PHYSICAL REVIEW A **78**, 012506 (2008)

Calculation of the electron-nucleus scalar-pseudoscalar interaction constant W_S for YbF and BaF molecules: A perturbative approach

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(Received 17 March 2008; published 16 July 2008)

The P,T-odd interaction constant, W_S, for the ground state of YbF and BaF molecules are calculated using the second-order many-body perturbation theory (MBPT) via Z-vector technique. The interaction constant W_S reported here agrees favorably well with other correlated calculations. We also address the convergence behavior of W_S with respect to the number of active orbitals used in the perturbative calculations.

DOI: 10.1103/PhysRevA.78.012506 PACS number(s): 11.30.Er, 31.30.J−, 12.38.Bx

I. INTRODUCTION

Heavy atoms and heavy-polar diatomic molecules are well understood to be the potential candidates for the experimental search of permanent electric dipole moments (EDMs) arising from the violations of space inversion symmetry (P) and time reversal invariance (T). At the level of presently accessible experimental sensitivity, the search for a nonzero electron EDM, arising particularly due to the nonvanishing P- and T-violating effects in these systems, would indicate the presence of the so-called "new physics" beyond the standard model (SM) of elementary particle physics [1], which is certainly of fundamental importance. Though there are well-known drawbacks and unresolved problems of the SM, experimental data available are not good enough to be in direct contradiction with this theory. It is also realized that some popular extensions of the SM, which explain some of its shortcomings are yet to be confirmed experimentally. For more details, we refer the reader to the original Refs. [2,3].

Calculations of the expectation values of suitable P- and T-violating operators and combining them with measured data can provide the P,T-odd coupling constants in molecules. These P- and T-violating operators are highly dominant around the nuclear region, which cannot be measured and their theoretical study is a nontrivial task. During the last several years the significance as well as requirement of *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 article, we consider one of the P,T-odd interaction constants W_S which is scalar-pseudoscalar (S-PS) in nature. The knowledge of W_S is necessary to link the experimentally determined P,T-odd frequency shift with the electron-nucleus (S-PS) coupling constant k_s, which can arise from the mixing of scalar and pseudoscalar particles in multi-Higgs-boson models.

The P,T-odd interaction constant W_S of YbF was first computed by Titov *et al.* [4] at the restricted active space (RAS) self-consistent field (SCF) level using generalized effective core potential (GRECP) method. Assuming that the valence-valence electron correlation effect is negligible, Parpia [5] estimated W_S from the all-electron unrestricted Dirac-Fock (UDF) method in 1998. The first *ab initio* many-body perturbation calculation of W_S was due to Quiney *et al.* [6] However, they consider only the core-polarization (CP) terms in their perturbative calculations of W_S. The first calculation of the P,T-odd interaction constant W_S for the BaF molecule was carried out by Kozlov *et al.* [7] at the SCF and RASSCF level using the GRECP method. In early 2007, we have also computed the P,T-odd interaction constant W_S for YbF and BaF molecules using the restricted active space (RAS) configuration interaction (CI) method [8].

In this paper, we report P,T-odd interaction constant W_S for the ground ($^2\Sigma_{1/2}$) state of YbF and BaF molecules estimated from the second-order many-body perturbation theory (MBPT) with all-electron DF orbitals. Since the second-order MBPT calculation includes all the terms correct up to second order, we believe that our predicted W_S for YbF and BaF should be quite reasonable at this level of approximation. Studies have shown [9] that the second-order MBPT is capable of providing reasonable estimate of the P,T-odd interaction constant W_d for these systems.

The organization of the paper is as follows. Section II briefly reviews the Z-vector method [10–12] which has been applied here to compute the P,T-odd constant W_d. The calculated results are presented and compared with other methods in the subsequent section.

