PHYSICAL REVIEW A **90**, 052513 (2014)

Ab initio study of radium monofluoride (RaF) as a candidate to search for parity- and time-and-parity–violation effects

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(Received 28 June 2014; published 17 November 2014)

Relativistic *ab initio* calculations have been performed to assess the suitability of RaF for experimental search of P- and T-and-P–violating interactions. The parameters of P- and T,P-odd terms of the spin-rotational Hamiltonian have been calculated for the $^2\Sigma$ electronic ground state of the ^{223}RaF molecule. They include the W_a parameter, which is critical in the experimental search for nuclear anapole moment, and the parameters W_d and W_{SP} required to obtain restrictions on the electric dipole moment of the electron and T,P-odd scalar-pseudoscalar interactions, respectively. The parameter X corresponding to the "volume effect" in the T,P-odd interaction of the ^{223}Ra nuclear Schiff moment with electronic shells of RaF has also been computed. Spectroscopic and hyperfine structure constants for ^{223}RaF and ^{223}Ra$^+$ have been computed as well, demonstrating the accuracy of the methods employed.

DOI: 10.1103/PhysRevA.90.052513 PACS number(s): 31.15.A−, 31.15.bw, 31.15.vn

I. INTRODUCTION

Manifestations of interactions which are not symmetric with respect to time (T) or spatial (P) inversions (T,P- and P-odd interactions) are of great interest in modern physics. Particularly, the observation of an electron electric dipole moment (eEDM) at a level significantly larger than $10^{-38}e$ cm would indicate the presence of new physics beyond the standard model. Popular extensions of the standard model of particle physics predict eEDM magnitudes of 10^{-26}–$10^{-29}e$ cm [1]. It was realized many years ago [2–7] (see also Refs. [8] and [9]) that very promising experiments in the search for the violation of fundamental symmetries could be performed on atoms, molecules, and solids containing heavy elements. Effects connected with parity-violating interactions can be considerably enhanced in such systems. However, the enhancement cannot be measured directly in a single experiment and, thus, should be calculated theoretically. Recently, a very strict upper bound on eEDM ($<8.7\times10^{-29}e$ cm) was obtained in ThO molecular beam experiments [10], based on the computed effective electric field (E_{eff}) acting on the unpaired electrons from Ref. [11]. It should be noted that another value of E_{eff} (and the corresponding recalculated limit on the eEDM) has recently been reported in Ref. [12]. A series of calculations E_{eff}(ThO) has been performed in Ref. [13], where an extensive analysis of uncertainties of previous calculations [11,12] has also been given.

Diatomic molecules containing heavy nuclei look very promising and, in fact, turn into the main probe for P- and T,P-violating effects in the low-energy sector. Recently, considerable effort has been put into *ab initio* calculations of the nuclear-spin-dependent (NSD) P-odd interaction constant W_a for RaF [14,15] (W_A in Ref. [16]). Here we present results of *ab initio* coupled-cluster calculations of W_a for ^{223}RaF, together with other T,P-odd parameters and spectroscopic constants of this radical at a high level of computational accuracy that can be reliably used in further research on RaF. Computed hyperfine structure (HFS) constants for ^{223}Ra$^+$ allow one to check the accuracy of the theoretical methods used.

II. THEORETICAL BACKGROUND

Following the designations in Ref. [15] for consistency with previous works, the term in the spin-rotational Hamiltonian associated with the NSD parity-violating effects is

$$\hat{h}^{I}_{\mathrm{PV}} = \frac{G_{\mathrm{F}}}{\sqrt{2}} \sum_{Nuc,i} k_{\mathcal{A},Nuc}\boldsymbol{\alpha}\cdot\boldsymbol{I}_{Nuc}\rho_{Nuc}(\boldsymbol{r}_i), \tag{1}$$

where Nuc labels all the system's nuclei, $k_{\mathcal{A},Nuc}$ are the dimensionless strength constants, $G_{\mathrm{F}} = 2.222\,49\times10^{-14}\ E_{\mathrm{h}}a_0^3$ is the Fermi coupling constant, E_{h} is the Hartree energy, $\boldsymbol{\alpha}$ is a one-electron operator made up of Dirac matrices

$$\boldsymbol{\alpha} = \begin{pmatrix} 0 & \boldsymbol{\sigma} \\ \boldsymbol{\sigma} & 0 \end{pmatrix}, \quad \boldsymbol{\sigma} = \begin{pmatrix} \sigma_x \\ \sigma_y \\ \sigma_z \end{pmatrix}$$

