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Re-appraisal of the P,T-odd interaction constant $W_{\rm d}$ in YbF: Relativistic configuration interaction approach

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Abstract. Restricted active space (RAS) configuration interaction (CI) approach is employed to compute the P,T-odd interaction constant $W_{\rm d}$ for the ground ($^2\Sigma_{1/2}$) state of YbF molecule. The present estimate of $W_{\rm d} = -1.164 \times 10^{25}$ Hz/e-cm is expected to provide a reliable limit on the electron's electric dipole moment (EDM), $d_{\rm e}$.

Keywords. Electron's electric dipole moment; parity and time reversal violations; relativistic electronic structure; *ab-initio* method.

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1. Introduction

It is well recognized that heavy atoms and heavy polar diatomics are the prime candidates of the experimental search for permanent electric dipole moments (EDMs) arising from the violations of space inversion symmetry (P) and time reversal invariance (T). The search for non-zero 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 interaction (see [1] and references therein) which is certainly of fundamental importance. Despite the well-known drawbacks and unresolved problems of the SM, very little experimental data are available which would be in direct contradiction with this theory. In turn, some popular extensions of the SM, which allow one to overcome it's disadvantages, are not yet confirmed experimentally (see [2,3] for details).

In order to interpret the measured data in terms of fundamental constants of the above-mentioned interactions, one must calculate those properties of the systems, which establish a connection between the measured data and the studied fundamental constants. These properties are described by the operators that are

prominent around the nuclear region; they cannot be measured and their theoretical study is a non-trivial 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 importance. In this paper, we will compute one of the P,T-odd interaction constants, the so-called $W_{\rm d}$, which is a measure of the effective electric field $\mathbf{E}$ at the un-paired electrons, for the ground state of YbF with reliable accuracy. The knowledge of $W_{\rm d}$ is necessary to link the experimentally determined P,T-odd frequency shift with the electron's EDM, $d_{\rm e}$. It is worthwhile to mention here that an experiment to measure the EDM of YbF is currently in progress [4].

The P,T-odd interaction constant $W_{\rm d}$ in YbF was first calculated by Kozlov based on a semi-empirical method [5,6] using the experimental hyperfine structure data. On the other hand, *ab-initio* calculation of the P,T-odd interaction constant $W_{\rm d}$ in YbF was first calculated by Titov *et al* [7] using generalized relativistic effective core potential (GRECP) as this procedure provides reasonable accuracy with small computational cost. Titov and co-workers have also reported the result of $W_{\rm d}$ computed using restricted active space self-consistent field (RASSCF) scheme [7,8] within GRECP approach. Assuming that the valence–valence electron correlation effect is negligible, Parpia [9] estimated $W_{\rm d}$ from all-electron unrestricted Dirac–Fock (DF) method (UDF) in 1998. In the same year Quiney *et al* [10] reported the P,T-odd interaction constant $W_{\rm d}$ computed at the core-polarization level (CP) with all-electron Dirac Hartree–Fock (DHF) orbitals, neglecting the effect of pair correlation (PC) and higher-order corrections to $W_{\rm d}$. The calculations cited above predict the values of P,T-odd interaction constant in the interval of -0.91×10^{25} to -1.26×10^{25} Hz/e-cm which is quite large. Therefore, more precise estimation of $W_{\rm d}$ is necessary to set a reliable limit on $d_{\rm e}$.

In our earlier communications, we have reported the P,T-odd interaction constant $W_{\rm d}$ for the ground ($^2\Sigma_{1/2}$) states of YbF [11] and BaF [12] molecules computed using all-electron DF orbitals at RASCI (comprised of 31 active electrons and 56 active orbitals of YbF) and second-order many-body perturbation theory level [13]. The present calculation is carried out with relatively large CI space (generated by distributing 31 active electrons and 76 active orbitals of YbF) to incorporate non-dynamical electron correlation effects more accurately. It is worth noting that deep-lying occupied and high-lying virtual orbitals are kept frozen in the present calculation using RASCI method.

In §2 we briefly present the working equation for the P,T-odd interaction constant $W_{\rm d}$. The computational details and results are presented in §3.