II. METHODOLOGY

The calculation of molecular properties can be regarded as a by product of the molecular electronic wave function calculation. Once the molecular electronic wave function Ψ is known, the properties of interest can be computed from the expectation value

$$\langle O\rangle = \langle\Psi|H'|\Psi\rangle, \tag{2.1}$$

where H' is an appropriate operator for the property of interest. For one-electron properties, Eq. (2.1) reduces to the contraction of a density matrix with property integrals. The property values can also be computed using perturbation theory. In this case, the property associated with H' is given by

$$\langle O\rangle = |dE/d\lambda|_{\lambda=0}, \tag{2.2}$$

where

$$E(\lambda) = \langle\Psi|H_0 + \lambda H'|\Psi\rangle, \tag{2.3}$$

in which H_0 is the unperturbed Hamiltonian. Differentiating Eq. (2.3), with respect to λ, we obtain

$$|dE/d\lambda|_{\lambda=0} = \langle\Psi|H'|\Psi\rangle + \left.\left\langle \frac{d\Psi}{d\lambda}|H_0|\Psi\right\rangle\right|_{\lambda=0} + \left.\left\langle \Psi|H_0|\frac{d\Psi}{d\lambda}\right\rangle\right|_{\lambda=0}, \tag{2.4}$$

which reduces to Eq. (2.1) when Ψ is an exact eigenfunction of H_0, i.e., when $d\Psi/d\lambda=0$. Under this circumstances the wave function is said to obey Hellmann-Feynmann theorem [13] for H'.

The simplest approach to compute the property is the finite difference approach [14], where $dE/d\lambda|_{\lambda=0}$ is estimated by finite differences, i.e.,

$$\left.\frac{dE}{d\lambda}\right|_{\lambda=0} = \frac{E(\bar{\lambda}) - E(0)}{\bar{\lambda}} \tag{2.5}$$

for small $\bar{\lambda}$. However, this approach is neither convenient nor simple for general application. The alternative to Eq. (2.5) is the "coupled perturb" approach where the non-Hellmann-Feynmann terms are computed explicitly via

$$\left.\frac{dE}{d\lambda}\right|_{\lambda=0} = \left.\frac{\partial E}{\partial\lambda}\right|_{\lambda=0} + \sum_k \left.\frac{\partial E}{\partial\alpha_k}\right|_{\alpha_k=\alpha_0} \times \left.\frac{d\alpha_k}{d\lambda}\right|_{\lambda=0}, \tag{2.6}$$

where $\{\alpha_0\}$ is the set of parameters in the optimization of unperturbed wave function Ψ. It immediately follows from the above equation that in order to compute the non-Hellmann-Feynmann terms in Eq. (2.4), we have to evaluate $\partial E/\partial\alpha_k$ and $d\alpha_k/d\lambda$. In the actual calculation, this is accomplished by the Z-vector method [10–12].

Since the basic formalism of the Z-vector method is available elsewhere [10,11], we briefly review this scheme. For convenience, we restrict our discussion on the evaluation of analytic energy derivative involving the electric field perturbation for the CI wave function. Let us consider the following first-order perturbed Hamiltonian operator H;

$$H = H_0 + \lambda_a H'_a + \lambda_f H'_f, \tag{2.7}$$

where H_0 is the unperturbed Hamiltonian and H'_a is the first-order change in the Hamiltonian due to nuclear perturbation, and H'_f is the first-order change due to electric field. The parameters λ_a and λ_f in Eq. (2.7) are the nuclear coordinate and electric field perturbations, respectively. Since the atomic orbital basis set depends only on the nuclear coordinate, H'_a affects the one-electron, two-electron, and overlap integrals. On the other hand, H'_f only affects the one-electron integrals. The electric dipole moment is defined by

$$\mu_f = -\frac{\partial E_{\text{total}}}{\partial F} = -\frac{\partial E_{\text{nuc}}}{\partial F} - \frac{\partial E_{\text{elec}}}{\partial F} = \mu_f^{\text{nuc}} + \mu_f^{\text{elec}}, \tag{2.8}$$

where F stands for the electric field along the f axis. Now, the first derivative of the electronic energy for the CI wave function with respect to the electric field perturbation can be written as [11]

$$\frac{\partial E_{\text{elec}}}{\partial F} = -\sum_{ij}^{\mathcal{M}} Q_{ij}h_{ij}^f - 2\sum_{ij}^{\mathcal{M}} U_{ij}^f X_{ij}, \tag{2.9}$$