with σ_x, σ_y, and σ_z being the 2×2 Pauli matrices and 0 a 2×2 zero matrix, $\boldsymbol{r_i}$ is the displacement of unpaired electron i from nucleus Nuc, and, finally, $\boldsymbol{I}_{Nuc}$ and $\rho_{Nuc}(\boldsymbol{r})$ are the dimensionless reduced nuclear spin operator and the nuclear density distribution (normalized to unity), respectively. Taking into account the fact that the matrix element of the NSD P-odd interactions scales as $\sim Z^2$ [17], our main concern in this particular case shifts to the NSD parity-violating effects due to the radium nucleus. With that in mind, Eq. (1) can be reduced to [16]

$$\hat{h}^{I}_{\mathrm{PV}} \approx k_{\mathcal{A},\mathrm{Ra}}\frac{G_{\mathrm{F}}}{\sqrt{2}}\boldsymbol{\alpha}\cdot\boldsymbol{I}_{\mathrm{Ra}}\rho_{\mathrm{Ra}}(\boldsymbol{r}). \tag{2}$$

For convenience, index Ra is omitted in discussions below ($k_{\mathcal{A},\mathrm{Ra}} \rightarrow k_{\mathcal{A}}$, etc.). It should be noted that different definitions

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and designations of $k_{\mathcal{A}}$ are used by different researchers (see Ref. [18] and references within). Aside from the nuclear anapole moment, the electroweak neutral coupling between the electron vector and the nucleon axial-vector currents also gives rise to the NSD PNC (parity nonconservation) effects [19]. However, the nuclear anapole moment contribution to the NSD interaction is expected to be dominant in RaF since it scales as $\sim A^{2/3}$, where A is atomic number [20] (of Ra, in our case). Finally we have a small contribution to the NSD PNC effects induced by the perturbation of the nuclear-spin-independent weak interaction by the hyperfine interaction which also scales as $\sim A^{2/3}$ [21].

Following Eqs. (1) and (2) in case of the $^2\Sigma$ electronic ground state of RaF, the NSD parity-violating interaction gives rise to a P-odd contribution to the effective spin-rotational Hamiltonian, which can be written as [22–24]

$$H_{\mathcal{A}}^{\text{eff}} = k_{\mathcal{A}} W_a (\boldsymbol{n} \times \boldsymbol{S}') \cdot \boldsymbol{I}, \tag{3}$$

where $\boldsymbol{S}'$ is the effective electron spin (as defined in Ref. [23]) and $\boldsymbol{n}$ is the unit vector directed along the molecular axis from the heavier (Ra) to the lighter (F) nucleus. The electronic parameter W_a can be written as

$$W_a = \frac{G_{\text{F}}}{\sqrt{2}} \langle \Psi_{^2\Sigma_{1/2}} | \rho(\boldsymbol{r}) \alpha_+ | \Psi_{^2\Sigma_{-1/2}} \rangle, \tag{4}$$

where Ψ is the electronic wave function of the considered RaF state and α_+ is defined as

$$\alpha_+ = \alpha_x + i\alpha_y = \begin{pmatrix} 0 & \sigma_x \\ \sigma_x & 0 \end{pmatrix} + i \begin{pmatrix} 0 & \sigma_y \\ \sigma_y & 0 \end{pmatrix}.$$

When W_a is accurately known from electronic structure calculations, one can determine the isotope-specific constant $k_{\mathcal{A}}$ from a successful molecular experiment.

To interpret results of complementary molecular experiments in terms of the eEDM one should know the effective electric field E_{eff} acting on the electron. In turn, E_{eff} can be expressed in terms of the T,P-odd interaction parameter W_d (discussed in Refs. [23,25–27]): $E_{\text{eff}} = W_d|\Omega|$, where $\Omega = \langle \Psi | \boldsymbol{J} \cdot \boldsymbol{n} | \Psi \rangle$ and $\boldsymbol{J}$ is the total electronic angular momentum ($\Omega = \pm 1/2$ for the considered $^2\Sigma$ electronic state of RaF). The parameter W_d itself is written as

$$W_d = \frac{1}{\Omega} \langle \Psi_{^2\Sigma_{1/2}} | \sum_i \frac{H_d(i)}{d_e} | \Psi_{^2\Sigma_{1/2}} \rangle, \tag{5}$$

where d_e is the value of the eEDM,

$$H_d = 2d_e \begin{pmatrix} 0 & 0 \\ 0 & \boldsymbol{\sigma} \cdot \boldsymbol{E} \end{pmatrix}, \tag{6}$$

$\boldsymbol{E}$ is the inner molecular electric field, and $\boldsymbol{\sigma}$ is the vector of Pauli spin matrices.