2. P,T-odd interaction constant $W_{\rm d}$

The general form of the interaction of an electron's EDM with an electric field is defined by the interaction operator

$$H_{\rm d} = -d_{\rm e}\beta\mathbf{\Sigma}\cdot\mathbf{E}, \tag{1}$$

where $d_{\rm e}$ is the magnitude of electron's EDM. β and $\mathbf{\Sigma}$ are the Dirac matrices. In the non-relativistic limit ($\beta = 1$) the above operator reduces to

$$H_{\rm d}^{\rm NR} = -d_{\rm e}\mathbf{\Sigma}\cdot\mathbf{E}. \tag{2}$$

According to the Schiff's theorem [14], the expectation value of this operator $H_{\rm d}^{\rm NR}$ vanishes. In relativistic consideration ($\beta = \gamma_0$) the expectation value of the interaction operator becomes non-zero which can be written as

$$H_{\rm d}^{\rm R} = -d_{\rm e}\gamma_0\mathbf{\Sigma}\cdot\mathbf{E}. \tag{3}$$

If we subtract the above two equations, i.e. $H_{\rm d}^{\rm R} - H_{\rm d}^{\rm NR}$, we get the non-vanishing part of the electron's EDM interaction as

$$H_{\rm d} = -d_{\rm e}(\gamma_0 - 1)\mathbf{\Sigma}\cdot\mathbf{E}. \tag{4}$$

Using the matrix form for the Dirac matrices γ_0 and $\mathbf{\Sigma}$, where

$$\gamma_0 = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \quad \text{and} \quad \mathbf{\Sigma} = \begin{pmatrix} \hat{\sigma} & 0 \\ 0 & \hat{\sigma} \end{pmatrix}, \tag{5}$$

we obtain the non-zero part of $H_{\rm d}$ as

$$H_{\rm d} = 2d_{\rm e}\begin{pmatrix} 0 & 0 \\ 0 & \hat{\sigma} \end{pmatrix}\cdot\mathbf{E}. \tag{6}$$

Here, we can see that, this electron's EDM interaction operator involves only the small component of Dirac wave function. In the case of molecule, $\mathbf{E}$ is given by

$$\mathbf{E} = \mathbf{E}_{\rm i}^{\rm mol} = \sum_m \mathbf{E}_i^m + \sum_{j\neq i}\mathbf{E}_{i,j}. \tag{7}$$

Here, $\mathbf{E}_i^m$ is the field due to the mth nucleus at the site of the ith electron and $\sum_{j\neq i}\mathbf{E}_{i,j}$ is the electric field due to the jth electron at the site of ith electron. Thus, for YbF molecule,

$$\mathbf{E}_i^{\rm mol} = \mathbf{E}_{\rm Yb} + \mathbf{E}_{\rm F} + \sum_{j\neq i}\mathbf{E}_{i,j}. \tag{8}$$

For our calculation of $W_{\rm d}$ we have neglected the last term of the above equation because the contribution of this last term is quite small compared to the first two terms. We have also assumed that, both Yb and F nuclei are uniformly charged spherical ball of negligible dimension. In this case we can evaluate the nuclear electric field using the Gauss law as

$$\vec{E}(\vec{r}) = \frac{Q}{r^2}\hat{r}\ \text{(a.u.)}, \tag{9}$$

where Q is the total charge inside the nucleus and $\hat{r}$ is the position vector of the electron from the centre of the nucleus. Using these approximations we obtain the molecular electric field at the un-paired electron to be (the contribution of all the paired electrons vanishes)

$$\mathbf{E}^{\rm mol} = \frac{Z_{\rm Yb}}{r_{\rm Yb}^2}\hat{r}_{\rm Yb} + \frac{Z_{\rm F}}{r_{\rm F}^2}\hat{r}_{\rm F}. \tag{10}$$

The P, T-odd constant $W_{\rm d}$ is evaluated from the following expression [8–10]:

$$W_{\rm d} = \frac{2}{d_{\rm e}}\langle\, ^2\Sigma_{1/2}|H_{\rm d}|\, ^2\Sigma_{1/2}\rangle. \tag{11}$$

Table 1. P,T-odd constant $W_{\rm d}$ (in 10^{25} Hz/e-cm) for the ground state of YbF molecule.

