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High-precision determination of Lorentz-symmetry-violating parameters in Ca^+

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We present high-precision calculations of local Lorentz invariance (LLI) violating parameters of the $3d\,^2D_{3/2;5/2}$ states in Ca^+. We have employed three variants of the relativistic coupled-cluster (RCC) theory to determine these coefficients by gradually including electron correlation effects through the single, double, and triple excitation determinants from the Dirac-Hartree-Fock wave function. A precise estimate of the energy shift due to LLI violation depends on accurate evaluations of the expectation values of the square of the momentum operator ($\langle p^2\rangle$) and a second rank tensor ($\langle T_0^{(2)}\rangle$). It is found that the $\langle T_0^{(2)}\rangle$ values converge smoothly with the systematic inclusion of higher-order correlation effects in an expectation value evaluation approach, however, that is not the case for $\langle p^2\rangle$. Similar trends were also observed in the finite-field approach. To circumvent these problems, we determine $\langle p^2\rangle$ values very precisely by developing and applying an analytic gradient approach in the RCC framework. Corrections due to the Breit and quantum electrodynamics interactions are also estimated. Further, these calculations are validated by evaluating the energies and the quadrupole moments of the above states at different levels of approximations.

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Local Lorentz symmetry invariance (LLI) and Einstein equivalence principle (EEP) are two very fundamental requirements to validate the standard model (SM) of particle physics and general theory of relativity [1–4]. It is believed that these fundamental theories are valid only at much larger than Planck scales, but they can break at very high energy ($\sim 10^{19}$ GeV) or due to spontaneous symmetry breaking [5–7]. Breaking of LLI also implies violation of combined charge conjugation, parity, and time-reversal (CPT) symmetries in a local quantum-field theory [5,8]. Probing such violation can validate models that are attempting to unify gravity with the SM [9]. Therefore, testing invariance of these theories quantitatively are now of general interest. Present accelerator facilities are incapable of testing physics at the order of 10^{19} GeV energy. Therefore, by combining high-precision data from table-top low-energy experiments with accurate quantum mechanical calculations one can infer deviations from known physics. Such departures can validate plausible new physics by relating them with relics from the Planck scale [1,7]. There has been widespread search for LLI and EEP violating physics in the last two decades but without unambiguous signature thus far. One of the most well-known tests of this type is Michelson-Morley (MM) like experiments to verify the isotropy of the speed of light [10,11]. In an atomic system, LLI should ensure that kinetic energy of an electron must be independent of the direction of its velocity.

In a recent work [12], violation of LLI for electrons is demonstrated by performing an analog of a MM experiment in the singly charged calcium ion (Ca^+). In this experiment, anisotropic electron momentum distributions in the manifolds of the $3d\,^2D_{5/2}$ state of $^{40}Ca^+$ were interfered by trapping a pair of ions in the Paul trap. The quantization axis was defined by applying a static magnetic field and interference was created in the Ramsey-type interferometric scheme by changing the direction of the magnetic field with respect to location of the sun. The energy difference between the $M_J = \pm 5/2$ and $M_J = \pm 1/2$ sublevels of the $3d\,^2D_{5/2}$ state was measured by creating a product state $|\Psi^P\rangle = \frac{1}{2}[|-1/2\rangle + |-5/2\rangle] \otimes [|+1/2\rangle + |+5/2\rangle]$ after applying $\pi/2$- and π- pulse lasers to the $4s\,^2S_{1/2} - 3d\,^2D_{5/2}$ transition. Under common noise induced by a fluctuating magnetic field, this product state was transformed to a mixed state $|\Psi^R\rangle = \frac{1}{2}[|-5/2, +5/2\rangle + |-1/2, +1/2\rangle]$ with 50% probability. Similarly, a mirror state $|\Psi^L\rangle = \frac{1}{2}[|+5/2, -5/2\rangle + |+1/2, -1/2\rangle]$ was created to measure the average frequency difference between the time evolution of these states. Measurements were performed for about 95 ms to suppress the systematics due to gradient of external magnetic fields. Repeating the experiment for about 23 h, a sensitivity of the oscillation frequency of 11 mHz was observed. This was then attributed to residual variation of the energy correlated with Earth's rotation to violation of LLI. To infer limits on various parameters describing LLI violation, the measured frequency was combined with the corresponding electronic calculations. In Ref. [12], theoretical results for both the $3d\,^2D_{3/2;5/2}$ states of Ca^+ were obtained by employing a variety of many-body methods including relativistic coupled-cluster (RCC) theory. Large discrepancies among these calculations were found and the final values were reported with relatively large error bars. In this Rapid Communication, we analyze these calculations further by accounting for higher-order corrections and adopting different procedures in the RCC theory to appraise limits on the LLI violating parameters scrupulously.

