^{(6)TJKL})$
7	$-\frac{2}{3}\langle \boldsymbol{p}_{pd}^2\rangle m_w^2(2a_{w\rm eff}^{(7)TTTTJ}\delta^{KL}+3a_{w\rm eff}^{(7)TTJKL})-\frac{2}{7}\langle \boldsymbol{p}_{pd}^4\rangle a_{w\rm eff}^{(7)MMJKL}$
8	$2\langle \boldsymbol{p}_{pd}^2\rangle m_w^3(c_{w\rm eff}^{(8)TTTTTJ}\delta^{KL}+2c_{w\rm eff}^{(8)TTJKL})+\frac{6}{7}\langle \boldsymbol{p}_{pd}^4\rangle m_w c_{w\rm eff}^{(8)TMMJKL}$

hydrogen maser by factors of about a billion for $k = 2$ and about 10^{18} for $k = 4$. Moreover, the reach for the a- and c-type coefficients in Table IX is also substantially enhanced relative to related measurements of the $1S$-$2S$ transitions in hydrogen and deuterium. The prospects for these boosted measurements with a deuterium maser therefore appear excellent as well.

VI. POSITRONIUM

Positronium is another hydrogenic system with potential for measurable signals from Lorentz and *CPT* violation. Studies of *CPT* violation in positronium decay have been published for both experiment [35] and theory [36]. Here, we offer some remarks on the potential role of positronium spectroscopy the search for Lorentz and *CPT* violation.

The perturbative corrections to the hydrogen spectrum obtained in Secs. II and III cannot generically be applied to determine shifts in the positronium spectrum because the large magnetic moment of the positron implies the fine and hyperfine structures in positronium are comparable and so the hierarchy of angular-momentum couplings of hydrogen and positronium are different. However, the $nS_{1/2}$ levels present an exception to this, as the two schemes for angular-momentum couplings coincide when $L = 0$. We therefore focus here on experimental scenarios involving transitions among the $nS_{1/2}$ levels. In particular, we consider potential signals for Lorentz and *CPT* violation in the hyperfine splitting of the $1S$ ground-state levels and in the $1S$-$2S$ transition.

The quantum states of free parapositronium ($S = 0$) or orthopositronium ($S = 1$) are eigenstates of the charge-conjugation operator C, so only C-even Lorentz-violating operators can contribute to the energy shifts. Examining Table I reveals that only the electron coefficients c_{ekjm}^{NR} can contribute to spin-independent shifts of the positronium ground-state splitting, while only $g_{ekjm}^{\mathrm{NR}(0B)}$ and $g_{ekjm}^{\mathrm{NR}(1B)}$ can contribute to spin-dependent ones. This basic feature means that positronium naturally disentangles *CPT*-even and *CPT*-odd operators in the electron sector in the nonrelativistic limit.

In the limit of a weak applied magnetic field, the frequency shift $\delta\nu_{\mathrm{Z}}$ of the hyperfine Zeeman transitions in positronium is given by

$$2\pi\delta\nu_{\mathrm{Z}} = -\frac{\Delta m_F}{\sqrt{3\pi}}\sum_{q=0}^{2}(\alpha m_{\mathrm{r}})^{2q}(1+4\delta_{q2}) \times (g_{e(2q)10}^{\mathrm{NR}(0B)} + 2g_{e(2q)10}^{\mathrm{NR}(1B)}). \tag{126}$$

