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Relativistic configuration-interaction study of the nuclear-spin-dependent parity-nonconserving electron-nucleus interaction constant W_A in BaF

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A fully relativistic restricted active space configuration-interaction method is employed to compute the P-odd electron-nucleus interaction constant W_A for the ground $(^2\Sigma_{1/2})$ state of BaF, which yields the result of $W_A=160$ Hz. Our present estimated result of the P-odd interaction constant W_A is in reasonable agreement with previous calculations. This result will be useful for the interpretation of the nuclear-spin-dependent parity-nonconservation experiment on BaF.

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It is well understood that possible P- and P,T-odd effects are strongly enhanced in diatomic radicals containing heavy atoms, and hence, heavy-polar diatomics are promising candidates for the search of symmetry violations [1]. For example, the search of permanent electric dipole moments (EDMs) arises from the violations of parity or space inversion symmetry (P) and time-reversal invariance (T), and nuclear anapole moments arise from the P-odd interactions within the nucleus. The search for nonzero P- and P,T-odd effects in these systems with the presently accessible (expected) level of experimental sensitivity would indicate the presence of the so-called "new physics" beyond the standard model (SM) of electroweak and strong interactions and shed light on parity nonconservation in nuclei (see Ref. [2] and references therein). This is undoubtedly of fundamental importance. Despite the well-known drawbacks and the unresolved problems of the SM, there is very little experimental data available which would be in direct contradiction with this theory. However, some popular extensions of the SM, which allow one to overcome its disadvantages, are not yet confirmed experimentally (see Refs. [3,4] for details).

The P-odd and P,T-odd coupling constants in molecules can be extracted by calculating the expectation values of appropriate symmetry violating operators and combining them with measured data. These properties are described by operators that are prominent in the nuclear region; they cannot be measured and their theoretical study is a challenging task. During the past several years the significance of (and requirement for) reliable *ab initio* electronic structure calculations accounting for both relativistic and correlation effects associated with these properties has acquired importance. In this Rapid Communication, we report the result of our nuclear-spin-dependent (NSD) P-odd interaction constant W_A for the ground state of BaF molecule using the relativistic configuration-interaction (CI) method. The knowledge of W_A is necessary to relate the experimentally measured data with the constant k_a arising from the NSD parity-nonconserving (PNC) interaction within the nucleus [5], just like the knowledge of P,T-odd constant W_d is necessary to relate the P,T-odd frequency shift with the electron EDM, d_e [6]. A proposed method to measure nuclear-spin-dependent parity-nonconservation in alkali-metal atoms is analyzed recently by Gomez *et al.* [7]. It is worthwhile to mention here that an experiment to measure the EDM of YbF molecule is currently in progress [6], and an experiment on BaF molecule for the search of nuclear anapole moment is also currently under way by DeMille and co-workers [8]. Therefore, the present calculation of the P-odd interaction constant W_A will be useful for the interpretation of the latter experiment.

For YbF molecule, the calculation of the P-odd interaction constant W_A was done by Kozlov and Ezhov [9] using a semiempirical method. An *ab initio* calculation of this constant was first done by Titov *et al.* [10] using the generalized relativistic effective core potential (GRECP) method which produces reasonably accurate results with relatively modest computational cost. They have reported the result of W_A computed at the level of self-consistent field (SCF) and restricted active space (RAS) self-consistent field (RASSCF) using the GRECP method. Further improvement of the calculation of the interaction constant W_A was carried out by Mosyagin *et al.* [11] using an effective operator (EO) technique in the framework of the GRECP method. For BaF, the first semiempirical calculation of the P-odd interaction constant W_A was done by Kozlov [1,12]. The *ab initio* calculation for the P-odd interaction constant W_A was performed by Kozlov *et al.* [13] using the GRECP method at the level of SCF and RASSCF approaches. They further improved their result using the EO technique. Some more references can be found in the review paper by Titov *et al.* [2]. We would like to emphasize here that there are no more theoretical calculations available for the P-odd interaction constant W_A in BaF using correlated many-body methods. Furthermore, it can be seen from Table III of Ref. [2] that the available theoretical results of W_A in BaF obtained from both semiempirical method and *ab initio* calculations within the framework of GRECP approach are not in close agreement with each other. On the other hand, proportionality of W_A with $\sqrt{AA_d}$ is not as good as the proportionality W_d with $\sqrt{AA_d}$ [where $A=(A_\parallel+2A_\perp)/3$ and $A_d=(A_\parallel-A_\perp)/3$], as discussed by Kozlov *et al.* [13], and hence, calculations of W_A using the semiempirical method may not be as accurate as the calculations of W_d using the same method. Therefore, calcula-

tions using the relativistic configuration-interaction approach would certainly improve the predictability of the P-odd constant W_A in BaF, as they would be based on firmer theoretical footing.

