Search for CP-violating nuclear magnetic quadrupole moment using the LuOH\(^+\) cation

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The CP-violating interaction of the nuclear magnetic quadrupole moment (MQM) of the \(^{175}\)Lu nucleus with electrons in the molecular cation LuOH\(^+\) is studied. The resulting effect is expressed in terms of CP-odd parameters, such as quantum chromodynamics angle \(θ\), quark EDM and chromo-EDM. For this we have performed a calculation of the nuclear MQM as well as the molecular constant that characterises the interaction of this MQM of \(^{175}\)Lu with electrons. Additionally, we predict the hyperfine structure constants for the ground electronic state of LuOH\(^+\). We conclude that LuOH\(^+\) is a promising system to measure the nuclear MQM.

I. INTRODUCTION

Study of the time-reversal (T) and spatial parity (P) violating forces inside the nucleus is of the key importance to test extensions of the standard model. According to the CPT theorem, T-violation implied also CP-violation, where C is the charge conjugation. As it was shown by A.D. Sakharov \(^1\), CP-invariance violation is one of the three necessary conditions to explain the baryon asymmetry of the Universe, also known as matter-antimatter asymmetry. Investigation of CP-violation in nature is closely related to the explanation of the predominance of baryon matter, which is called “one of the great mysteries in physics” \(^2\) and can not be explained within the standard model.

As it was realized in the second half of the 20th century, atoms and molecules are very promising systems to search for the CP- and T,P-violating interactions. Indeed, the best limitation on the electron electric dipole moment has been established in the molecular experiment using the neutral \(^{232}\)ThO molecule \(^3\). A very sensitive experiment to search for the electron EDM has also been performed using the trapped \(^{180}\)Hf\(^+\) molecular cations \(^4\).

The present study is devoted to another source of CP-violation, the nuclear magnetic quadrupole moment (MQM). It is induced by CP-violating internal nuclear interactions and therefore can serve as an indicator of invariance violation in the hadron sector. As it is shown below, nuclear MQM is proportional to the CP-violating parameters of the standard model. Therefore, its measurement can be used to determine these parameters indirectly.

Recently, it was noted \(^3,6\) that linear triatomic molecules with heavy atoms such as YbOH have certain advantages to search for T,P-violating effects over corresponding isoelectronic diatomic molecules. In such molecules, there is a small energy gap between levels of opposite parity due to the \(l\)-doubling effect \(^6\). This allows one to fully polarize them using a relatively weak electric field. Additionally, the \(l\)-doublet can be used to suppress systematic errors arising from magnetic fields, regardless of the electronic state. Another feature of linear triatomics is their ability to be cooled by the laser-cooling technique. The ytterbium monohydroxide molecule has been studied by several theoretical groups \(^5,10\). It can be cooled to temperatures lower than 1 mK \(^11\). This allows one to increase the coherent time significantly and increase sensitivity to T,P-odd effects which is inversely proportional to this time.

In the present paper, we study another triatomic system — the \(^{175}\)LuOH\(^+\) molecular cation. The \(^{175}\)Lu nucleus has the spin \(I = 7/2 > 1\) and therefore can have the CP-violating nuclear MQM. Experimentally, \(^{175}\)Lu is an appealing species as the atomic ion Lu\(^+\) can be directly laser cooled and stored under ultra-high vacuum in an ion trap \(^12\). The molecular ion LuOH\(^+\) could then be created by reacting the cold Lu\(^+\) with, e.g., water or methanol. Remaining Lu\(^+\) ions can be used to sympathetically cool the LuOH\(^+\) molecules. The LuOH\(^+\) molecule has a simple electronic structure, with a single valence electron and a \(2Σ_{1/2}\) ground state, which facilitates state preparation via optical pumping schemes, and state detection of the molecule can be achieved by performing resonant dissociation followed by observing Lu\(^+\) fluorescence, or via quantum logic spectroscopy using Lu\(^+\) as a logic ion \(^13\).
II. NUCLEAR MAGNETIC QUADRUPOLE MOMENT

We perform calculation of MQM using the technique used in Ref. [15]. Nucleus $^{175}$Lu is deformed, therefore, we use deformed oscillator Nilsson model for proton and neutron orbitals. Formula for the contribution of a Nilsson orbital to the nuclear MQM has been derived in Ref. [18]. Summation over nucleons gives the following result for the $^{175}$Lu collective MQM:

$$M = 15M_P^p + 32M_p^o,$$  \hspace{1cm} (1)

where $M_P^p$ and $M_p^o$ are the single-particle matrix elements for protons and neutrons which depend on the form of the T,P-odd interaction. For comparison we also calculated $^{173}$Yb collective MQM:

$$M = 14M_P^p + 23M_p^o,$$  \hspace{1cm} (2)

The coefficient before the neutron contribution (equal to 23) is now slightly different from the value in Ref. [18] (formerly 26) due to a small contribution of deep neutron orbitals accounted in the present work.