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The electronic quantum electrodynamics (QED) Lagrangian, in a coordinate system in which a hypothetical LLI violation in light is manifested, is given by [8,13]

$$\mathcal{L} = \tfrac{1}{2}\iota\bar{\psi}_e(\gamma_\nu + c'_{\mu\nu}\gamma^\mu)\overleftrightarrow{D}^\nu\psi_e - m_e\bar{\psi}_e\psi_e, \tag{1}$$

where ψ_e is the Dirac spinor for an electron, m_e is electron mass, γ are Dirac matrices, $\bar{\psi}_e\overleftrightarrow{D}^\nu\psi_e = \bar{\psi}_e D^\nu\psi_e - \psi_e D^\nu\bar{\psi}_e$ with the covariant derivative D^ν, and $c'_{\mu\nu}$ is a frame-dependent dimensionless matrix involving even and odd components with $\mu, \nu = 0, 1, 2, 3$ being the space-time coordinates. The $c'_{\mu\nu} = c_{\mu\nu} + k_{\mu\nu}/2$ matrix actually carries LLI violation information for both the electron (denoted by $c_{\mu\nu}$ component) and photon (denoted by $k_{\mu\nu}$ component). In the Ca^+ experiment, $c'_{\mu\nu}$ was specified in the sun-centered celestial-equatorial frame (SCCEF). The time-dependent values of this tensor can transform from SCCEF to the local laboratory frame on Earth due to its rotation. Hence, they can vary in time when measurements are performed in the laboratory. In an atomic system, this can give rise to an interaction Hamiltonian for a bound electron with momentum $\vec{p}_e$ [14,15] ,

$$H^{\rm LLI} = -\Gamma_L\frac{\vec{p}_e^{\,2}}{2m_e} - \frac{1}{6m_e}C_0^{(2)}T_0^{(2)}, \tag{2}$$

where $\Gamma_L = C_0^{(0)} - \frac{2U}{3c^2}c_{00}$ for speed of light c, $(2U/3c^2)c_{00}$ representing the gravitational redshift anomaly for the Newtonian potential U, and $C_0^{(0)} = c_{00} + \frac{2}{3}(c_{11} + c_{22} + c_{33})$; $C_0^{(2)} = c_{11} + c_{22} - 2c_{33}$, and $T_0^{(2)} = c\gamma^0(\gamma^j p_j - 3\gamma^3 p_3)$. The first-order energy shift due to the above Hamiltonian is given by $\delta E^{(1)} = \langle H^{\rm LLI}\rangle$. By combining the measured value of $\delta E^{(1)}$ with atomic calculations of $\langle\vec{p}_e^{\,2}\rangle$ and $\langle T_0^{(2)}\rangle$ in a given state, it is possible to infer the LLI violating $C_0^{(0)}$ and $C_0^{(2)}$ parameters. These two parameters can be deduced by determining $\delta E^{(1)}$ values at least either in two independent atomic states or differential shifts between two atomic transitions.

The coupled-cluster theory is one of the leading quantum many-body methods, referred to as the gold standard for treating electron correlation, and has been applied to the atoms, molecules, condensed matter systems, and nuclei [16–18]. Thus, it can be anticipated that $\langle\vec{p}_e^{\,2}\rangle$ and $\langle T_0^{(2)}\rangle$ values can be estimated precisely using RCC theory. Besides, it was demonstrated recently by employing RCC theory at various levels of approximation that trends of electron correlation effects vary diversely in the determination of properties having different radial and angular factor dependencies [19]. Therefore, it is necessary to verify convergence in the calculation of any property with the inclusion of higher-order effects to gauge its accuracy. The exact wave functions of the $3d\,^2D_{3/2;5/2}$ states in Ca^+ can be expressed in the RCC theory as (e.g., see [19])