As expected, only contributions from coefficients controlling *CPT* violation appear. In contrast, in a strong applied magnetic field the quantum states of the system are no longer eigenstates of the charge-conjugation operator due to mixing of the entangled spin-triplet and spin-singlet levels. In this Paschen-Back limit, both *CPT*-odd and *CPT*-even Lorentz-violating operators contribute to the frequency shift,

$$2\pi\delta\nu_{\mathrm{PB}} = -\frac{1}{\sqrt{3\pi}}\sum_{q=0}^{2}(\alpha m_{\mathrm{r}})^{2q}(1+4\delta_{q2}) \times [(\Delta S_e + \Delta S_{\bar{e}})(g_{e(2q)10}^{\mathrm{NR}(0B)} + 2g_{e(2q)10}^{\mathrm{NR}(1B)}) - (\Delta S_e - \Delta S_{\bar{e}})(H_{e(2q)10}^{\mathrm{NR}(0B)} + 2H_{e(2q)10}^{\mathrm{NR}(1B)})], \tag{127}$$

where ΔS_e and $\Delta S_{\bar{e}}$ denote the electron and positron spin changes, respectively.

Current precision measurements of the positronium hyperfine structure lie in the ppm range, with an absolute uncertainty of order 1 MHz [99]. For example, this implies a potential reach of about 10^{-17} GeV for the coefficients $g_{e010}^{\mathrm{NR}(0B)}$ and $2g_{e010}^{\mathrm{NR}(1B)}$, about 10^{-6} GeV^{-1} for $g_{e210}^{\mathrm{NR}(0B)}$ and $2g_{e210}^{\mathrm{NR}(1B)}$, and about 10^{5} GeV^{-3} for $g_{e410}^{\mathrm{NR}(0B)}$ and $2g_{e410}^{\mathrm{NR}(1B)}$. While these sensitivities are about 9 orders of magnitude below those presented in Table III obtained via spectroscopy with a hydrogen maser taking only one coefficient nonzero at a time, the actual combinations of coefficients in the positronium and hydrogen observables are distinct. This confirms that positronium hyperfine measurements can be used to separate *CPT*-even and *CPT*-odd spin-dependent effects in the electron sector.

Positronium also has the advantage of being a purely leptonic atom, allowing precision tests of quantum electrodynamics or new physics via the direct comparison between experiment and theory. Paralleling the discussion for hydrogen, isotropic coefficients for Lorentz violation can be expected to shift the value of experimental measurements of the $1S$-$2S$ transition in positronium relative to the Lorentz-invariant theory. Comparing experiment to theory therefore provides a constraint on Lorentz violation in the electron sector.

The Lorentz-violating frequency shift for the $1S$-$2S$ transition in positronium is given by

$$2\pi\delta\nu = \frac{3}{2}(\alpha m_{\mathrm{r}})^2\left(\overset{\circ}{c}{}_{e,2}^{\mathrm{NR}} + \frac{67}{12}(\alpha m_{\mathrm{r}})^2\overset{\circ}{c}{}_{e,4}^{\mathrm{NR}}\right). \tag{128}$$

As expected, it contains only *CPT*-even effects. The observed difference between the theoretical and experimental values of the positronium $1S$-$2S$ frequency is 5.8 ± 3.3 MHz [100]. Identifying this difference with the frequency shift (128) yields the result

$$\overset{\circ}{c}{}_{e,2}^{\mathrm{NR}} + \frac{67}{12}(\alpha m_{\mathrm{r}})^2\overset{\circ}{c}{}_{e,4}^{\mathrm{NR}} \simeq (4.5 \pm 2.5) \times 10^{-6}\ \mathrm{GeV}^{-1}, \tag{129}$$

representing a 1.8 sigma effect. It can conservatively be taken as indicating an experimental reach of about 10^{-5} GeV^{-1} to the coefficients $\overset{\circ}{c}{}^{\rm NR}_{e,2}$ and about 10^{5} GeV^{-3} to $\overset{\circ}{c}{}^{\rm NR}_{e,4}$. Improvements of about a factor of 5 in the experimental sensitivity are within reach of future experiments [101].