Methods	$W_{\rm d}$
Semi-empirical [6]	−1.26
GRECP-RASSCF [7]	−0.91
DHF+CP [10]	−1.20
UDF (unpaired electron) [9]	−0.962
UDF (all electrons) [9]	−1.203
GRECP-RASSCF-EO [8]	−1.206
DF [11]	−0.963
RASCI [11]	−1.088
MBPT(2) [13]	−1.043
RASCI (present work)	−1.164

3. Results and discussion

The P,T-odd constant $W_{\rm d}$ for the ground $^2\Sigma_{1/2}$ state of YbF is calculated using the RASCI method. The basis set and geometry used in this calculation are identical with our previous calculations [11]. The RASCI method has been discussed earlier and used successfully for the study of molecular properties [15–17]. In any RASCI calculation, the total active orbitals are 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. However, for all the active spaces used in the present calculations, we have considered (a) all the 31 active occupied spinors containing 31 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 DF reference configuration. Although, from methodology point of view, both the present calculations and our earlier calculations [11] are the same, there are some technical differences, which makes a significant difference in the result of $W_{\rm d}$ obtained from both these calculations. In the present calculations, we have employed a sufficiently large CI space and considered all possible single and double excitations, within the active space, with respect to the DF reference function. This is in contrast with our earlier calculations, where we used a relatively small CI space and considered all possible single, double and some triple excitations, within the active space, with respect to the DF reference function. For example, the active spaces for YbF molecule considered in the present calculations are composed of 31 electrons and a maximum of 76 active orbitals, whereas the active spaces considered in the earlier calculations [11] are composed of 31 electrons and a maximum of 56 active orbitals.

The P,T-odd constant $W_{\rm d}$ for the ground state of YbF estimated from the present RASCI calculation is compared with other calculations [7–10] as well as with our previous calculations [11,13] and the semi-empirical result [6] in table 1. As can be

seen in table 1, the present estimated value of W_d using the same RASCI method, but with a slightly different technique (as discussed above) is improved over our earlier calculation [11] and the magnitude of the computed quantity is increased by around 6% over our earlier result [11]. The present estimated result of W_d is off by ∼3% from the estimation of Mosyagin *et al* [8] at the level of RASSCF with the EO technique within the GRECP approach (GRECP-RASSCF-EO) and differs by ∼7% from the latest semi-empirical result of Kozlov [6]. However, accuracy of the semi-empirical method is expected to be 80% as Kozlov pointed out in his calculation [6]. Similarly, our present estimated result of W_d is off by ∼3% from the calculation of Quiney *et al* [10] at the level of first-order CP with all-electron DHF orbitals (DHF+CP) and Parpia's all-electron UDF [9] calculation. Note that although the CP contribution is the most important, the effects of PC and higher-order terms are non-negligible. We also emphasize that the inclusion of electron correlation through UDF method is generally not recommended as the UDF theory suffers from spin contamination.

The inclusion of electron correlation to W_d via CI method is straightforward but computationally challenging as large number of electrons and orbitals need to be included in the CI space. In this article, we analyse the effect of electron correlation using RASCI method. There are 39 doubly and one singly occupied orbitals in YbF of which the 25th occupied orbital of YbF corresponds to 5s occupied spin orbital of Yb. As the contribution of 5s orbital of Yb to W_d is quite significant [5–7], this orbital is included in our CI space. The occupied orbitals above 25th are also included in the RASCI space 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. [9]).) Thus, altogether 31 active electrons (16α and 15β) are included in CI space. In the present calculations for the constant W_d, we consider six sets of RASCI space which are constructed from 31 active electrons and 26, 36, 46, 56, 66 and 76 active orbitals to analyse the result of W_d. From this analysis we find that, when we include more active orbitals in the CI space, the magnitude of W_d for YbF increases gradually and reaches a value of 1.164×10^{25} Hz/e-cm for active space containing 76 active orbitals. Therefore, we believe that considering a large CI space is quite important to study the P, T-odd constant W_d. Furthermore, we find that contribution of triple excitation, omitted in the present calculation, but considered in our earlier calculation [11] is quite negligible.

4. Conclusion

A fully relativistic RASCI method with a sufficiently large active space is employed to estimate the P, T-odd interaction constant W_d for the ground ($^2\Sigma_{1/2}$) state of YbF molecule, which yield the result of W_d to be -1.164×10^{25} Hz/e-cm for YbF. The active space employed in the present calculations is quite large, and all the single and double excitations, within the active space, with respect to the DF reference function are considered in the present calculation to incorporate important core–core, core–valence and valence–valence electron correlation effects. Therefore, we strongly believe that the present estimate will be important to provide a reliable limit on d_e. We also observed that the present estimated result of W_d obtained

using the RASCI method is improved to some extent as compared to our earlier calculation [11], which is now reasonably close to the latest semi-empirical result [6] and other theoretical calculations [8,9]. Furthermore, we conclude from the present and our earlier calculations [11] that the influence of triple excitation is quite negligible for the computed quantity W_{d}. However, a significantly large CI space is rather important.

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