$$|\Psi_v\rangle = e^T\{1 + S_v\}|\Phi_v\rangle, \tag{3}$$

where $|\Phi_v\rangle = a_v^+|\Phi_0\rangle$ with the Dirac-Hartree-Fock (DHF) wave function $|\Phi_0\rangle$ of the Ca^{2+} ground-state configuration and the corresponding valence orbital $v = 3d_{3/2;5/2}$. In the above expression, T is the RCC excitation operator embodying electron correlation effects from $|\Phi_0\rangle$ and the S_v operator incorporates core-valence and valence electron correlation effects from $|\Phi_v\rangle$. To demonstrate the role of electron correlation effects for accurate evaluations of $\langle\vec{p}_e^{\,2}\rangle$ and $\langle T_0^{(2)}\rangle$, we want to give results at various levels of approximation in the RCC theory, as described below, and compare them with the values obtained using the DHF method and the second-order relativistic many-body perturbation theory [RMBPT(2) method].

Excitation levels by the RCC operators are denoted by

$$T = T_1 + T_2 + \cdots + T_n, \tag{4}$$

and

$$S_v = S_{1v} + S_{2v} + \cdots + S_{nv}, \tag{5}$$

where subscript $k = 1, 2, \ldots n$ stands for level of excitation with $n = 18$ indicating number of core electrons. Due to computational challenges, RCC theory is often approximated to the dominantly contributing single and double excitations (RCCSD method). With the availability of modern supercomputers, it has become possible to apply RCC theory with single, double, and triple excitations (RCCSDT method) and occasionally up to quadruple and pentuple excitations by freezing low-lying core orbitals. Here, we consider up to the RCCSDT method to demonstrate convergence in the results by exciting all the core electrons. We also present results only by considering the linear terms in the RCCSD method (denoted by RLCCSD method) to highlight contributions due to the nonlinear terms. Similarly, we give results by suppressing T_3 but including only S_{3v} in the RCCSDT method (referred to as the RCCSDTv method) to show importance of correlation effects through both the T_3 and S_{3v} operators. Amplitudes of these RCC operators, and energies are obtained by solving

$$\langle\Phi_0^L|\bar{H}_N^{at}|\Phi_0\rangle = \delta_{L,0}\Delta E_0, \tag{6}$$

and

$$\langle\Phi_v^L|\bar{H}_N^{at}\{1 + S_v\}|\Phi_v\rangle = \Delta E_v\langle\Phi_v^L|\{\delta_{L,0} + S_v\}|\Phi_v\rangle, \tag{7}$$

with $\bar{H}_N^{at} = e^{-T}H_N^{at}e^T$ for the normal ordered atomic Hamiltonian H_N^{at}, superscript L indicating $L^{\rm th}$ excited determinant, ΔE_0 the correlation energy of Ca^{2+}, and ΔE_v the electron affinity (EA) of the electron in the v orbital of Ca^+. The energies are determined by

$$\Delta E_0 = \langle\Phi_0|\overline{H}_N^{at}|\Phi_0\rangle, \tag{8}$$

and

$$\Delta E_v = \langle\Phi_v|\overline{H}_N^{at}\{1 + S_v\}|\Phi_v\rangle. \tag{9}$$

In the RCCSD method, when partial valence triple excitations are included through Eq. (9), we refer to it as the RCCSD(T) method. After obtaining wave functions, we calculate expectation value of an operator O as

$$< O >= \frac{\langle\Phi_v|\{1 + S_v^\dagger\}e^{T^\dagger}Oe^T\{1 + S_v\}|\Phi_v\rangle}{\langle\Phi_v|\{1 + S_v^\dagger\}e^{T^\dagger}e^T\{1 + S_v\}|\Phi_v\rangle}. \tag{10}$$

In this expectation value evaluation (EVE) expression, both $e^{T^\dagger}Oe^T$ and $e^{T^\dagger}e^T$ contain finite terms in the RLCCSD method but they are nonterminating when all nonlinear terms are included in the RCC theory. To account for contributions that are significant from these nonterminating series, we have used the generalized Wick's theorem to divide them into effective one-body, two-body, and three-body terms in order to compute both the nonterminating series systematically as described in [20]. We also calculate the above expression retaining

TABLE I. The $\langle|p^2|\rangle$ values and $\langle||T^{(2)}||\rangle$ reduced matrix elements in atomic units from the EVE approach of RCC theory. Corrections from the Breit and lower-order QED interactions are added subsequently. The results for $\langle|p^2|\rangle$ show peculiar trends, but the $\langle||T^{(2)}||\rangle$ values converge after inclusion of triples. We have also quoted values from different methods used in Ref. [12] and experimental $\langle|p^2|\rangle$ values as two times the EAs [22] in the nonrelativistic limit of VT.

