

Calculation of the parity- and time-reversal-violating interaction in ^{225}RaO

A. D. Kudashov,^{1,2,*} A. N. Petrov,^{1,2,†} L. V. Skripnikov,^{1,2,‡} N. S. Mosyagin,^{1,2} A. V. Titov,^{1,2,§} and V. V. Flambaum³

¹Department of Physics, Saint Petersburg State University, Saint Petersburg, Petrodvoretz 198904, Russia

²Federal State Budgetary Institution "Petersburg Nuclear Physics Institute," Gatchina, Leningrad District 188300, Russia

³School of Physics, The University of New South Wales, Sydney 2052, Australia

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The ten-electron generalized relativistic effective core potential and the corresponding correlation spin-orbital basis sets are generated for the Ra atom and the relativistic coupled-cluster calculations for the RaO molecule are performed. The main goal of the study is to evaluate the T, P -odd parameter X characterized by the molecular electronic structure and corresponding to a "volume effect" in the interaction of the ^{225}Ra nucleus Schiff moment with electronic shells of RaO. Our final result for $X(^{225}\text{RaO})$ is -7532 which is surprisingly close to that in ^{205}TlF but has a different sign. The obtained results are discussed and the quality of the calculations is analyzed. The value is of interest for a proposed experiment on RaO [Phys. Rev. A **77**, 024501 (2008)] due to a very large expected Schiff moment of the ^{225}Ra nucleus.

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Introduction. Study of fundamental interactions, which break both the time-reversal invariance (T) and spatial parity inversion symmetry (P), or T, P -odd interactions, is a way to study so-called "new physics" [1,2] beyond the standard model of electroweak and strong interactions. Despite well-known drawbacks and unresolved problems of the standard model (radiative corrections to the Higgs mass are quadratically divergent; the rather artificial Higgs mechanism of symmetry breaking is not yet proved experimentally; the origins of CP violation, where C is the charge conjugation symmetry, are not well understood; the CP violation according to the CPT theorem is equivalent to the T violation problem, etc.) there are very few experimental data available which are in contradiction with this theory.

In turn, some popular extensions of the standard model, which allow one to overcome its disadvantages, are not confirmed experimentally. Since considerable enhancement of the T, P violation effects is expected in polar diatomic molecules comprising a heavy atom, such systems have been a research subject for a couple of decades. It is also believed that the standard model gives the baryon-to-photon ratio ten orders of magnitude smaller than the observed value. This is a strong argument in favor of an additional source of CP violation which may be detected using atomic and molecular experiments searching for T, P violating interactions. Thus, finding a molecule that exhibits the strongest T, P -odd effects may be crucial for observation of these effects experimentally.

Following [3], the effective interaction with the Ra nucleus Schiff moment in RaO can be written in the form

$$H_{\text{eff}} = -6SX\vec{\sigma}_N \cdot \vec{\lambda}, \quad (1)$$

where $\vec{\sigma}_N$ is the Ra nuclear-spin operator, $\vec{\lambda}$ is the unit vector along the internuclear axis z from Ra to O, S is the Schiff moment of Ra, X is determined by the electronic structure of

the molecule:

$$X = \frac{2\pi}{3} \left[\frac{\partial}{\partial z} \rho_\psi(\vec{r}) \right]_{x,y,z=0}, \quad (2)$$

where $\rho_\psi(\vec{r})$ is an electronic density calculated from the four-component wave function ψ . The amplitude of the T, P -odd spin-axis interaction, $6SX$, in RaO was estimated by Flambaum [4] to be 500 times larger than that in TlF [5]. Such an enhancement in RaO is based first on the ^{225}Ra nucleus Schiff moment [6,7] being about 200 times greater than that of ^{205}Tl [8–10] and second on a semiempirical estimate $X(^{225}\text{RaO}) = 2.2X(^{205}\text{TlF})$.