Another T,P-odd interaction is the scalar-pseudoscalar nucleus-electron neutral current interaction, which is given by the following operator (see Ref. [8]):

$$H_{\text{SP}} = i \frac{G_{\text{F}}}{\sqrt{2}} Z k_{\text{SP}} \gamma_0 \gamma_5 \rho(\mathbf{r}), \tag{7}$$

where γ_0 and γ_5 are the Dirac matrices and k_{SP} is a dimensionless coupling constant.

To extract the fundamental k_{SP} constant from an experiment one needs to know the factor W_{SP} (designated $W_{\text{T,P}}$ in Refs. [11,28] or W_{s} in Ref. [15]), which is determined by the electronic structure of a studied molecule on a given nucleus:

$$W_{\text{SP}} = \frac{1}{\Omega} \langle \Psi_{^2\Sigma_{1/2}} | \sum_i \frac{H_{\text{SP}}(i)}{k_{\text{SP}}} | \Psi_{^2\Sigma_{1/2}} \rangle. \tag{8}$$

Another experimentally detectable source of T,P invariance in RaF might be the EDM induced by the Schiff moment of the Ra nucleus, S [29,30]. Due to nuclear octupole deformations [31,32] S(Ra) should be exceptionally large, e.g., exceeding S(Tl) by $\sim$200 times. The most stringent constraint on the atomic EDM to date comes from experiments on ^{199}Hg [33]. According to Ref. [34], the Schiff moment of ^{225}Ra may surpass that of ^{199}Hg by 2 orders of magnitude, making Ra a very promising candidate for further EDM experiments. The atomic EDM is further enhanced in Ra since the Schiff moment contribution increases faster than Z^2. In RaF the observable T,P-odd effect associated with the Schiff moment can be expressed in terms of the following effective Hamiltonian [35,36]:

$$H_X = 6S(\text{Ra}) X \boldsymbol{\sigma}_{\text{Ra}} \cdot \boldsymbol{n}, \tag{9}$$

where $\boldsymbol{\sigma}_{\text{Ra}}$ is the Ra nuclear spin operator and X is determined by the electronic structure of the radical:

$$X = \frac{2\pi}{3} \left[\frac{\partial}{\partial z} \rho_e(\boldsymbol{r}) \right]_{x,y,z=0}, \tag{10}$$

where $\rho_e(\boldsymbol{r})$ is the electronic density calculated from the four-component wave function $\Psi_{^2\Sigma}$.

The operators corresponding to the constants (4), (5), (8), and (10) are most sensitive to the wave function of the valence electrons (electron spin density) in the region near the heavy nucleus. Thus, the standard way to verify the accuracy of the computed electron spin density in the core region (the region near the heavy nucleus) is to calculate the HFS tensor, which can be measured experimentally (see, e.g., Ref. [26]). In case of RaF, the tensor has two independent components, which can be written as $A_\parallel$ and $A_\perp$,

$$A_\parallel = \frac{\mu(\text{Ra})}{I\Omega} \langle \Psi_{^2\Sigma_{1/2}} | \sum_i \left(\frac{\boldsymbol{\alpha}_i \times \boldsymbol{r}_i}{r_i^3} \right)_z | \Psi_{^2\Sigma_{1/2}} \rangle, \tag{11}$$

$$A_\perp = \frac{\mu(\text{Ra})}{I} \langle \Psi_{^2\Sigma_{1/2}} | \sum_i \left(\frac{\boldsymbol{\alpha}_i \times \boldsymbol{r}_i}{r_i^3} \right)_+ | \Psi_{^2\Sigma_{-1/2}} \rangle, \tag{12}$$

with μ(Ra) being the magnetic moment of a Ra isotope with nuclear spin quantum number I, and are heavily determined by the core region of the electronic wave function.

III. ELECTRONIC STRUCTURE CALCULATIONS

In this work, we are mostly concerned with quantities, which are mean values of the operators heavily concentrated in the atomic core of Ra and sensitive to variation of core-region densities of the valence electrons (the "atom in a compound" or AiC properties [37] below). Efficient computations of AiC properties can be performed by the two-step approach [26,38] utilizing the generalized relativistic effective core potential (GRECP) method [39–41]. In the first (molecular) step the GRECP is used to exclude the inner-core electrons from a correlation calculation and obtain an accurate description of the valence part of the wave function in an economical way, thus dramatically reducing the computational cost of the relativistic molecular calculation. Second, a nonvariational restoration procedure is employed [26] to recover the valence wave function in the inner-core region of a heavy atom. The two-step approach has been used in various calculations of AiC properties [11,27,44–49] and has proven to be a reliable source of theoretical data for experimental investigations [50]. The GRECP from Ref. [48] was used for Ra in this work.