We start from a contact T,P-odd nuclear potential

$$V^{TP}_{p,n} = \eta_{p,n} \frac{G}{2\sqrt{2}m_p} (\sigma \cdot \nabla \rho),$$  \hspace{1cm} (3)

acting on the valence nucleon. Here $\eta_{p,n}$ is the dimensionless strength constant, $\rho$ is the total nucleon number density, $G$ is the Fermi constant, $m_p$ is the proton mass. Using Eq. (3) and values of $M_P^o = -0.76\eta_p \cdot 10^{-34} e \cdot cm^2 + 2.1d_p \cdot 10^{-14} cm$ and $M_p^o = 0.80\eta_p \cdot 10^{-34} e \cdot cm^2 + 2.1d_n \cdot 10^{-14} cm$ from Refs. [18, 19] we obtain:

$$M = (2.6\eta_n - 1.1\eta_p) \cdot 10^{-33} e \cdot cm^2 + (0.67d_n + 0.31d_p) \cdot 10^{-12} cm,$$  \hspace{1cm} (4)

where $d_n$ and $d_p$ are neutron and proton electric dipole moments. The $T$-, $P$- odd nuclear potential Eq. (3) is dominated by the neutral $\pi_0$ exchange between the nucleons and the strength constants $\eta$ may be expressed in terms of $\pi NN$ couplings (see details in Ref. [19]):

$$\eta_n = -\eta_p \approx 5 \times 10^6 g (\tilde{g}_1 + 0.4\tilde{g}_2 - 0.2\tilde{g}_0),$$  \hspace{1cm} (5)

where $g$ is the strong $\pi NN$ coupling constant and $\tilde{g}_0, \tilde{g}_1, \tilde{g}_2$ are three $T_-, P$-odd $\pi NN$ coupling constants, corresponding to the different isotopic channels. Substitution of these $\eta_{n,p}$ into Eq. (4) gives:

$$M = g (1.8\tilde{g}_1 + 0.73\tilde{g}_2 - 0.37\tilde{g}_0) \times 10^{-26} e \cdot cm^2 + (0.67d_n + 0.31d_p) \cdot 10^{-12} cm,$$  \hspace{1cm} (6)

Constants of the $T_-, P$-odd $\pi NN$ interaction $\tilde{g}$ and nucleon EDMs may be expressed in terms of more fundamental $T_-, P$- violating parameter, QCD constant $\bar{\theta}$, or EDM $d$ and chromo-EDM $\bar{d}$ of $u$ and $d$ quarks [20, 21]

$$\tilde{g}_0(\bar{\theta}) = -0.21\bar{\theta},$$

$$g\tilde{g}_1(\bar{\theta}) = 0.046\bar{\theta},$$

$$d_n = -d_p = 1.2 \cdot 10^{-16} \bar{\theta} \cdot e \cdot cm,$$

$$g\tilde{g}_0(d_u, d_d) = 0.8 \times 10^{15} (d_u + d_d) \text{ cm}^{-1},$$

$$g\tilde{g}_1(d_u, d_d) = 4 \times 10^{15} (d_u - d_d) \text{ cm}^{-1},$$

$$d_p(d_u, d_d, d_u, d_d) = 1.1e (d_u + 0.5d_d) + 0.8d_u - 0.2d_d,$$

$$d_n(d_u, d_d, d_u, d_d) = 1.1e (d_d + 0.5d_u) - 0.8d_d + 0.2d_u.$$

The substitutions to Eq. (6) give the following results for MQM:

$$M(\bar{\theta}) \approx 1.6 \cdot 10^{-27} \bar{\theta} e \cdot cm^2,$$

$$M(\bar{d}) \approx 0.7 \times 10^{-10} (\bar{d}_u - \bar{d}_d) e \cdot cm$$  \hspace{1cm} (8)