In this Rapid Communication, we estimate the P-odd interaction constant W_A for the ground ($^2\Sigma_{1/2}$) state of BaF molecule using a restricted active space configuration-interaction (RASCI) method with all-electron Dirac-Fock orbitals. The active space used for this system in the present calculation is sufficiently large to incorporate the important core-core, core-valence, and valence-valence electron correlation effects, and hence, should be capable of providing a reliable estimate of W_A. Earlier calculations of some P,T-odd constants based on the RASCI method [14–16] shows that it can produce results of such constants which are in reasonable agreement with other theoretical results.

The expression for the P-odd interaction constant W_A is given by [9,17]

$$\langle {}^2\Sigma_{1/2}|H_A|{}^2\Sigma_{1/2}\rangle = W_A k_A [\mathbf{n}\times\mathbf{S}]\cdot\mathbf{I}, \tag{1}$$

where $\mathbf{S}$ is the effective electron spin, $\mathbf{I}$ is the spin of the Ba nucleus, and $\mathbf{n}$ is the unit vector directed along the molecular axis from Ba to F. The nuclear-spin-dependent P-odd Hamiltonian H_A arising due to the interaction of the nuclear anapole moment with electrons in an atom or molecule is defined as

$$H_A = \frac{G_F}{\sqrt{2}} k_A \mathbf{I}\cdot\sum_e \alpha_e \rho_N(r_e), \tag{2}$$

where $\alpha=\gamma_0\gamma$ is the four-component Dirac matrices and the term $\rho_N(r_e)$ is the nuclear charge density normalized to unity. G_F is the Fermi constant and k_A is the dimensionless constant proportional to the anapole moment of Ba nucleus [18]. The ground-state wave functions $|{}^2\Sigma_{1/2}\rangle$ for the BaF molecule is obtained using the RASCI method. It may be noted that the matrix elements of the Hamiltonian H_A are nonzero only for off-diagonal elements (i.e., nonzero between $\omega=+1/2$ and $\omega=-1/2$ and vice versa) where ω is the projection of the angular momentum of the unpaired electron on the molecular axis.

The P-odd interaction constant W_A for the ground-state of BaF is calculated using the RASCI method with all-electron fully relativistic Dirac-Fock orbitals. The basis set and geometry used in this calculation are identical with our previous calculation of the P,T-odd constant W_d [15] and electron-nucleus scalar pseudoscalar interaction constant W_s [16]. The active space employed in this calculation is composed of 17 electrons and a maximum of 76 orbitals. The RASCI method has been discussed earlier and used successfully for the study of molecular properties [19–21]. Therefore, it is desirable to use this method for the calculation of the P-odd constant W_A in BaF. In any RASCI calculations, the total active orbitals are generally divided into three active subspaces: (a) RAS1 with a restricted number of holes allowed, (b) RAS2 where all possible configurations are permitted, and (c) RAS3 with an upper limit on the number of electrons allowed. There is no unique way of choosing the three active subspaces and it is on the choice of the researcher. However, for all the active spaces used in our calculations, we have considered (a) all the 17 active occupied spinors containing 17 electrons in RAS1 with a maximum of two holes allowed, (b) 7 active virtual spinors in RAS2, and (c) the remaining active virtual spinors in RAS3 with a maximum of two electrons are permitted. The basic idea behind this choice is to consider all possible single and double excitations, within the active space, with respect to the Dirac-Fock reference configuration.

TABLE I. P-odd interaction constant W_A for the ground $^2\Sigma_{1/2}$ state of BaF molecule.

Methods	W_A (Hz)
Semiempirical [1][a]	240
Semiempirical [1][b]	210
Recent result [8][c]	164
SCF [13]	111
RASSCF [13]	107
SCF-EO [13]	181
RASSCF-EO [13]	175
DF (this work)	135
RASCI (this work)	160

[a]Semiempirical result estimated from the experimental hyperfine structure data of Ryzlewicz *et al.* [23].
[b]Semiempirical result estimated from the experimental hyperfine structure data of Knight *et al.* [22].
[c]Recent result taken from the values quoted by DeMille *et al.* in Table I of Ref. [8].