Two methods were employed to treat electron correlation and relativistic effects: (i) a relativistic two-component Fock-space coupled-cluster approach with single- and double-cluster amplitudes (FS-RCCSD) [51] and (ii) a spin-orbit direct configuration interaction (SODCI) approach [52–54] (modified in Ref. [55] to account for spin-orbit interaction in the configuration selection procedures).

The FS-RCCSD scheme begins with a one-component self-consistent-field calculation of the reference wave function (in this case a closed-shell RaF^+ reference state) followed by the two-component RCCSD calculations of RaF taking account of single- and double-cluster amplitudes. Ten electrons of radium $6s^2 6p^6 7s^2$) and nine electrons of fluorine ($1s^2 2s^2 2p^5$) were treated explicitly in the correlation calculations.

The AiC properties are calculated via the finite-field method [56,57]. Triple-cluster amplitudes and basis set enlargement corrections for values obtained within the FS-RCCSD are computed using the scalar-relativistic CFOUR [58] code via interface to the nonvariational one-center restoration code developed in Ref. [46]. Corrections for triple-cluster amplitudes were estimated using CCSD and CCSD(T) approximations, while the basis set enlargement corrections were obtained from CCSD calculations with normal and enlarged basis sets. Final absolute values of AiC properties defined by Eqs. (5), (8), (10), and (11) are obtained as

$$\begin{aligned}\mathrm{Y(FINAL)} = {} & \mathrm{Y(FS{-}RCCSD)} \\ & + [\mathrm{Y(CCSD_{enlarged})} - \mathrm{Y(CCSD)}] \\ & + \{\mathrm{Y[CCSD(T)]} - \mathrm{Y(CCSD)}\}. \qquad (13)\end{aligned}$$

TABLE I. Equilibrium internuclear distance R_e (in units of the Bohr radius a_0), harmonic vibrational wave number $\omega_e x_e$ (in cm^{-1}), and vibrational anharmonicity $\omega_e x_e$ (in cm^{-1}) of $^{223}\mathrm{RaF}$.

Method	R_e	ω_e	$\omega_e x_e$
CCSD(T) [16][a]	4.26	–	–
FS-RCCSD-1 [59][b]	4.24	428	–
FS-RCCSD-2 [59][b]	4.29	431	–
	This work		
FS-RCCSD	4.23	435	1.53

[a] Two-component relativistic coupled-cluster approach with single, double, and perturbative triple excitations.

[b] FS-RCCSD-1 from Ref. [59] refers to four-component Fock-space coupled-cluster calculations with single- and double-cluster amplitudes (as implemented in the DIRAC program package [60]) with Dyall's relativistic basis set and FS-RCCSD-2 with the RCC-ANO basis set by [61]. The active space in FS-RCCSD-1 and FS-RCCSD-2 was restricted by energy for Dyall's basis set up to 10 E_h (10 hartree) and for the RCC-ANO basis set up to 1000 E_h.

TABLE II. Hyperfine coupling constants A (given in MHz) for $^{223}\mathrm{Ra}^+$.

	$A(^2S_{1/2})$	$A(^2P_{3/2})$	$A(^2P_{1/2})$
This work	3379	64	657
Experiment [63,64]	3404(2)	57(8)	667(2)

The GRECP and RCCSD methods with scalar-relativistic corrections for triple-cluster amplitudes and basis set enlargement were also used to calculate the ground-state potential curve of the RaF radical, which was then used to compute the spectroscopic constants (R_e, ω_e, $\omega_e x_e$) of RaF (Table I) via the Simons-Parr-Finlan potential [62]. HFS constants A for different states of the $^{223}\mathrm{Ra}^+$ ion were obtained within the FS-RCCSD method (Table II). The magnetic moment $\mu = 0.271$ (in nuclear magnetons) and the nuclear spin $I = 3/2$ were implied for the $^{223}\mathrm{Ra}$ nucleus. Basis sets $(20s,20p,10d,8f,5g)/[6s,8p,4d,2f,1g]$ [48] and $(10s,5p,2d)/[4s,3p,2d]$ (aug-cc-pVDZ basis set [65]) were used for Ra and F, respectively, except when computing basis set enlargement corrections, in which case basis sets $(15s,15p,10d,8f,5g)$ and $(11s,6p,3d,2f)$ (uncontracted aug-cc-pVTZ [65]) were used. Also in atomic calculations of $^{223}\mathrm{Ra}^+$, basis set $(20s,20p,10d,8f,5g)/[6s,8p,5d,5f,1g]$ was employed. All molecular calculations of AiC properties were carried out for the equilibrium internuclear distance, $R_e = 4.23a_0$ (2.24 Å), the results are given in Table III; the results of FS-RCCS calculations are also presented to demonstrate double-cluster amplitudes' corrections.