III. ELECTRONIC STRUCTURE

A. Geometry optimization

Nuclear configuration of triatomic molecule has three degrees of freedom: two interatomic bond lengths and one bond angle. According to our calculations, the LuOH$^+$ cation has a linear geometry in the ground electronic state $^4\Sigma_{1/2}$. Taking this into account, one can determine equilibrium geometry parameters as a minimum
point of the energy function $E = E(R(\text{Lu–O}), R(\text{O–H}))$. Solution of the electronic problem with various parameters $R(\text{Lu–O})$ and $R(\text{O–H})$ has been performed within the relativistic 4-component coupled cluster approach with single, double and perturbative triple cluster amplitudes CCSD(T) \[24\] [26]. The inner electrons of Lu with lowest orbital energies (1s$^2$2s$^2$2p$^6$) were excluded from this correlation calculation, as well as virtual orbitals with energies greater than 600 Hartree. For comparison, the orbital energy of 3s electrons of the Lu atom, which is the lowest active shell, is –94 Hartree. Dependence of electronic properties on energy cutoff was studied extensively in Refs. [27, 28]. In the calculations the Gaussian-type basis set has been employed. The Dyall’s CV3Z basis set for Lu atom [29] and the aug-cc-pVTZ-DK basis sets [30–32] for the oxygen and hydrogen atoms were used. Both the Dirac–Fock and CCSD(T) calculations were performed using the local code [33]. The obtained equilibrium geometry parameters are: $R$(Lu–O) = 1.873(20)Å and $R$(O–H) = 0.958(20)Å.

### B. $W_M$ calculation

The T,P-violating interaction of the nuclear MQM with electrons is described by the following Hamiltonian:

$$H_{\text{MQM}} = -\frac{M}{2I(2I-1)}T_{i,k} \cdot \frac{3}{2} \frac{[\alpha \times r_i] \cdot r_k}{r_k^5},$$

where $T_{i,k} = I_i I_k + I_i I_k - \frac{3}{2} I(I + 1) \delta_{i,k}$, $I$ is the nuclear spin of $^{175}$Lu, $M$ is the magnetic quadrupole moment of the $^{175}$Lu nucleus, $\alpha$ are Dirac matrices and $r$ is the electron radius-vector with respect to the heavy atom nucleus under consideration. The electronic part of the Hamiltonian \[9\] is characterized by the magnetic constant $W_M$ \[34, 35\]:

$$W_M = \frac{3}{2\Omega} \langle \Psi \sum_i \left( \frac{\alpha_i \times r_i}{r_i^3} \right) \cdot r_\zeta \vert \Psi \rangle,$$

where $\Psi$ is the electronic wavefunction, index $i$ runs over all the electrons, index $\zeta$ means projection on the molecular axis and $\Omega$ is the projection of the total electronic angular momentum $J^*$ on the molecular axis. The ground electronic state of the LuOH$^+$ cation has $\Omega = 1/2$. $W_M$ constant can not be measured but is required for interpretation of the experimental data in terms of the nuclear MQM. In order to test accuracy of the obtained $W_M$ value we have performed calculation of the ground electronic state hyperfine structure constants, which can be measured directly.

| Basis set on Lu [29] | Basis set on O and H [30–32] | $W_M$, $A_{\|}$, $A_{\perp}$ | $10^{33}$ | 10$^6$ | MHz | MHz |
|----------------------|-----------------------------|-----------------------------|---------|---------|-----|-----|
| AE2Z                | aug-cc-pVDZ-DK              | –1.224                      | 7882    | 7618    |     |     |
| AE3Z                | aug-cc-pVDZ-DK              | –1.248                      | 8011    | 7740    |     |     |
| AE4Z                | aug-cc-pVDZ-DK              | –1.244                      | 8012    |         |     |     |
| AE3Z                | aug-cc-pVTZ-DK              | –1.251                      | 8024    | 7752    |     |     |
| AE4Z                | aug-cc-pVTZ-DK              | –1.249                      | 8026    |         |     |     |