Measuring the free-fall acceleration of positronium has been proposed as a test of the gravitational couplings of matter and antimatter [102], in a spirit similar to the proposals for antihydrogen discussed in Sec. IV D. Following the line of reasoning leading to Eq. (96), we find that nonzero isotropic coefficients for Lorentz violation lead to a fractional change in the gravitational acceleration of positronium given by

$$\left.\frac{\delta g}{g}\right|_{Ps} \approx \frac{8}{3}\,\overset{\circ}{c}{}^{\rm NR}_{e,0}. \tag{130}$$

Note this depends only on C-even Lorentz violation. The prospective measurements of the positronium gravitational acceleration at the 10% level could therefore either provide direct sensitivity to CPT-even Lorentz violation in the electron sector or help disentangle CPT-even and CPT-odd effects obtained in other experiments.

VII. HYDROGEN MOLECULES

High-precision molecular spectroscopy presents an interesting alternative potential arena for tests of Lorentz and CPT symmetry, albeit one that remains largely unexplored to date. Although the primary focus of the present work is hydrogenic systems, some of the tools developed here can be applied in the context of comparatively simple molecules and molecular ions such as H_2, H_2^+, HD, and HD^+. In this section, we offer a few comments about the prospects for measuring nonrelativistic spherical coefficients for Lorentz and CPT violation in these systems.

Corrections to the energy levels and internuclear distances of H_2, H_2^+, HD, and HD^+ arising from Lorentz and CPT violation in the electron sector of the minimal SME have previously been studied by Müller *et al.* [23]. In this work, the unperturbed molecular states are approximated by a wave function ansatz of the form $\phi_\gamma(\boldsymbol{r}_{a1})\phi_\gamma(\boldsymbol{r}_{b2}) + \phi_\gamma(\boldsymbol{r}_{b1})\phi_\gamma(\boldsymbol{r}_{a2})$ for H_2 or HD and $\phi_\gamma(\boldsymbol{r}_{a1}) + \phi_\gamma(\boldsymbol{r}_{b1})$ for H_2^+ or HD^+, where $\phi_\gamma(r) \equiv \exp(-\gamma r)$ and the displacements between the pointlike nuclei $f = a, b$ and the electrons $j = 1, 2$ are denoted by r_{fj}. The electron wave functions depend on two parameters, the bond length R of the molecule and the fall-off parameter γ, both of which are fixed by minimizing the expectation value of the electron Hamiltonian in the Born-Oppenheimer approximation.

Here, we extend this methodology to nonrelativistic spherical coefficients with $k = 2$ in the electron sector, which includes operators of arbitrary nonminimal dimension d. Incorporating coefficients with $k > 2$ is also of interest in principle, but it turns out that the higher powers of the momentum operator accompanying the larger values of k become unbounded with the simple wave function ansatz adopted here. A more sophisticated ansatz is likely to overcome this issue and would be of interest to investigate but lies beyond our present scope.

The relevant perturbation Hamiltonian $\delta h_e^{\rm NR}$ for Lorentz and CPT violation in the electron sector is given by Eqs. (3)–(6) with $w = e$ and $k = 2$. Using the appropriate ansatz for the wave function and working in a frame in which the z axis is aligned along the displacement $\boldsymbol{R}$ between the positions of the two nuclei, we find the energy shift of the ground state of H_2 due to Lorentz and CPT violation is given by

$$\langle \delta h_e^{\rm NR}\rangle_{H_2} = \frac{-1}{\sqrt{\pi}}\langle p^2 \mathcal{V}_{e200}^{\rm NR} + \sqrt{5}(p_z^2 - p_x^2)\mathcal{V}_{e220}^{\rm NR}\rangle, \tag{131}$$

while the shift for H_2^+ takes the form

$$\begin{aligned}\langle \delta h_e^{\rm NR}\rangle_{H_2^+} = {}& \frac{-1}{\sqrt{4\pi}}\langle p^2 \mathcal{V}_{e200}^{\rm NR} + \sqrt{5}(p_z^2 - p_x^2)\mathcal{V}_{e220}^{\rm NR}\rangle \\ & - \langle\sigma^3\rangle\sqrt{\frac{3}{4\pi}}\Big\langle \mathcal{T}_{e010}^{\rm NR(0B)} + p_z^2 \mathcal{T}_{e210}^{\rm NR(0B)} \\ & + 2p_x^2 \mathcal{T}_{e210}^{\rm NR(1B)} + \sqrt{\frac{7}{3}}(p_z^2 - p_x^2)\mathcal{T}_{e230}^{\rm NR(0B)}\Big\rangle.\end{aligned} \tag{132}$$