	$\langle\|p^2\|\rangle$		$\langle\|\|T^{(2)}\|\|\rangle$		Reference
Method	$3D_{3/2}$	$3D_{5/2}$	$3D_{3/2}$	$3D_{5/2}$	
DHF	3.050	3.039	5.454	7.116	This work
	3.05	3.04	5.45	7.12	[12]
RMBPT(2)	1.279	0.794	7.052	9.092	This work
RPA	0.66	0.66	5.72	7.47	[12]
CI+SD	0.73	0.73	6.89	8.98	[12]
RLCCSD	−0.037	−0.887	7.551	9.682	This work
All-order	0.83	0.83	7.09	9.25	[12]
RCCSD^2	0.421	−0.298	7.295	9.375	This work
RCCSD	0.392	−0.311	6.956	8.878	This work
RCCSD(T)	0.389	−0.318	6.975	8.901	This work
RCCSDpT	0.244	−0.412	6.965	8.875	This work
RCCSDTv	0.065	−0.630	6.953	8.867	This work
RCCSDT	0.011	−0.787	6.961	8.879	This work
	Relativistic corrections				
+Breit	0.012	−0.786	6.966	8.889	This work
+QED	0.012	−0.786	6.967	8.890	This work
Final	Unsure	Unsure	6.97(5)	8.89(7)	This work
	0.75(9)	0.75(9)	7.09(12)	9.25(15)	[12]
VT	0.748	0.748			[22]

only the terms that appear in the RLCCSD method but use amplitudes from the RCCSD method (RCCSD^2 method). This can demonstrate roles of nonlinear terms in the determination of wave functions. Again, we include contributions from the valence triple excitations perturbatively in the above expression after evaluating wave functions using the RCCSD(T) method (RCCSDpT method) to show differences in the results due to inclusion of triple effects through the perturbative approach and in the exact form in the RCCSDT method. It is worth mentioning here that we compute these terms adopting exclusion-principle-violating (EPV) Goldstone diagrams [21]. The unphysical contributions involved in this approach can cancel out through the direct and exchange terms in the exact formulation of RCC theory, but it can result in some errors in an approximated method. Such errors can be minimized by including higher-level terms. All the above exercises to perform calculations at different levels of approximations are intended to help us in a comprehensive understanding of roles of electron correlation effects to explain the reasons for discrepancies in results among various many-body methods.