where Q is the one-electron density matrix [15] and h_{ij}^f is the dipole moment matrix. The Lagrangian matrix for the CI wave function X is given by

$$\mathbf{X} = \sum_{ij}^{\mathcal{M}} Q_{ij}h_{ij} + \sum_{ijkl}^{\mathcal{M}} G_{ijkl}(ij|kl) \tag{2.10}$$

in which h_{ij} and $(ij|kl)$ are the one- and two-electron matrix elements and G is the two-electron density matrix [15]. The U_{ij}^f matrices, which are related to the first derivative of molecular orbital ($\mathcal{M}$) coefficients with respect to the electric field are obtained by solving the coupled perturbed Hartree-Fock (CPHF) equations in the following matrix form:

$$\mathbf{A}\mathbf{U}^f = \mathbf{B}^f. \tag{2.11}$$

For a closed-shell SCF wave function matrices $\mathbf{A}$ and $\mathbf{B}$ can be written as

$$Aij,kl = \delta_{ij}\delta_{kl}(\epsilon_j - \epsilon_i) - [4(ij|kl) - (ik|jl) - (il|jk)] \tag{2.12}$$

and

$$B_{ij} = h_{ij}^f, \tag{2.13}$$

respectively, where ϵ's are single particle orbital energies. The one- and two-electron integrals appearing in Eqs. (2.12) and (2.13) are defined in terms molecular orbitals as

$$h_{ij} = \int \phi_i^*(1)h(1)\phi_j(1)d\tau_1, \tag{2.14}$$

$$(ij|kl) = \int\int \phi_i^*(1)\phi_j^*(1)\frac{1}{r_{12}}\phi_k(2)\phi_l(2)d\tau_1 d\tau_2. \tag{2.15}$$

Now the second term of Eq. (2.9) may be written as [11]

$$2\sum_{ij}^{\mathcal{M}} U_{ij}^f X_{ij} = 2\mathbf{X}^T\mathbf{U}^f, \tag{2.16}$$

where $\mathbf{X}^T$ is the transpose of $\mathbf{X}$ matrix. Combining Eqs. (2.11) and (2.16), the second term of Eq. (2.9) can be written as

$$2\sum_{ij}^{\mathcal{M}} U_{ij}^f X_{ij} = 2\mathbf{X}^T\mathbf{A}^{-1}\mathbf{B}^f = 2\mathbf{Z}^T\mathbf{B}^f, \tag{2.17}$$

where the $\mathbf{Z}$ vector in this equation is defined by

$$\mathbf{Z}^T = \mathbf{X}^T \mathbf{A}^{-1}, \tag{2.18}$$

which in turn may be written as

$$\mathbf{A}^T \mathbf{Z} = \mathbf{X}. \tag{2.19}$$

Once **Z** is known, the corrections due to first-order changes of the $\mathcal{M}$ coefficients may be evaluated as

$$2\sum_{ij}^{\mathcal{M}} U_{ij}^f X_{ij} = 2\sum_{ij}^{\mathcal{M}} B_{ij}^f Z_{ij}. \tag{2.20}$$

The advantage of the Z vector is now obvious. In Eq. (2.11) the simultaneous equations were to be solved for three degrees (x, y, and z) of freedom, while in Eq. (2.19) they are solved only for one degree of freedom. It is worth noting that the Z-vector method, *in principle*, is applicable whenever equations of the form (2.19) and (2.20) are valid.

III. RESULTS AND DISCUSSIONS

The expression for the P,T-odd interaction constant W_S is given in many articles [4–6,8],

$$W_S = \frac{2}{k_s}\langle {}^2\Sigma_{1/2}|H_s|{}^2\Sigma_{1/2}\rangle, \tag{3.1}$$

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

$$H_s = i\frac{G_F}{\sqrt{2}} Zk_s \sum_e \beta_e \gamma_e^5 \rho_N(r_e), \tag{3.2}$$

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 second-order perturbation theory.

