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Ab initio calculation of the electron-nucleus scalar-pseudoscalar interaction constant W_s in heavy polar molecules

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A fully relativistic restricted active space configuration interaction method is employed to compute the P,T-odd interaction constant W_s for the ground $(^2\Sigma_{1/2})$ state of YbF and BaF molecules, which yield the results $W_s=-41.2$ kHz and -9.7 kHz for YbF and BaF, respectively. Our present estimated results of the P,T-odd interaction constant W_s is in reasonable agreement with previous calculations.

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I. INTRODUCTION

It is widely recognized that heavy atoms and heavy-polar diatomics are important candidates for the experimental search of permanent electric dipole moments (EDM's) arising from the violations of space inversion symmetry (P) and time reversal invariance (T). The search for nonzero 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 (see [1] and references therein). This is undoubtedly of fundamental importance. Despite the well-known drawbacks and 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 [2,3] for details).

The P- and T-odd coupling constants in molecules can be extracted by calculating the expectation values of suitable P- and T-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 challenging task. During the last several years the significance of (and requirement for) *ab initio* calculation of electronic structure providing a high level of reliability and accuracy in accounting for both relativistic and correlation effects associated with these properties has gained in importance. In this paper, we will compute one of the P,T-odd interaction constants W_s, for the ground state of YbF and BaF molecules with reliable accuracy of the method, arising due to the electron-nucleus scalar-pseudoscalar (S-PS) interaction. Knowledge of W_s is necessary to link the experimentally determined P,T-odd frequency shift with the electron-nucleus coupling constant k_s, which can arise from the mixing of scalar and pseudoscalar particles in multi-Higgs-boson models.

An experiment to measure the EDM of YbF is currently in progress [4]. The P,T-odd interaction constant W_s in YbF was first calculated by Titov *et al.* [5] using generalized relativistic effective core potential (GRECP) method as this procedure provides reasonable accuracy with small computational cost. Titov and co-workers have also reported W_s computed using a restricted active space self-consistent field (RASSCF) scheme [5] with GRECP orbitals. Assuming that the valence-valence electron correlation effect is negligible, Parpia [6] estimated W_s from the all-electron unrestricted Dirac-Fock (UDF) method in 1998. In the same year Quiney *et al.* [7] reported the P,T-odd interaction constant W_s computed at the core-polarization level with all-electron DF orbitals. Though the effect of pair correlation and higher-order effects to W_s are non-negligible, these terms were not included in the calculations of Quiney *et al.* Similarly, for the BaF molecule, the first calculation of the P,T-odd interaction constant W_d was carried out by Kozlov *et al.* [8] using the GRECP at the level of SCF and RASSCF approaches.

In this paper, we estimate the P,T-odd interaction constant W_s for the ground $(^2\Sigma_{1/2})$ state of YbF and BaF molecules using a RAS configuration interaction (CI) method with all-electron Dirac-Fock orbitals. The active space used for both systems in this calculation is sufficiently large to incorporate important core-core, core-valence, and valence-valence electron correlation effects and, hence, should be capable of providing a reliable estimate of W_s.

II. EXPRESSION FOR THE P,T-ODD INTERACTION CONSTANT W_s

The expression for the P,T-odd interaction constant W_s is given in many articles [5–7]:

$$W_s = \frac{2}{k_s}\langle ^2\Sigma_{1/2}|H_s|^2\Sigma_{1/2}\rangle. \tag{1}$$

where k_s is the electron-nucleus S-PS coupling constant. The interaction Hamiltonian H_s is defined as

$$H_s = i\frac{G_F}{\sqrt{2}}Zk_s\sum_e \beta_e\gamma_e^5\rho_N(r_e), \tag{2}$$

where β and γ^5 are the four-component Dirac matrices and $\rho_N(r_e)$ is the nuclear charge density normalized to unity. G_F is the Fermi constant and k_s is a dimensionless S-PS interaction constant, which is defined as $Zk_s=(Zk_{s,p}+Nk_{s,n})$ where, $k_{s,p}$ and $k_{s,n}$ are electron-proton and electron-neutron coupling constants, respectively. The ground-state wave functions $|^2\Sigma_{1/2}\rangle$ for YbF and BaF molecules are obtained using the RASCI method.