### C. $A_{\|}$ and $A_{\perp}$ calculation

Magnetic dipole hyperfine structure of the $^2\Sigma_{1/2}$ state is described by the following constants

$$A_{\|} = \frac{\mu}{10} \langle \Psi_{^2\Sigma_{1/2}} \vert \sum_i \left( \frac{\alpha_i \times r_i}{r_i^3} \right) \cdot |\Psi_{^2\Sigma_{1/2}}\rangle,$$

$$A_{\perp} = \frac{\mu}{7} \langle \Psi_{^2\Sigma_{1/2}} \vert \sum_i \left( \frac{\alpha_i \times r_i}{r_i^3} \right) \cdot |\Psi_{^2\Sigma_{1/2}}\rangle.$$

Here $\mu = 2.2327(11)\mu_N$ \[36\] is the magnetic moment of the $^{175}$Lu nucleus, $I$ is nuclear spin, which is equal to 7/2, and index “+” denotes the following linear combination: $a_+ = a_x + ia_y$, where $xy$-plane is perpendicular to the molecular axis. As one can see from Eqs. \[10\] – \[12\], the values of $W_M$, $A_{\|}$ and $A_{\perp}$ constants are mainly determined by the behavior of the electronic wavefunction in the core region of heavy atom. These are examples of so-called atoms-in-compounds properties \[37, 38\]. The $A_{\|}$ and $A_{\perp}$ parameters can be used to estimate indirectly the $W_M$ uncertainty if the value of hyperfine splitting is measured \[38, 39\].

To compute matrix elements \[10\]–\[12\] the code developed in Refs. \[40, 41\] was used.

### IV. RESULTS AND DISCUSSION

In order to check the convergence of the $W_M$ and hyperfine constants values with respect to the basis set size we have performed calculations using five basis sets (see Table I) of different quality. Inner core electrons $1s^22s^22p^6$ of Lu were excluded from these calculations. Energy cutoff of virtual orbitals was set to 1000 Hartree in these calculations. One can see a good convergence with respect to the basis set size.

The final calculated values of the $W_M$, $A_{\|}$ and $A_{\perp}$ constants are given in Table III. The main calculation has been performed using the basis set that corresponds to the AE3Z on Lu \[29\] and aug-cc-pVTZ-DK \[30–32\] on.
light atoms. All electrons were correlated in this calculation and the energy cut-off for virtual orbitals was set to 11000 Hartree \([27, 28]\). We have also applied the basis set correction calculated as the difference between results obtained using the AE4Z(Lu)&aug-cc-pVTZ-DK(O,H) and AE3Z(Lu)&aug-cc-pVTZ-DK(O,H) basis sets employing the CCSD(T) method with excluded ls2s2p6 electrons of Lu. As one can see from Table I the ratio \(\frac{A_{\perp}}{A_{||}}\) is almost independent on the basis set. Hence, the values of \(A_{\perp}\) in Table II were obtained by the scaling of the corresponding values of \(A_{||}\) with the factor \(\frac{A_{\perp}}{A_{||}} \approx 0.966\).

Contribution of the Gaunt interaction has been calculated within the AE3Z basis set for Lu and the CV2Z \([42]\) basis set for O and H atoms. For this calculation we have used the code, developed in \([43]\). The Gaunt correction, obtained within the CCSD(T) approach, is \(+0.0135 \cdot 10^{33}\text{Hz/(e}\cdot\text{cm}^2\) for \(W_{M}\) and \(-15.9\text{MHz}\) for \(A_{||}\); it is close enough to the one, obtained at the Dirac-Fock level \(+0.0126 \cdot 10^{33}\text{Hz/(e}\cdot\text{cm}^2\) and \(-14.0\text{MHz}\), respectively). These calculations were performed within the MRCC code \([14, 40]\). The uncertainty of the calculated \(W_{M}\) value can be estimated to be lower than 5%.

### Table II. Calculated \(W_{M}\), \(A_{||}\) and \(A_{\perp}\) constants for the ground state of the LuOH\(^{+}\) molecule.

| Contribution | \(W_{M}\), \(10^{33}\text{Hz cm}^2\) | \(A_{||}\), MHz | \(A_{\perp}\), MHz |
|--------------|-------------------------------|----------------|----------------|
| Dirac-Fock   | \(-1.120\)                    | 6640           | 6414           |
| 79e-CCSD     | \(-1.294\)                    | 8227           | 7946           |
| 79e-CCSD(T)  | \(-1.268\)                    | 8156           | 7878           |
| Gaunt correction | +0.014                     |                |                |
| Basis set correction | +0.003                  |                |                |
| Final result | \(-1.251\)                    | 8142           | 7864           |

The final \(W_{M}\) value is about 16\% higher than \(W_{M}\)(YbOH) \([7, 14]\). Note that the difference in constants of fundamental symmetry violating interactions in a neutral molecule and isoelectronic cation can be even larger \([35]\).