IV. RESULTS AND DISCUSSIONS

The goal of this study was to assess the possibility of using RaF in search of P- and T,P-symmetry violation in molecules. While providing a higher level of precision, our results mostly support those published recently [14–16,59], confirming RaF as a versatile multipurpose probe in the search for fundamental symmetry violation in low-energy sectors. Triple-cluster amplitudes and basis set enlargement corrections to W_a and $A_\perp$ cannot be obtained within the scalar-relativistic approach employed herein, because these properties require mixing of the states with different projections of the total electronic angular momentum, which is not implemented in the codes used. As for other parameters from Table III, it is clear that the aforementioned corrections contribute less than 4% to the final values. There are no obvious reasons to expect that further enlargement of the basis set and accounting for quadruple amplitudes will influence the results by more than 5%. Taking into account our previous findings for RaO [48], $X(\mathrm{RaF}) \approx 0.6X(\mathrm{RaO})$, making RaF less sensitive to T,P-odd effects associated with the Schiff moment than RaO. HFS constants of $^{223}\mathrm{Ra}^+$ were computed to demonstrate the accuracy of our approach and, as seen from Table II, one might safely assume 10% theoretical uncertainty of our final results [our value of $A(^2P_{3/2})$ is within the error margin of the experimental one].

TABLE III. *Ab initio* calculations of AiC properties and spectroscopic constants for the $^2\Sigma$ ground state of RaF (the ^{223}Ra isotope was considered in this work): P-odd interaction constant W_a (Hz), T,P-odd interaction constants W_d ($10^{25}e^{-1}$ Hz cm^{-1}), W_{SP} (kHz) and X (a_0^{-4}); hyperfine constants $A_{||}$ (MHz) and $A_{\perp}$ (MHz); and the total angular momentum projection quantum number J_x.

Method	W_a	W_d	W_{SP}	X	$A_{\|\|}$	$A_{\perp}$	J_x
DHF [16][a]	1364	–	–	–	–	–	–
GHF-ZORA [14][b]	1300	(−)2.20[c]	−150[d]	–	1900	1860	–
GHF-ZORA scaled[e]	2100	–	–	–	–	–	–
GKS-LDA [15][f]	1470	–	–	–	–	–	–
			This work				
SODCI	1540	−2.40	−131	−3700	1790	1720	0.491
FS-RCCS	1455	−2.25	−122	−5620	1700	1630	0.487
FS-RCCSD	1700	−2.65	−144	−4300	2100	2020	0.491
CCSD	–[g]	−2.36	−128	−3090	2090	–[g]	–[g]
CCSD(T)	–	−2.33	−127	−3000	2110	–	–
$\text{CCSD}_{\text{enlarged}}$[h]	–	−2.30	−125	−3140	2080	–	–
Final	1700	−2.56	−139	−4260	2110	2020	0.491

[a] Four-component Dirac-Hartree-Fock.

[b] Two-component generalized Hartree-Fock (GHF) in zero-order regular approximation (ZORA).

[c] Computed via $|E_{\text{eff}}/\Omega| = |W_d|$ with the value of $|E_{\text{eff}}|$ estimated in Ref. [59] using the GHF-ZORA value of W_{SP} and the approximate ratios between W_{SP} and W_d.

[d] GHF-ZORA value from Ref. [59].

[e] Spin-polarization is included using scaling relations between hyperfine tensor components and P-odd properties (see Ref. [59]).

[f] Two-component density functional theory calculations within the generalized Kohn-Sham (GKS) framework with the local-density approximation (LDA) exchange-correlation functional.

[g] Computation of the parameter is not implemented in the current version of the code.

[h] CCSD with larger basis sets.

ACKNOWLEDGMENTS

The authors acknowledge Saint Petersburg State University for a research grant 0.38.652.2013. The work of A.D.K., A.N.P., L.V.S. and A.V.T. is supported by RFBR (Russian Foundation for Basic Research) Grant No. 13-02-01406. The work of N.S.M. is supported by RFBR under Grant No. 13-03-01307. L.V.S. is also supported by a grant from the President of RF (Russian Federation), Grant No. MK-5877.2014.2. The molecular calculations were partly performed at the Supercomputer "Lomonosov." The work of T.A.I. and R.B. is supported by the State Initiative for the Development of Scientific and Economic Excellence (LOEWE) in the LOEWE-Focus ELCH.

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