In Table I, we present $\langle\vec{p}_e^{\,2}\rangle$ and $\langle T_0^{(2)}\rangle$ values of the $3d\,^2D_{3/2;5/2}$ states in Ca^+ that are obtained by employing the aforementioned RCC methods along with the results that are reported in [12]. In the table, the methods from top to bottom can be viewed as encompassing more physical effects than the previous method. The results are also quoted after adding corrections from the Breit interaction and QED effects subsequently. In the earlier study [12], it was found that RPA values are smaller than the All-order results. These All-order values were obtained by employing RCC theory with the similar approximation to our RLCCSD method (SD method) but by including perturbative triples and scaling the dominant terms of the higher-order RCC theory. A hybrid method of configuration interaction and the SD (CI+SD) method was also employed in that work giving intermediate values between the RPA and All-order calculations. In the above work, the final values were given in atomic units (a.u.) as $\langle\vec{p}_e^{\,2}\rangle = 0.75(9)$ for both the states, and the reduced matrix elements as $\langle 3D_{3/2}||T_0^{(2)}||3D_{3/2}\rangle = 7.09(12)$ and $\langle 3D_{5/2}||T_0^{(2)}||3D_{5/2}\rangle = 9.25(15)$. The $\langle\vec{p}_e^{\,2}\rangle$ values were actually taken as twice the EA from the National Institute of Science and Technology (NIST) database [22] in the nonrelativistic limit of the Virial Theorem (VT). Our RLCCSD and RCCSD^2 results for $\langle T_0^{(2)}\rangle$ are found to be closer to the final values of Ref. [12], but the $\langle\vec{p}_e^{\,2}\rangle$ values differ significantly. Further attempt to include higher-order correlation effects through the nonlinear terms in the RCCSD, RCCSDTv, and RCCSDT methods lower the $\langle T_0^{(2)}\rangle$ values in both the states but we find that the $\langle\vec{p}_e^{\,2}\rangle$ values show peculiar trends. We ascribe this unusual behavior in $\langle\vec{p}_e^{\,2}\rangle$ to two reasons; first the correlation effects are found to be very large (as seen from the difference between the DHF and RCC results) and secondly, truncation in Eq. (10) may cause instability in the calculations due to EVE diagrams. By analyzing finite-size basis functions used in the calculations and trends in the correlation effects from the RCCSD to RCCSDT methods, we recommend the final values for $\langle T_0^{(2)}\rangle$ as 6.97(5) a.u. and 8.89(7) a.u. in the $3d\,^2D_{3/2}$ and $3d\,^2D_{5/2}$ states, respectively. They are accurate to within 1%, whereas the EVE approach is unable to provide reliable results for $\langle\vec{p}_e^{\,2}\rangle$. In an attempt to get $\langle\vec{p}_e^{\,2}\rangle$ reliably, we also used the finite-field (FF) approach in which the effective Hamiltonian is considered as $H_N = H_N^{at} + \lambda\vec{p}_e^{\,2}$ for an arbitrary small perturbative parameter λ and express the EA value obtained using this effective Hamiltonian as

$$\Delta E_v = \Delta E_v^{(0)} + \lambda\Delta E_v^{(1)} + O(\lambda)^2. \tag{11}$$

Hereafter superscripts (0) and (1) represent results from H_N^{at} and its first-order correction, respectively. From the above expression, we can get

$$\langle\vec{p}_e^{\,2}\rangle \equiv \Delta E_v^{(1)} \simeq \left.\frac{\partial\Delta E_v}{\partial\lambda}\right|_{\lambda=0}, \tag{12}$$

by neglecting $O(\lambda)^2$ contributions. The $\langle\vec{p}_e^{\,2}\rangle$ values obtained from the FF approach with $\lambda = 1.0\times10^{-5}$ are given in Table II for both the $3d\,^2D_{3/2}$ and $3d\,^2D_{5/2}$ states at different levels of RCC theory along with the DHF and RMBPT(2) methods. We observe that when triples are included in various forms through the amplitude equations, the results dwindle gradually. It should be noticed that $O(\lambda)^2$ contributions are being neglected to estimate the $\langle\vec{p}_e^{\,2}\rangle$ values. Given the fact that this property shows strong correlation effects in the EVE approach, neglecting higher-order corrections in the FF approach may be leading to large uncertainties.

To circumvent the problems from the EVE and FF procedures for reliable determination of $\langle\vec{p}_e^{\,2}\rangle$, we have developed and applied the analytic gradient (AG) approach as discussed

TABLE II. Comparison of the $\langle|p^2|\rangle$ values in atomic units in the FF and AG frameworks of the RCC theory at different levels of approximation. Corrections from higher-order relativistic effects are also quoted. As seen, FF values do not converge after inclusion of triples while AG procedure offers converged values decisively in the RCC theory.

	FF approach		AG approach	
Method	$3D_{3/2}$	$3D_{5/2}$	$3D_{3/2}$	$3D_{5/2}$
DHF	0.646	0.645	3.050	3.039
RMBPT(2)	0.728	0.726	2.142	1.889
RLCCSD	0.741	0.739	0.591	0.589
RCCSD	0.725	0.723	0.785	0.779
RCCSD(T)	0.718	0.716	0.750	0.745
RCCSDTv	0.240	−0.009	0.677	0.673
RCCSDT	0.203	−0.035	0.658	0.656
	Relativistic corrections			
+Breit	0.205	−0.033	0.660	0.658
+QED	0.205	−0.033	0.661	0.658
Final	Unsure	Unsure	0.660(5)	0.660(5)

TABLE III. Demonstration of convergence of EA and Θ values of the $3d\,^2D_{3/2;5/2}$ states in Ca^+ using different approximations of RCC theory compared to their available experimental values. It clearly suggests the importance of including triples for studying properties of the considered states.