The resulting energy shift caused by the interaction can be parameterized in the following way:

\[
\delta E = C(J, F, \Omega) \cdot |W_{M}M|, \tag{13}
\]

with the parameter \(C(J, F, \Omega)\) dependent on the sublevel of hyperfine structure considered; \(J\) and \(F\) are the total electronic and the total angular momenta respectively. For the ground and the lowest excited hyperfine structure levels this parameter may be estimated as 0.1 \([47]\). Thus, one can expect the energy shift caused by CP-odd constants \(\tilde{d}\) and \((\tilde{d}_u - \tilde{d}_d)\) to be respectively

\[
\delta E(\tilde{d}) \approx 2 \cdot 10^5 \tilde{d} \text{ Hz} \tag{14}
\]

\[
\delta E(\tilde{d}_u - \tilde{d}_d) \approx 9 \cdot 10^{28} \frac{\tilde{d}_u - \tilde{d}_d}{\text{cm}} \text{ MHz}. \tag{15}
\]

Substitution of current limitations for \(\tilde{d}\) and \((\tilde{d}_u - \tilde{d}_d)\), taken from Ref. \([48]\) \((|\tilde{d}| < 2.4 \times 10^{-10}, |\tilde{d}_u - \tilde{d}_d| < 6 \times 10^{-27} \text{ cm})\), leads to the upper limits \(|\delta E(\tilde{d})| \leq 48\text{MHz}\) and \(|\delta E(\tilde{d}_u - \tilde{d}_d)| \leq 54\text{MHz}\).

These values are of the same order of magnitude as the current sensitivity achieved in measurements of the energy shift produced by the electron electric dipole moment in the ThO molecule \([3]\). Taking also into account the large coherence time one may expect that \(^{175}\text{LuOH}^+\) promises to give new restrictions for mentioned CP-odd fundamental parameters. Finally, it can be noted that the nuclear electric quadrupole moment of \(^{176}\text{Lu}\) is 1.4 times higher than the one of \(^{175}\text{Lu}\), one should expect the nuclear MQM ratio of these isotopes to be the same order of magnitude. Hence, the \(^{176}\text{LuOH}^+\) ion may be also considered as a prospective system for nuclear MQM search.

### ACKNOWLEDGMENTS

We are grateful to Igor Samsonov and Alexander Oleynichenko for useful discussions. Electronic structure calculations in the paper were carried out using resources of the collective usage center “Modeling and predicting properties of materials” at NRC “Kurchatov Institute” - PNPI.

Molecular coupled cluster electronic structure calculations have been supported by the Russian Science Foundation Grant No. 18-12-00227. Calculations of the \(W_{M}\) matrix elements were supported by the foundation for advancement of theoretical physics and mathematics “BASIS” grant according to the research project No. 18-1-3-55-1. Calculation of the Gaunt interaction matrix elements has been supported by RFBR grant No. 20-32-70177. The calculations of the nuclear structure were supported by the Australian Research Council Grant No. DP150101405 and New Zealand Institute for Advanced Study.

\[\text{[1]}\] A. D. Sakharov, JETP Lett. 5, 27 (1967).
\[\text{[2]}\] L. Canetti, M. Drewes, and M. Shaposhnikov, New Journal of Physics 14, 095012 (2012).
\[\text{[3]}\] V. Andreev, D. G. Ang, D. DeMille, J. M. Doyle, G. Gabrielse, J. Haeberer, N. R. Hutzler, Z. Lasner, C. Meisenhelder, B. R. O’Leary, et al., Nature 562, 355 (2018).
\[\text{[4]}\] W. B. Cairncross, D. N. Gresh, M. Grau, K. C. Cossel, T. S. Roussy, Y. Ni, Y. Zhou, J. Ye, and E. A. Cornell, Phys. Rev. Lett. 119, 153001 (2017).
\[\text{[5]}\] T. A. Isaev and R. Berger, Phys. Rev. Lett. 116, 063006 (2016).