In the above equations, $\mathcal{V}_{ekj0}^{\rm NR}$, $\mathcal{T}_{ekj0}^{\rm NR(0B)}$, and $\mathcal{T}_{ekj0}^{\rm NR(1B)}$ are related to the electron coefficients for Lorentz and CPT violation via Eq. (6). The derivation of these results takes advantage of axial symmetry to replace factors of p_y^2 with p_x^2 for convenience.

Numerical values for the expectation values of the momenta in the above expressions are compiled in Table I of Ref. [23]. These tabulated values must be divided by a factor of two before substitution in Eq. (131) to match our use of $\boldsymbol{p}$ for the electron momentum, but they can be used directly in Eq. (132). For H_2^+, the expectation values of the electron spin operator $\boldsymbol{\sigma}$ appearing in Eq. (132) can be taken in the electron spin state to an excellent approximation because the two protons are in a symmetric singlet. Note that in principle operators with E-type parity might contribute to the shift (132). However, these are associated with the difference between $\langle\sigma^1\rangle$ and $\langle\sigma^2\rangle$. The symmetry of the system suggests equality of these expectation values and hence a zero contribution. This symmetry might fail in a more realistic model, but any corresponding effects are likely to be suppressed.

The analogue of the shift (132) for HD^+ is also of potential interest. However, the spin state of the electron in HD^+ is nontrivial, so expectation values involving all the components of $\boldsymbol{\sigma}$ play a role. The contributions from σ^m with $m = \pm 1$ for this case are given by

$$\langle \delta h_e^{\rm NR}\rangle_{HD^+} \supset -\sqrt{\frac{3}{4\pi}}\sum_m \langle\sigma^m\rangle \Big\langle \sum_k p_x^k \mathcal{T}_{ek1m}^{\rm NR(0B)} + (p_z^2 - p_x^2)\mathcal{T}_{e21m}^{\rm NR(1B)}\Big\rangle - \sqrt{\frac{7}{6\pi}}\sum_m \langle\sigma^m\rangle\langle (p_z^2 - p_x^2)\mathcal{T}_{e23m}^{\rm NR(0B)}\rangle, \tag{133}$$

where the sum over m spans the values $m = \pm 1$ and the sum over k the values $k = 0, 2$. The expectation values are understood to be taken in the electron part of the full spin wave function.

In addition to shifting the ground-state energy, the presence of Lorentz and *CPT* violation also modifies other physical quantities [23]. The bond length R is changed by an amount δR, which can be expressed as

$$\delta R = -\frac{1}{\partial_R^2 \epsilon_0}\partial_R \langle \delta h_e^{\rm NR}\rangle, \tag{134}$$

where the unperturbed ground-state energy ϵ_0 can be taken as the minimum of the expectation value of the Hamiltonian in the absence of Lorentz violation. The vibrational spectrum of the molecule within the electronic ground state is also shifted. An expression for this shift can be obtained by approximating the vibrating molecule as a harmonic oscillator and calculating the effective change $\delta\omega_v$ in the resonance frequency ω_v due to Lorentz and *CPT* violation. This yields

$$\delta\omega_v = \frac{\omega_v}{2\partial_R^2\epsilon_0}(\partial_R^3\epsilon_0\delta R + \partial_R^2\langle\delta h_e^{\rm NR}\rangle). \tag{135}$$