In the Rapid Communication we have performed *ab initio* calculations of the T, P -odd parameter $X(^{225}\text{RaO})$, excitation energies of the Ra atom and some spectroscopic properties of the ^{225}RaO molecule.

Methods. It follows from Eq. (2) that the volume effect is localized on the nucleus and determined by polarization of the valence electrons. Earlier it was demonstrated by our group [11] that calculation of such core properties can be performed efficiently in two steps. First, electron correlation for valence and outer-core electrons is accounted for, whereas the inner-core electrons are excluded from this calculation using the generalized relativistic effective core potential (GRECP) method [12,13], which yields a very accurate valence region wave function by the most economical way. Second, since the heavy atom's inner core wave function cannot be accurately obtained within the GRECP method, it has to be recovered using a nonvariational restoration procedure [11]. The two-step approach has recently been used in Refs. [14–18] for calculation of other core properties, such as hyperfine constants, electron electric dipole moment enhancement factor, etc., in molecules and atoms.

The fully relativistic Fock-space coupled-cluster code with single and double cluster amplitudes (FS-RCCSD) [19,20] was applied to take account of both the electron correlation and relativistic effects. Triple cluster amplitudes and basis set enlargement corrections to X were obtained using scalar-relativistic approach within CFOUR [21] and MRCC [22,23]

*kudashovad@gmail.com

†alexandernp@gmail.com

‡leonidos239@gmail.com

§http://www.qchem.pnpi.spb.ru

TABLE I. Transition energies (TE) from GRECP-FS-RCCSD calculations of the lowest-lying states of the Ra atom for ten correlated electrons. All values are in cm^{-1} .

Leading conf.	Term	Basis set					Expt. [25,26]
		A	B	C	D	E	
$7s_{1/2}^2 \rightarrow$							
$7s_{1/2}^1 7p_{1/2}^1 (J=0)$		12435	12920	13072	13164	13029	13078
$7s_{1/2}^1 7p_{1/2}^1 (J=1)$		13386	13840	13995	14136	13953	13999
$7s_{1/2}^1 7p_{3/2}^1 (J=1)$		21546	21258	21045	21714	21000	20715
$7s_{1/2}^1 7p_{3/2}^1 (J=2)$		16262	16660	16756	16996	16714	16689
$7s_{1/2}^1 6d_{3/2}^1 (J=1)$		15579	14112	13892	14964	13753	13716
$7s_{1/2}^1 6d_{3/2}^1 (J=2)$		15969	14434	14199	15318	14049	13994
$7s_{1/2}^1 6d_{5/2}^1 (J=2)$		19864	17943	17553	18946	17340	17081
$7s_{1/2}^1 6d_{5/2}^1 (J=3)$		16901	15191	14925	16207	14761	14707

codes via interface to our nonvariational one-center restoration codes developed in Ref. [17].

GRECP generation and atomic calculations. The GRECP for Ra is generated to simulate interactions of ten explicitly treated electrons, the valence and outer-core ($6s6p7s$) ones, with the inner-core $1s - 5d$ electrons, which are excluded from calculations.

Basis sets for Ra were constructed using the generalized correlated scheme [24]; as a result, five correlation spin-orbital basis sets were generated, which are designated here as A, B, C, D, and E. Each one is constructed of optimized primitive $20s$, $20p$, $10d$, $8f$, and $5g$ Gaussian-type functions contracted to $[4s4p3d1f1g]$, $[5s6p4d3f1g]$, $[6s7p5d4f2g]$, $[6s8p4d2f1g]$, and $[6s8p5d5f3g]$ sets, respectively. These basis sets were obtained in a series of atomic two-component GRECP calculations, with correlations included by the FS-RCCSD method [20], and optimized to reproduce the $7s^2 \rightarrow 7s7p$ and $7s^2 \rightarrow 7s6d$ transition energies of the atom as accurately as possible.