A. YbF molecule

The P,T-odd interaction constant W_S for the ground state of YbF is calculated using the second-order MBPT with all-electron Dirac-Fock orbitals. The basis set and geometry employed in these calculations can be found in Ref. [16]. The result of W_S estimated from the second-order MBPT is compared with other theoretical calculations and with our earlier RASCI calculation [4–6,8,17] in Table I. It can be seen from Table I that our DF estimate is in accord with those reported by Titov *et al.* [4] and UDF calculation of Parpia [5], but differs substantially from Quiney *et al.*'s value. This discrepancy arises because Quiney and co-workers consider only a single combination of symmetry type in their calculations.

We also notice that the correlation contribution to W_S reported by Quiney *et al.* differs from ours as well from Parpia's UDF estimate. According to Quiney *et al.*, the correlation contribution to W_S is ~90%, whereas the corresponding UDF estimate of Parpia is ~27%. The present calculation, on the other hand, indicates that the correlation contribution to W_S is ~8.5%. It is worth mentioning that our perturbative calculation of W_S is accomplished via the Z-vector method which allows one to include all the terms correct upto second order in an efficient way.

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

Methods	W_S (kHz)
Semiempirical [17]	−43.0
CRECP and SCF [4]	−33.0
GRECP and RASSCF [4]	−33.0
DHF [6]	−22.0
DHF+CP [6]	−42.0
UDF (unpaired electron) [5]	−34.6
UDF (all electrons) [5]	−44.0
DF [8]	−34.2
RASCI [8]	−41.2
MBPT (this work)	−37.1

There are 39 doubly and one singly occupied orbitals in YbF of which the 25th occupied orbital of YbF corresponds to the $5s$ occupied spin orbitals of Yb. As the contribution of the $5s$, $5p$, and $4f$ orbitals of Yb to W_S is quite significant [4,17,18], these orbitals are kept active in perturbative treatment. The occupied orbitals above the 25th are also kept active from energy consideration. [Note that the $4f$ orbitals of Yb and the $2p$ orbitals of F in YbF are energetically quite close (see Table 12 of Ref. [5]).] Therefore, we have considered 31 active electrons and 96 active orbitals in this perturbative calculation to analyze the convergence of W_S. The present calculation clearly demonstrates that our second-order MBPT estimate of W_S converges smoothly and quite faster, which can be seen from Fig. 1. However, our earlier RASCI calculations was exhibiting a slight fluctuation of around ±2% in the result of W_S with respect to the variation in the size of the active space and orbitals. In fact, the magnitude of W_S for YbF was reaching a maximum value of 41.2 kHz for active space containing 76 active orbitals and with a further increase of active virtual orbitals, the magnitude of W_S was decreasing by around ~3.5% in our previous RASCI calculations [8]. However, this kind of oscillating behavior is not observed in the present calculation based on second-order MBPT, but the value of W_S is roughly ~10% less in magnitude than the RASCI result.

B. BaF molecule

For the ground state of the BaF molecule also, the P,T-odd constant W_S is calculated using the second-order MBPT with all-electron Dirac-Fock orbitals at the experimental geometry R_e=2.16 Å [19]. Here also we have used the uncontracted Gaussian basis set and the details can be found in Ref. [20]. Similarly, the active space employed for the BaF molecule in this perturbative calculation of W_S is composed of 17 active electrons and 96 active orbitals to analyze the convergence.