The rotational spectrum within the electronic ground state is shifted by the Lorentz and *CPT* violation as well. In the rigid rotor approximation, this shift can be understood as an effective change $\delta\omega_r$ in the rotation frequency ω_r given by

$$\delta\omega_r = -\frac{2\omega_r}{R}\delta R. \tag{136}$$

In the limit of zero nonminimal coefficients, all the above results reduce to the minimal-SME expressions presented in Ref. [23]. The nonminimal terms introduce several qualitatively novel features. One is the dependence of the bond length of H_2^+ on the electron spin state in the presence of Lorentz and *CPT* violation. Another noteworthy effect is the occurrence of contributions from coefficients with $j = 2$ and $j = 3$ to the ground-state energies of all the molecular species. This implies, for example, a signal involving sidereal variations at the third harmonic of the sidereal frequency, which could be detected in measurements of suitable rovibrational transitions. Including terms with values $k > 2$ would result in effects from coefficients with $j \geq 4$ as well, together with the concomitant sidereal signals at higher harmonics. In contrast, as discussed in Sec. II C, the ground state in atomic hydrogen only receives contributions from coefficients with $j \leq 1$.

Rovibrational transitions with unchanged electronic state in HD^+ are dipole allowed. Current experiments with HD^+ have reached an impressive relative uncertainty of about 10^{-9} [103]. The long lifetime of rovibrational excited states suggests considerable room for improvement remains, and indeed it is believed possible in principle for future experiments to achieve relative uncertainties of about 5×10^{-17} for H_2^+ and of order 10^{-18} for HD^+ [104]. For illustrative purposes here, consider future prospective relative uncertainties of about 10^{-14} in frequency measurements. Using the expressions (131) and (132), we find this corresponds to experimental sensitivities of about 10^{-9} GeV^{-1} to the nonrelativistic spherical coefficient with $k = 2$. For the coefficients with $j = 2$ and $j = 3$, a glance at Table VII reveals that this represents a sharper measurement by at least one order of magnitude than would be available using atomic hydrogen.

The discussion in this subsection suffices to confirm that spectroscopy of hydrogen molecules has the potential to provide competitive searches for Lorentz and *CPT* violation in coming years. Several improvements on the theoretical treatment can be envisaged. A comparatively straightforward one would be to adopt improved unperturbed electron ground states. For example, a more detailed form of the H_2^+ wave function has been available for many decades [105], and high-accuracy computations of various systematic effects now exist [106]. This or related improvements in the ground-state wave functions could also make feasible the calculations for coefficients with $k > 2$. Another improvement would be to incorporate contributions from the nucleons. The perturbative rovibrational shifts established above can be traced to the effective shift of the nucleon separation $\boldsymbol{R}$. However, in reality these transitions drastically change the vibrational states of the nucleons, which could plausibly lead to signals allowing sensitive measurements of coefficients in the proton and neutron sectors of the SME.

VIII. SUMMARY

In this paper, we studied spectroscopic searches for Lorentz and *CPT* violation using hydrogen, antihydrogen, deuterium, positronium, and hydrogen molecules and molecular ions. Our considerations begin in Sec. II with a treatment of theoretical aspects for hydrogen spectroscopy. The leading-order perturbative Hamiltonian (2) is constructed in the nonrelativistic limit, incorporating coefficients for Lorentz and *CPT* violation of arbitrary mass dimension d. These coefficients can be expressed in a spherical basis and separated into ones controlling *CPT*-even and *CPT*-odd effects, as presented in Eq. (6). The

symmetries of the hydrogen atom restrict the possible perturbative contributions to certain coefficients, listed in Table I along with some of their key features. The formalism permits determining the general matrix elements (18) of the full perturbation Hamiltonian δh_H^{NR}. The result is used in Sec. II C 2 to establish analytical expressions for the perturbative energy shifts. We follow this with a discussion of the general features of effects on the hyperfine Zeeman transitions, including notably the sidereal variations (35) and the annual variations discussed in Sec. II D 2.