The P-odd interaction constant W_A estimated using the RASCI method is compared with the results of both semiempirical method and other theoretical calculations [1,13] in Table I. As can be seen from that table, the present DF estimate of $W_A=135$ Hz is $\sim$21(25)% off from the SCF (RASSCF) result of Kozlov*et al.* [13] and $\sim$35(43)% off from the semiempirical results of Kozlov and Labzowsky [1], estimated from two different sources of experimental hyperfine structure data of Knight *et al.* [22] (Ryzlewicz *et al.* [23]). However, our RASCI result of $W_A=160$ Hz is in better agreement and differs by $\sim$11(8)% from the SCF- EO (RASSCF-EO) result of Kozlov *et al.* [13] and $\sim$23(33)% from the semiempirical results of Kozlov and Labzowsky [1], estimated from same sources of hyperfine structure data of Knight *et al.* [22] (Ryzlewicz *et al.* [23]). Our RASCI result of W_A is almost the same (differs by only 4 Hz) as the value quoted by DeMille *et al.* in a recent paper (see Table I of Ref. [8]). Further, we would like to mention that no further calculations for W_A are available using other correlated many-body methods.

Inclusion of the electron correlation in the calculation of the P-odd and P,T-odd interaction constants such as W_A, W_s, and W_d using the RASCI method is straight forward but computationally challenging because one must consider a large number of electrons and orbitals in the RASCI space. There are 32 doubly and one singly occupied orbitals in BaF of which the 25th occupied orbital of BaF corresponds to the 5s occupied spin orbitals of Ba. As the contribution of the 5s

and $5p$ orbitals of Yb to W_d and W_s is quite significant [10] in the case of YbF, in this case also we have included the $5s$ and $5p$ orbitals of Ba in our active space for the calculation of W_A for the ground-state of BaF molecule. The occupied orbitals above $5s$ are also included in the active space from energy considerations. Thus, altogether 17 active electrons (9α and 8β) are included in the active space for the RASCI calculation. In the present calculations for W_A, we consider five similar sets of active space which are constructed from 17 active electrons and 36, 46, 56, 66, and 76 active orbitals to analyze the convergence of W_A in BaF. We find that when we include more active virtual orbitals in the CI space, the magnitude of W_A for BaF increases gradually and reaches a value of 160 Hz for the active space containing 76 active orbitals. We have further observed that the variation in the result of W_A for the last three active spaces containing 56, 66, and 76 orbitals is quite negligible. The maximum magnitude of this oscillation is around 1.3% or roughly 2 Hz. Therefore, we believe that the result for W_A in our calculation has more or less converged.

The main advantage of our method to calculate the constant W_A over the other two methods that have been employed earlier is that it takes into account relativistic effects in an *ab initio* manner. However, it does not calculate the core polarization effects in a very efficient manner. It is not possible at this stage to quantify the exact accuracy of our method because of the lack of accurate experimental data for quantities such as the hyperfine constants, and its proportionality with the computed quantity is not quite exact. However, an approximate error estimate of our present work can be obtained from a more exhaustive calculation, where we consider 35 active electrons (including $4s$, $4p$, and $4d$ electrons of Ba) in the active space keeping the same number of virtual orbitals. We find that the correlation contribution of these core electrons (with $n=4$ of Ba) to the computed quantity W_A is $\sim 2.5\%$. The correlation contribution from the remaining core electrons excluded in the present calculation would at the most be of the same size. Hence, all the frozen-core electrons in our calculation can give rise to an error of around 5%, and the excluded virtual orbitals can be expected to produce an error of $\sim 1\%$. Therefore, the estimated error in our calculation for the computed quantity W_A is around 6%, within the framework of RASCI with single and double excitations. There may be further errors due to the neglected triples, quadruples, and higher-order excitations, but we cannot estimate that. Nevertheless, it is expected to be small. Some more errors may arise due to the incompleteness of the basis set, which we have analyzed to some extent at present and in an earlier calculation of the parameter W_d [15] and have found that the error due to this is negligible. Therefore, we believe that the total error in our calculation of the computed quantity W_A is within 10%.

A fully relativistic restricted active space configuration-interaction method is employed to estimate the nuclear-spin-dependent P-odd interaction constant W_A of the ground $(^2\Sigma_{1/2})$ state of BaF, which gives the result $W_A=160$ Hz. To our knowledge, this is the first calculation for the constant W_A using a relativistic CI approach. This calculation will be useful for the interpretation of the nuclear-spin-dependent parity-nonconservation experiment on BaF by DeMille and co-workers. Like our earlier calculations of W_d [14,15] and W_s [16] the present calculation of W_A is also in reasonable agreement with semiempirical and other *ab initio* calculations.

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