Our FS-RCCSD results are compared to experimental data [25,26] in Table I. A reasonable level of accuracy has been achieved with C and E basis sets. The use of the D basis set leads to satisfactory results as far as $7s^2 \rightarrow 7s7p$ transition energies are concerned. However, a lack of f and g functions apparently causes considerable errors in $7s^2 \rightarrow 7s6d$ transition energies.

Molecular calculations. To perform a relativistic Fock-Space coupled-cluster calculation of RaO, the basis set D was used instead of E, thus excluding several d , f , and g basis functions to reduce the computational efforts. Note that the major contribution to the X value is determined by the $s-p$ orbital mixing, therefore such simplification is justified here. The $(10s5p2d1f)/[4s3p2d1f]$ basis set from the MOLCAS 4.1 library was used for oxygen.

A one-component self-consistent-field (SCF) calculation of the $(1\sigma \dots 5\sigma)^{10}(1\pi 2\pi)^8$ ground state of RaO is performed first. It is followed by two-component RCC calculations taking account of single and double (RCCSD) cluster amplitudes. To estimate the convergence of the results with respect to the basis set enlargement we have performed two scalar-relativistic calculations using the coupled-cluster method with single and

TABLE II. Calculated properties of RaO: equilibrium internuclear distance (R_e), harmonic frequency (w_e), and vibrational anharmonicity ($w_e x_e$).

R_e (a.u.)	3.852
w_e (cm^{-1})	598
$w_e x_e$ (cm^{-1})	-1.09

double cluster amplitudes in the basis set D and in enlarged basis set (uncontracted basis set D) using CFOUR code [21].

Correction for the contribution of the triple cluster amplitudes was also estimated. For this we have performed (i) a scalar-relativistic calculation using the coupled clusters with single and double cluster amplitudes and (ii) a scalar-relativistic calculation using the coupled clusters with single, double, and triple cluster amplitudes (CCSDT). The final X value is obtained as

$$X(\text{FINAL}) = X(\text{RCCSD}) + X(\text{CCSDuncon.}) + X(\text{CCSDT}) - 2X(\text{CCSD}). \quad (3)$$

The GRECP/RCCSD method was also used to calculate the ground-state potential curve of the RaO molecule, which was then used to obtain spectroscopic properties of RaO. The results are listed in Table II. All molecular calculations of X were carried out for the equilibrium internuclear distance, $R_e = 3.852$, given also in Table II.

Results and discussions. Although triple and higher cluster amplitudes in the valence region are important for chemical and spectroscopic properties in general, it can be concluded from Table III that GRECP/RCCSD calculation includes all major correlation contributions to X , since triple cluster amplitudes contribute only about 6%. Even smaller correction was found for basis set enlargement. We do not expect that further enlargement of the basis set and accounting for quadrupole amplitudes will change the result by more than 1%. The influence of the inner core-valence electron correlation on X value was estimated in Ref. [27] to be no more than 2% for TlF. Taking into account essentially different electronic structures of TlF and RaO we believe that our final result for X is reliably valid within 10% accuracy.

One of the goals of this work is to determine whether or not the RaO molecule is a feasible candidate for experimental research of T , P -odd effects. The corrected value $X(^{225}\text{RaO}) \approx -X(^{205}\text{TlF})$, according to our calculations, is not as large as could be expected from the usual Z scaling (see [28] and references therein). The estimation based on Z scaling determines

TABLE III. Parameter X calculated for the ^{225}RaO ground state $R_e = 3.852$ a.u. Only the RCCSD result takes into account the spin-orbit interaction. All values are in a.u.