The potential applications of our methodology to measurements using hydrogen spectroscopy are discussed in Sec. III. We first address the issue of possible signals for free hydrogen in Sec. III A, and then consider spectroscopy in an external magnetic field. We derive the explicit formula (49) for the Lorentz- and CPT-violating shift of the hyperfine Zeeman frequency, and we combine it with published results from experiments searching for sidereal variations using a hydrogen maser [14–16] to place the constraint (52) on a combination of nonrelativistic coefficients controlling spin-dependent effects. Taken one coefficient at a time, this constraint yields the results displayed in Table III. The prospects for hyperfine Zeeman measurements using annual variations and studies on a space-based platform are discussed in Secs. III B 4 and III B 5. We then turn to precision spectroscopy with nL-$n'L'$ transitions in hydrogen. The frequency shift for any hydrogen transition of this type with $J = 1/2$, $\Delta J = 0$ arising from isotropic Lorentz and CPT violation is given by Eq. (60). In Sec. III C 3, we consider various options for using annual variations of the $1S$-$2S$ transition frequency to measure coefficients for Lorentz and CPT violation. Results from an existing experiment of this type [18] are used to place first constraints on various nonminimal Cartesian coefficients with mass dimensions $5 \leq d \leq 8$, as reported in Table VI. In Sec. III D the possibility of measuring nonrelativistic coefficients with $j \geq 2$ using these types of transitions is discussed, and estimates for the reach of future analyses are presented in Table VII.

Antihydrogen spectroscopy in the context of the search for Lorentz and CPT violation is the topic of Sec. IV. The implementation of the CPT transformation on the hydrogen spectrum is provided in Sec. IV A. For hyperfine Zeeman transitions, the induced frequency shift is presented in Eq. (77), while for Paschen-Back transitions it is given in Eq. (81). The $1S$-$2S$ transition in free antihydrogen is shown to depend only on nonminimal coefficients for Lorentz and CPT violation, with the corresponding frequency shift specified in Eq. (84). For all these cases, we provide estimates of attainable sensitivities both from direct measurements and from comparisons with hydrogen spectroscopy. In Sec. IV D, the prospects for detecting an anomalous gravitational response of antihydrogen is considered. Insight into the role of nonminimal operators is obtained by constructing a generalization of the isotropic parachute model [86]. Sensitivity estimates for future experiments are obtained.

Deuterium spectroscopy is the focus of Sec. V. We obtain the corrections to the $1S$-$2S$ transition frequency arising from isotropic Lorentz and CPT violation in Eq. (103). Associated signals are discussed in Sec. V C. The observed difference between the square of the charge radii of the proton and deuteron [61,98] is used to derive the constraint (114) on nonrelativistic coefficients. Another interesting approach to using deuterium spectroscopy to search for Lorentz and CPT violation is performing hyperfine Zeeman measurements with a deuterium maser. The implications of this are discussed in Sec. V D, where we show that the Lorentz and CPT reach of a deuterium maser represents in principle an improvement of many orders of magnitude over that of a hydrogen maser.

Some aspects of positronium spectroscopy in the context of the search for Lorentz and CPT violation are considered in Sec. VI. We obtain expressions for the measurable frequency shifts and use the observed difference between theoretical and experimental values of the $1S$-$2S$ transition frequency to deduce the measurement (129) of isotropic coefficients in the electron sector. Finally, spectroscopy with hydrogen molecules and molecular ions is the subject of Sec. VII. We determine the energy shifts (131) and (132) for the ground states of these systems, and we discuss the sensitivities and potential advantages of the corresponding frequency measurements.

The discussions in this paper provide a working summary of the prospects for observing Lorentz and CPT violation using precision spectroscopy of a number of comparatively simple systems. Although our analysis has led to a variety of new or improved constraints, many coefficients for Lorentz and CPT violation remain unmeasured at present. The numerous potential signals identified and impressive attainable sensitivities in future experiments offer strong motivation for further analyses, along with encouragement for a potential breakthrough discovery in this foundational subject.

ACKNOWLEDGMENTS

This work was supported in part by the Department of Energy under Grant No. DE-SC0010120 and by the Indiana University Center for Spacetime Symmetries.

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