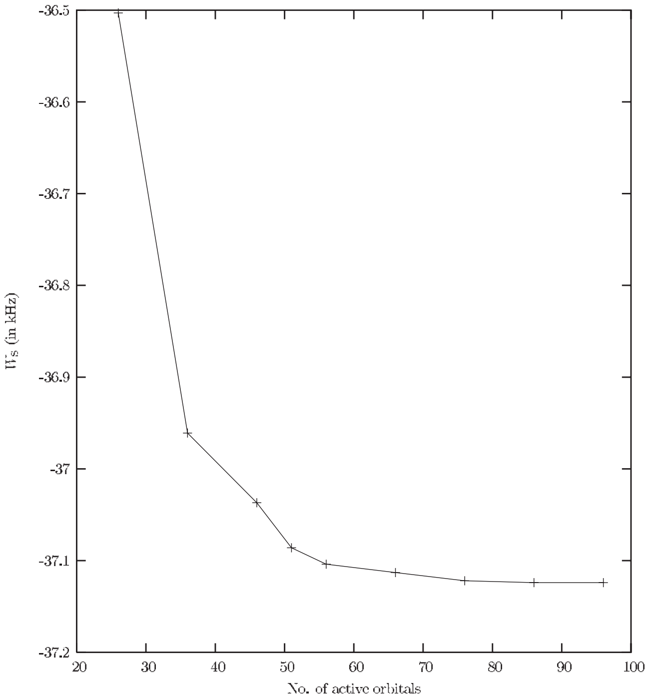

FIG. 1. Plot of W_S for YbF obtained from MBPT(2) vs the number of active orbitals.

The P,T-odd interaction constant W_S for BaF estimated from the second-order MBPT is compared with other calculations [7,8,21] in Table II. In the case of the BaF molecule also, we observed the similar trend as in the case of YbF molecule, i.e., the estimated result of W_S using MBPT converges smoothly and is quite stable with respect to the variation of the size of the active space, which was showing slight fluctuation in our previous calculation using RASCI method [8], with the variation of W_S was roughly ±1.2%. Furthermore, we analyzed the result of W_S with the inclusion of 35 electrons in the active space and found that the variation in the result of W_S is almost negligible in the present calculation. Therefore, we believe that the result of W_S estimated using second-order MBPT is quite stable as compared to our earlier RASCI calculations [8], with respect to the choice of active space, and hence, seems to be quite reasonable. However, in the case of the BaF molecule also, the magnitude of W_S is around ~13% less than the RASCI result.

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

Methods	W_S (kHz)
Semiempirical[a] [21]	−11.0
SCF [7]	−6.1
RASSCF [7]	−5.9
DF [8]	−7.7
RASCI [8]	−9.7
MBPT (this work)	−8.4

[a] Semiempirical results estimated from the experimental hyperfine structure data of Knight *et al.* [22]

IV. CONCLUSION

A fully relativistic second-order many-body perturbation theory is employed to compute the P,T-odd interaction constant W_S of the ground state of YbF and BaF, which yield the results W_S=−37.1 kHz and −8.4 kHz for YbF and BaF, respectively, which seems to be quite reasonable, but is little less in magnitude from earlier RASCI calculations [8]. To our knowledge, this is the first calculation for the P,T-odd constant W_S using a second-order MBPT. Since the nondynamical electron correlation effect can be incorporated more effectively through RASCI method, one expects more reliable estimate of W_S and other P,T-odd constants from RASCI approach. However, our previous calculations using RASCI method shows that this method is quite sensitive to the choice of active orbitals in the active space, where as second-order MBPT is quite stable with respect to this choice. Further, the result of W_S obtained using second-order MBPT converges smoothly and quite faster. Similar smooth convergence as well as stability was also observed in our previous calculation of the P-T-odd interaction constant W_d using the second-order MBPT [9]. Thus, we believe that our second-order estimate of W_S should be quite reliable.

Finally, we emphasize that though the present calculation agrees favorably with earlier theoretical results, more sophisticated theoretical treatment is still necessary to improve the accuracy of W_S. State-of-the-art many-body methods such as multireference many-body perturbation theory and/or coupled cluster method may be used to access higher-order dynamical and nondynamical electron correlation effects and accuracy of the present estimate. These schemes are, however, technically difficult to implement and is beyond the scope of the present work.

ACKNOWLEDGMENTS

The authors wish to thank Professor Hans Joergen Jensen and his group for providing us their DIRAC04 [23] code which is adapted with our codes. This work was partly supported by KSKRA (Grant No. 2007/11/1-BRNS/515) awarded to M.K.N. by the BRNS, Department of Atomic Energy, India. R.K.C. acknowledges the Department of Science and Technology, India (Grant No. SR/S1/PC-32/2005).

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