Method	X
Hartree-Fock	-9609
RCCSD	-7696
CCSD	-7648
CCSDT	-7209
CCSD uncontracted	-7923
FINAL	-7532

only a “systematic” variation with increasing Z , and does not take into account some particular changes from one element to the next in the Periodic Table and features of chemical bonding with different elements (F in the case of TIF and O in the case of RaO). A very large estimated Schiff moment of ^{225}Ra [6,7] will strengthen the T, P -odd interactions in RaO by two orders of magnitude. The best upper bound on the nuclear T, P -odd interactions can be obtained using the limit on the ^{199}Hg EDM, $|d(^{199}\text{Hg})| < 3.1 \times 10^{-29} e \text{ cm}$ [29], and the atomic calculation that links the atomic EDM with the Schiff moment of ^{199}Hg nucleus [27], $d(^{199}\text{Hg}) = -2.8 \times 10^{-17} [S(^{199}\text{Hg})/e \text{ fm}^3] e \text{ cm}$. Combining these values, the current upper limit on $|S(^{199}\text{Hg})|$ is $1.1 \times 10^{-12} / e \text{ fm}^3$. Using the corresponding experimental datum for TIF [30] and the most accurate calculated value for X [5] one can obtain the upper limit on $|S(^{205}\text{Tl})|$ as $1.7 \times 10^{-10} / e \text{ fm}^3$. Supposing the same accuracy for a “speculative” RaO experiment as for TIF (performed 22 years ago), the same limit on $|S(^{225}\text{Ra})|$ will be obtained. However, taking into account the relation $S(^{225}\text{Ra})/S(^{199}\text{Hg}) \approx 200$ [6–10] and the upper bound on $|S(^{199}\text{Hg})|$ we obtain $|S(^{225}\text{Ra})| < 2.2 \times 10^{-10} / e \text{ fm}^3$ which is only slightly (1.3 times) worse than that expected from the speculative RaO experiment. However, considering the impressive progress in molecular spectroscopy during the last decades one can expect an order of magnitude or even better sensitivity of the RaO experiment than that attained on TIF.

Analysis of contributions to X . In the present Rapid Communication an analysis of contributions to X based on the one-center representation of the one-particle density matrix has been performed assuming the scalar-relativistic approximation used in the Rapid Communication to construct initial (reference) Hartree-Fock wave function and molecular orbitals. The analysis is similar to that performed by our group for Eu^{2+} in Ref. [17]. It should be noted that such one-center density matrix analysis is free from those rotations in the space of molecular orbitals which do not change the wave function of a considered state (e.g., rotations between the doubly occupied orbitals) and can also be easily performed in the case of a correlated wave function, i.e., beyond the one-configuration approximation. A mean value of the one-electron operator X can be evaluated as follows:

$$\langle X \rangle = \sum_{pq} D_{pq} X_{qp}, \quad (4)$$

where X_{pq} are matrix elements of X , D_{pq} are matrix elements of the one-particle density matrix, and indices p, q enumerate all the atomic basis functions centered on Ra and O assuming the conventional molecular orbital (MO) linear combination of atomic orbitals (LCAO) approximation used in the RaO calculation. For a qualitative analysis of contributions to X it is reasonable to rewrite Eq. (4) in terms of only *atomic orbitals* of Ra, both occupied and virtual, which can be calculated using the Hartree-Fock method for a single Ra atom since such an analysis can be performed excluding one more ambiguity caused by overlapping of the atomic orbitals on different centers.

Represent the molecular density matrix D_{pq} in a “sufficiently complete” basis set of these atomic orbitals with indices i, j , running over all the occupied and virtual orbitals of Ra, i.e., decompose all original basis functions p, q (centered either on

TABLE IV. Parameter X calculated for the ^{225}RaO ground state $R_e = 3.852 \text{ a.u.}$ Individual shell contributions are calculated from the spin-averaged GRECP/SCF orbitals. All values are in a.u.

Shell: main contribution	X
$1\sigma^2 : 1s^2(\text{O})$	−50
$2\sigma^2 : 6s^2(\text{Ra})$	3862
$3\sigma^2 : 2s^2(\text{O})$	9936
$4\sigma^2 : 6p_z^2(\text{Ra})$	−14426
$5\sigma^2 : 2p_z^2(\text{O})$	−9036
$1\pi^4 : 6p_x^2 6p_y^2(\text{Ra})$	50
$2\pi^4 : 2p_x^2 2p_y^2(\text{O})$	54
Total SCF (spin averaged)	−9609

Ra or O) into one-center functions i, j . Then the mean value for X can be rewritten in the form

$$\langle \tilde{X} \rangle = \sum_{ij} \tilde{D}_{ij} X_{ji}, \quad (5)$$

where X_{ij} are matrix elements of X in the enlarged basis set of Ra orbitals, described above. $\langle \tilde{X} \rangle$ can be slightly different from $\langle X \rangle$ due to incompleteness of the used enlarged Ra basis set. In practice however, this difference can be made negligible.