	Electron affinity (in cm^{-1})		Θ value (in a.u.)	
Method	$3D_{3/2}$	$3D_{5/2}$	$3D_{3/2}$	$3D_{5/2}$
DHF	72617.49	72593.39	1.712	2.451
RMBPT(2)	82128.31	82051.23	1.287	1.845
RLCCSD	83538.93	83448.59	1.243	1.782
RCCSD	81753.82	81670.99	1.305	1.870
RCCSD(T)	80863.66	80783.04	1.297	1.860
RCCSDTv	81885.55	81805.00	1.292	1.852
RCCSDT	81938.03	81860.75	1.290	1.847
	Relativistic corrections			
+Breit	81976.09	81914.00	1.281	1.844
+QED	81982.01	81919.47	1.280	1.843
Final	81982(150)	81919(150)	1.280(7)	1.843(7)
Experiment	82101.68 [22]	82040.99 [22]		1.83(1) [23]

below. In this approach, we perturb the wave function and energy explicitly due to $\vec{p}_e^{\,2}$ as

$$|\Psi_v\rangle = \left|\Psi_v^{(0)}\right\rangle + \lambda\left|\Psi_v^{(1)}\right\rangle + \cdots, \tag{13}$$

$$\Delta E_v = \Delta E_v^{(0)} + \lambda\Delta E_v^{(1)} + \cdots, \tag{14}$$

and obtain $\langle\vec{p}_e^{\,2}\rangle \equiv \Delta E_v^{(1)}$ directly by solving

$$\left(H_N^{at} - \Delta E_v^{(0)}\right)\left|\Psi_v^{(1)}\right\rangle = \left(\Delta E_v^{(1)} - \vec{p}_e^{\,2}\right)\left|\Psi_v^{(0)}\right\rangle, \tag{15}$$

where $|\Psi_v^{(1)}\rangle$ is the first-order perturbed wave function to $|\Psi_v^{(0)}\rangle$. In the RCC theory, it yields

$$\left|\Psi_v^{(1)}\right\rangle = e^{T^{(0)}}\left((1+T^{(1)})S_v^{(0)} + S_v^{(1)}\right)|\Phi_v\rangle. \tag{16}$$

Amplitudes of the perturbed RCC operators are obtained by solving the following equations:

$$\left\langle\Phi_0^L\right|\bar{H}_N^{at}T^{(1)} + \bar{\vec{p}}^{\,2}|\Phi_0\rangle = 0, \tag{17}$$

and

$$\left\langle\Phi_v^L\right|\left(\bar{H}_N^{at} - \Delta E_v^{(0)}\right)S_v^{(1)} + \left(\bar{H}_N^{at}T^{(1)} + \bar{\vec{p}}^{\,2} - E_v^{(1)}\right) \times\left\{1 + S_v^{(0)}\right\}|\Phi_v\rangle = 0, \tag{18}$$

where $\bar{\vec{p}}^{\,2} = e^{-T^{(0)}}\vec{p}^{\,2}e^{T^{(0)}}$. It follows that

$$\Delta E_v^{(1)} = \langle\Phi_v|\bar{H}_N^{at}S_v^{(1)} + \left(\bar{H}_N^{at}T^{(1)} + \bar{\vec{p}}^{\,2}\right)\left\{1 + S_v^{(0)}\right\}|\Phi_v\rangle. \tag{19}$$

From a careful scrutiny, one can easily see that λ does not appear anywhere in the evaluations of $\Delta E_v^{(1)}$ and $|\Psi_v^{(1)}\rangle$ in the AG approach in contrast to the FF procedure. Moreover, all the terms involved in the AG approach terminate. We have given the $\langle\vec{p}_e^{\,2}\rangle$ values from this approach in Table II at different approximations of the RCC theory including their DHF and RMBPT(2) values. These calculations show convergence in the values gradually in the inclusion of nonlinear terms both in the RCCSD and RCCSDT methods. The reason for the discrepancies between the results from the AG approach and those that are inferred using VT (given in Table I) could be due to neglecting relativistic effects and assumption of the isotropic nature of electronic orbitals by VT. The final values are estimated as 0.660(5) a.u. for both the $3d\,^2D_{3/2}$ and $3d\,^2D_{5/2}$ states after including the Breit and QED corrections. These are about 1% accurate, as compared to the previously reported values with 12% uncertainty [12].