TABLE I. P,T-odd interaction constant W_s for the ground $^2\Sigma_{1/2}$ state of the YbF molecule.

Methods	W_s (kHz)
Semiempirical [10]	−43.0
GRECP-SCF [5]	−33.0
GRECP-RASSCF [5]	−33.0
DHF [7]	−22.0
DHF+CP [7]	−42.0
UDF (unpaired electron) [6]	−34.6
UDF (all electrons) [6]	−44.0
DF (this work)	−34.2
RASCI (this work)	−41.2

III. RESULTS AND DISCUSSION OF THE YbF MOLECULE

The P,T-odd interaction constant W_s for the ground state of YbF is calculated using the RASCI method with all-electron fully relativistic Dirac-Fock orbitals. The basis set and geometry used in this calculations are identical with our previous calculation [9] of the P,T-odd constant W_d. The active space employed in this calculation is composed of 31 electrons and 86 orbitals.

The P,T-odd constant W_s estimated from the RASCI method is compared with other calculations [5–7,10] in Table I. As can be seen in Table I the present DF estimate of W_s is in close agreement with the DF value of the calculation of Titov *et al.* [5], off by only ∼3% and almost the same as the unpaired electron contribution of Parpia's calculation [6]. At this juncture we emphasize that the DF estimate of W_s reported by Quiney *et al.* [7] differs by almost ∼35% from our estimate as well as from that of Titov *et al.* [5], because a single combination of symmetry type is considered in their calculations [7]. However, at the post-Dirac-Fock level Quiney *et al.* show that the contribution of first-order *core polarization* (CP) is almost 90%. On the other hand, Paripa's UDF calculation indicates that the correlation contribution is ∼27%. Note that although the CP contribution is the most important, the effects of pair correlation (PC) and higher-order terms are non-negligible. We also emphasize that the inclusion of electron correlation through unrestricted DF is *generally* not recommended as the unrestricted Dirac-Hartree-Fock theory suffers from spin contamination. Our present calculation using the RASCI method estimates W_s to be −41.2 kHz, which differs by ∼6% from Parpia's UDF calculation and off by ∼4% from the latest semiempirical calculation of Kozlov [10].

The inclusion of electron correlation in the calculations of the P,T-odd constants like W_d and W_s via CI is straightforward but computationally demanding as a large number of electrons and orbitals need to be included in the RASCI space. In this paper, we analyze the effect of electron correlation using the RASCI method. There are 39 doubly and one singly occupied orbitals in YbF of which the 25th occupied orbitals of YbF corresponds to the 5s occupied spin orbitals of Yb. As the contributions of the 5s and 5p orbitals of Yb to W_d and W_s are quite significant [5,10,11], these orbitals are included in the RASCI space. The occupied orbitals above 5s are also included in the RASCI space from energy considerations. [Note that the 4f orbitals of Yb and the 2p orbitals of F in YbF are energetically quite close (Table 12 of Ref. [6])]. Thus, altogether 31 active electrons (16 α and 15 β) are included in the CI space. In the present calculations for W_s, we consider six sets of RASCI space which are constructed from 31 active electrons and 36, 46, 56, 66, 76, and 86 active orbitals to analyze the convergence of W_s. From this analysis we find that, when we include more active virtual orbitals in the CI space, the magnitude of W_s for YbF increases gradually and reaches a maximum value of 41.2 kHz for the active space containing 76 active orbitals. However, with a further increase in the number of active virtual orbitals, the magnitude of W_s decreases by around 3.5%. Therefore, we predict that the uncertainty in our calculation is roughly 4%–5% due to the incompleteness of the basis.

TABLE II. P,T-odd interaction constant W_s for the ground $^2\Sigma_{1/2}$ state of the BaF molecule.

Methods	W_s (kHz)
Semiempirical [14][a]	−11.0
SCF [8]	−6.1
RASSCF [8]	−5.9
DF (this work)	−7.7
RASCI (this work)	−9.7

[a] Semiempirical result estimated from the experimental hyperfine structure data of Knight *et al.* [15].