Applying this scheme to RaO we obtain the following contributions: the main one (more than 50%) is due to a polarization of outer-core $6p_z$ orbital of Ra (the z axis coincides with the axis of the RaO molecule) into $7s, 8s \dots$. The rest are due to mixing of $7s, 8s, 9s \dots$ orbitals of Ra with different p_z orbitals of Ra which can partially consist of orbitals of oxygen (in terms of the basis set p, q used in RaO calculations).

It should be noted that this kind of analysis cannot be performed directly for individual contributions from *canonical* molecular orbitals (see Table IV) due to the above-mentioned large unitary rotations between atomic orbitals of radium (leading to mutually compensated unphysical contributions) and their overlapping with orbitals of oxygen. These circumstances result in the presence of several leading contributions. This is opposite the case of TIF (see Ref. [5]) where, due to the relatively simple electronic structure, such orbital analysis was successfully applied with only one leading contribution.

Analysis of X sign. The different sign of the X in TIF and RaO molecules can be explained in a simple qualitative analysis. The valence electronic configurations of Ra and Tl are $6s^2 6p^6 7s^2$ and $6s^2 6p^1$, respectively. TIF has ionic bonding, the $6p$ valence orbital of thallium becomes mainly unoccupied due to interaction with fluorine. Thus, qualitatively, the electronic configurations of the TIF molecule can be written as $\text{Tl}^+(6s^2)\text{F}^-(2s^2 2p^6)$. Electronic structure of RaO is more complicated. Calculation shows that its configuration is rather close to $\text{Ra}^+(6s^2 6p^6)(\pi^4)\text{O}^-(2s^2 2p_z^2)$, where π is three quarters $2p_{x(y)}(\text{O})$ and one quarter $6d_{xz(yz)}(\text{Ra})$. According to the Mulliken population analysis, an effective configuration of Ra in RaO is $6s^2 6p^6 6d^1$. Thus, due to the interaction with oxygen, the $7s$ valence orbital of Ra becomes mainly unoccupied in RaO. Following the density matrix analysis

the leading contribution to X in TIF and RaO is due to the polarization of $6s$ and $6p$ orbitals, correspondingly (see above).

Taking account of the leading contributions to X (TIF) and X (RaO) discussed earlier we can write

$$X(\text{TIF}) = 2\langle 6s|V|6p\rangle\langle 6s|W|6p\rangle/\Delta E_{\text{TIF}}, \quad (6)$$

$$X(\text{RaO}) = 2\langle 6p|V|7s\rangle\langle 6p|W|7s\rangle/\Delta E_{\text{RaO}}, \quad (7)$$

where $\Delta E_{\text{TIF}} = E_{6s} - E_{6p}$, $\Delta E_{\text{RaO}} = E_{6p} - E_{7s}$, V is the polarization operator, W is an operator for the X property localized on the Ra and Tl nuclei [see Eq. (2)]. Note that ΔE_{TIF} and ΔE_{RaO} have the same signs. Let us choose the phase of

orbitals so that the first extremum would have a positive sign for all the functions of Ra and Tl. Then the matrix elements $\langle 6s|W|6p\rangle$ and $\langle 6p|W|7s\rangle$, localized on the nucleus, will have the same signs. However, the terms $\langle 6s|V|6p\rangle$ and $\langle 6p|V|7s\rangle$, localized in the valence region, will have different signs, which explains the opposite signs of X (TIF) and X (RaO).

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