We also validate our calculations of $\langle\vec{p}_e^{\,2}\rangle$ and $\langle T_0^{(2)}\rangle$ by reproducing some of the measured quantities employing the above approximated RCC methods. For this purpose, we determine EAs and electric quadrupole moments (Θ) of the $3d\,^2D_{3/2;5/2}$ states of Ca^+. EAs are taken as input to obtain wave functions in our RCC theory and, again, evaluation of EAs depends on the accuracies of the $\langle\vec{p}_e^{\,2}\rangle$ values. Similarly, we assess accuracies of $\langle T_0^{(2)}\rangle$ with that of Θ values as both are described by rank-two operators. In Table III, we have quoted the EA and Θ values from different many-body methods and compared them with the available experimental results [22,23]. We find quite a good agreement between our calculations and experimental values. From the calculations, it can be seen that the EAs improve drastically from the RCCSD method to the RCCSDT method. In fact, we also find significant improvement in the Θ values due to triples and this is more precise than measurement. This implies inclusion of triples is crucial for studying properties of the $3D_{3/2;5/2}$ states in Ca^+. It now asserts the validity of our $\langle\vec{p}_e^{\,2}\rangle$ and $\langle T_0^{(2)}\rangle$ calculations. Substituting these values, we get changes in energies in the above states as

$$\delta E_{3D_{3/2}} = \left[-2.17(2)\Gamma_L + \left(2.13(2) - 1.71(1)M_J^2\right)C_0^{(2)}\right], \tag{20}$$

and

$$\delta E_{3D_{5/2}} = \left[-2.17(2)\Gamma_L + \left(2.08(2) - 0.713(6)M_J^2\right)C_0^{(2)}\right], \tag{21}$$

in units of $\times 10^{15}$ Hz for the corresponding sublevel M_J. This in combination with the measurement can provide stringent

limits on the LLI coefficients $C_0^{(0)}$ and $C_0^{(2)}$. It yields the difference between the $M_J = 5/2$ and $M_J = 1/2$ sublevels of the $3d\,^2D_{5/2}$ state as

$$\delta E_{3D_{5/2}}(M_J = 5/2) - \delta E_{3D_{5/2}}(M_J = 1/2) = -4.28(4) C_0^{(2)} \times 10^{15}\ \text{Hz}. \quad (22)$$

Considering its experimental value as 11 mHz, we get

$$C_0^{(2)} \simeq 2.6 \times 10^{-18}, \quad (23)$$

after 95 ms of averaging [12]. This limit can be used further in the SCCEF by expressing it as

$$C_0^{(2)} = A + \sum_j (C_j \cos(\omega_j T) + S_j \sin(\omega_j T)), \quad (24)$$

where C_j, S_j, and ω_j are the amplitudes and angular frequency that are listed in Ref. [12] and T is the time since vernal equinox of 2014. It would be desirable to carry out similar measurement in the $3d\,^2D_{3/2}$ state to affirm the above result and to infer limit on $C_0^{(0)}$.

In summary, we have employed the RCC theory with single, double, and triple excitations to determine energy shifts in the $3d\,^2D_{3/2;5/2}$ states of $^{40}Ca^+$ due to LLI violation. This is necessary for accurate evaluations of the expectation values of the square of the momentum operator and a second rank tensor. We have estimated them to within 1% accuracies by analyzing the calculations in different frameworks of the RCC theory. As a result, the energy shifts due to the LLI interaction Hamiltonian are also obtained to within 1% accuracies. Combining our calculation with the measurement in the $3d\,^2D_{5/2}$ state, a precise limit on the $C_0^{(2)}$ coefficient pertaining to the LLI tensor $c_{\mu\nu}$ is quoted. We also suggest that a similar measurement could be carried out for the $3d\,^2D_{3/2}$ state to impose a stringent limit on $C_0^{(0)}$.

Computations were carried out using the Vikram-100 high-performance computer of Physical Research Laboratory, Ahmedabad, India.

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