IV. RESULTS AND DISCUSSION OF THE BaF MOLECULE

For the ground state of the BaF molecule also, the P,T-odd constant W_s is calculated using the RASCI method with all-electron Dirac-Fock orbitals at the experimental geometry R_e=2.16 Å [12]. Here also, we have used the uncontracted Gaussian basis set which is identical to our previous calculation [13] of the P,T-odd constant W_d. The active space employed for BaF molecule is composed of 17 electrons and 96 active orbitals.

The P,T-odd interaction constant W_s estimated from the RASCI is compared with other calculations [8,14] in Table II. As can be seen in Table II the present DF estimate of W_d is ∼20% (23%) off from the SCF (RASSCF) result of Kozlov *et al.* [8] and ∼42% off from the semiempirical result of Kozlov and Labzowsky [14] while our RASCI result is only off by ∼13% from the semiempirical result of Kozlov and Labzowsky [14], which is estimated from the experimental hyperfine structure data of Knight *et al.* [15]. At this juncture, we emphasize that no more theoretical calculations for W_s are available using other correlated many-body methods.

In this calculation also, we incorporate the effect of electron correlation using the RASCI method. 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 [5] 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_s for the ground state of the 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_s also, we consider six similar sets of active space which are constructed from 17 active electrons and 46, 56, 66, 76, 86, and 96 active orbitals to analyze the convergence of W_s in BaF.

V. CONCLUSION

A fully relativistic restricted active space configuration interaction method is employed to estimate the P,T-odd interaction constant W_s of the ground ($^2\Sigma_{1/2}$) states of YbF and BaF, which yields the results $W_s = -41.2$ kHz and -9.7 kHz for YbF and BaF, respectively. To our knowledge, this is the first calculation for the constant W_s using a relativistic CI approach. Like our earlier calculations of W_d [9,13] the present calculations of W_s are also fairly close to previous calculations and semiempirical results.

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[1] A. V. Titov, N. S. Mosyagin, T. A. Isaev, and D. DeMille, Prog. Theor. Chem. Phys. **15**, 253 (2006).
[2] E. D. Commins, Adv. At., Mol., Opt. Phys. **40**, 1 (1999).
[3] W. Bernreuther and M. Suzuki, Rev. Mod. Phys. **63**, 313 (1991).
[4] B. E. Sauer *et al.*, in *Atomic Physics 20*, edited by C. Roos, H. Haeffner, and R. Blatt, AIP Conf. Proc. No. 869 (AIP, Melville, NY, 2006), p. 44.
[5] A. V. Titov, N. S. Mosyagin, and V. F. Ezhov, Phys. Rev. Lett. **77**, 5346 (1996).
[6] F. A. Parpia, J. Phys. B **31**, 1409 (1998).
[7] H. M. Quiney, H. Skaane, and I. P. Grant, J. Phys. B **31**, L85 (1998).
[8] M. G. Kozlov, A. V. Titov, N. S. Mosyagin, and P. V. Souchko, Phys. Rev. A **56**, R3326 (1997).
[9] M. K. Nayak and R. K. Chaudhuri, Chem. Phys. Lett. **419**, 191 (2006).
[10] M. G. Kozlov, J. Phys. B **30**, L607 (1997).
[11] M. G. Kozlov and V. F. Ezhov, Phys. Rev. A **49**, 4502 (1994).
[12] K. P. Huber and G. Herzberg, *Molecular Spectra and Molecular Structure: Constants of Diatomic Molecules* (Van Nostrand, New York, 1979), Vol. 4.
[13] M. K. Nayak and R. K. Chaudhuri, J. Phys. B **39**, 1231 (2006).
[14] M. G. Kozlov and L. N. Labzowsky, J. Phys. B **28**, 1933 (1995).
[15] L. B. Knight, W. C. Easley, and W. Weltner, J. Chem. Phys. **54**, 322 (1971).
[16] H. J. Aa. Jensen, T. Saue, and L. Visscher with contributions from V. Bakken, E. Eliav, T. Enevoldsen, T. Fleig, O. Fossgaard, T. Helgaker, J. Laerdahl, C. V. Larsen, P. Norman, J. Olsen, M. Pernpointner, J. K. Pedersen, K. Ruud, P. Salek, J. N. P. Van Stralen, J. Thyssen, O. Visser, and T. Winther, Computer code DIRAC 04, 2004 (http://dirac.chem.sdu.dk).