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A relativistic coupled-cluster calculation of the electron-nucleus scalar-pseudoscalar interaction constant W_s in YbF

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The scalar-pseudoscalar (S-PS) interaction, which has been predicted between the electrons and nuclei of atoms and molecules, violates parity (P) and time (T) reversal symmetries. The electric dipole moment of the electron (eEDM) and the S-PS interaction together give rise to an energy shift in paramagnetic polar molecules, which in principle can be measured. The determination of the S-PS interaction constant, $k_{s,A}$, for an atom A could be a sensitive probe of physics beyond the standard model (SM). The upper limit for it can be obtained by combining the results of the measured energy shift mentioned above and the accurate quantum chemical calculation of the S-PS coefficient, $W_{s,A}$. In this work, we use a method based on the four-component relativistic coupled-cluster singles and doubles (RCCSD) method to calculate this coefficient for YbF, one of the most promising candidates for the search of the eEDM and the S-PS interaction. We obtain $W_{s,\mathrm{Yb}} = -40.5$ [kHz] with an estimated error of less than 10% for YbF. We also calculate the effective electric field (E_{eff}), the molecular dipole moment (DM), and the parallel component of the hyperfine coupling constant ($A_{//}$) by the RCCSD method. The discrepancies in the results of these calculations with those of accurate measurements are used to estimate the accuracy of our calculation of $W_{s,\mathrm{Yb}}$.

I. INTRODUCTION

The dominant sources of parity (P) and time-reversal (T) violations in paramagnetic atoms and molecules are the electric dipole moment of the electron (eEDM) and the electron-nucleus scalar-pseudoscalar (S-PS) interaction [1,2]. They are sensitive probes of physics beyond the Standard Model (SM) [3]. The interaction of the eEDM with internal electric fields and the S-PS interaction give rise to a combined energy shift in paramagnetic molecules, which could be measured. The result of such a measurement combined with the calculations of quantities associated with the eEDM or the S-PS interaction, could give an upper limit for the eEDM or S-PS coupling constant.

The S-PS interaction between an electron and a nucleus originates at the level of elementary particles from a similar interaction involving electrons and quarks [4]. It is mediated by a neutral particle like a Higgs boson, which has scalar and pseudoscalar components [4]. Such an interaction does not occur in the SM of particle physics which contains only a single scalar Higgs boson. However, it is predicted by a number of multi-Higgs models including the minimal supersymmetric standard model (MSSM) [4,5] and the aligned two-higgs-doublet model (A2HDM) [6]. The contribution of the S-PS electron-nucleus interaction to P and T violation in atoms and molecules can be larger than that of the electron EDM for certain parameters of these models [4-6]. These models can also predict the baryonic asymmetry of the universe arising from CP violation due to the exchange of neutral Higgs bosons [5,7]

The current best upper limit on the S-PS electron-nucleus interaction coupling constant comes from the results of the measurement [8] and electronic structure calculations [9,10] on ThO. Efforts are under way to improve the energy shift measurement on YbF by laser cooling this molecule. It is expected that this would result in an improvement in the sensitivity of the limit on the S-PS coupling constant by three and two orders of magnitude compared to the current values obtained from YbF and ThO respectively [11]. It would therefore be appropriate to improve the accuracy of the calculation associated for the S-PS interaction in YbF.

The focus of the present paper is the theoretical determination of the S-PS coefficient, $W_{s,A}$ for YbF, which is currently one of the leading candidates for observing the energy shift due to the eEDM and the S-PS interaction [12]. It is a natural sequel to our previous work on the evaluation of the effective electric field (E_{eff}) interacting with the eEDM. We used a four-component relativistic coupled-cluster singles and doubles (RCCSD) method that we had developed for our present calculation of $W_{s,A}$ [13]. The result of this calculation is more accurate than previous calculations of $W_{\mathrm{s},A}$ for YbF. The accuracy of our calculation is discussed by considering the differences between the results of our calculations of the molecular dipole moment (DM), and the parallel component of the hyperfine coupling constant ($A_{//}$) and their measured values as well as pertinent theoretical issues.

II. THEORY

The expression for the scalar-pseudoscalar interaction Hamiltonian in a molecule is given by [2]

$$\hat{H}_{\mathrm{S-PS}} = \left[i\frac{G_{\mathrm{F}}}{\sqrt{2}} \sum_{A}^{N_{\mathrm{n}}} \sum_{j}^{N_{\mathrm{e}}} k_{\mathrm{s},A} Z_A \beta \gamma^5 \rho_A(\mathbf{r}_{Aj}) \right]. \quad (1)$$

Here, i is the imaginary unit, G_{F} is the Fermi coupling constant in atomic units ($2.22249\times10^{-14}/E_{\mathrm{h}}\cdot a_0^3$), and β and γ^5 are the Dirac matrices. N_{n} and N_{e} represent the total number of nuclei and electrons, and A and j are the label indices for nuclei and electrons. $k_{\mathrm{s},A}$ is a dimensionless S-PS interaction constant of an atom A, which is defined as,

$$Z_A k_{\mathrm{s},A} = Z_A k_{\mathrm{s,p}} + N_A k_{\mathrm{s,n}}. \quad (2)$$

Here, Z_A is the atomic number and N_A is the number of neutron in the target atom. $k_{\mathrm{s,p}}$ ($k_{\mathrm{s,n}}$) is the S-PS coupling constant of an electron and a proton (neutron). ρ in Eq(1) is the nuclear charge density normalized to unity. In the present work, we used the Gaussian-type distribution function as follows,

$$\rho_A(r) = \left(\frac{\eta_A}{\pi}\right)^{\frac{3}{2}} \exp(-\eta_A r^2). \quad (3)$$

$$\eta_A = \frac{3}{2}(R_{rms}^{A})^{-2}. \quad (4)$$

Here, R_{rms}^{A} is the root-mean-squared nuclear charge radius of atom A.

The observed energy shift (ΔE) caused by the S-PS interaction and the definition of $W_{\mathrm{s},A}$ coefficient is expressed as

$$\begin{aligned}\Delta E &= 2\left\langle \Psi \middle| \hat{H}_{\mathrm{S-PS}} \middle| \Psi \right\rangle \\ &= 2\sum_{A}^{N_{\mathrm{n}}} k_{\mathrm{s},A} \left\langle \Psi \middle| i\frac{G_{\mathrm{F}}}{\sqrt{2}} \sum_{j}^{N_{\mathrm{e}}} \beta\gamma^5 \rho_A(\mathbf{r}_{Aj}) \middle| \Psi \right\rangle \\ &= \sum_{A}^{N_{\mathrm{n}}} k_{\mathrm{s},A} W_{\mathrm{s},A}, \end{aligned} \quad (5)$$

where $|\Psi\rangle$ represents the electronic wave function. Both $k_{\mathrm{s},A}$ and $W_{\mathrm{s},A}$ depend on the atom and its isotope. For diatomic systems, there are two atomic contributions in ΔE, but the contribution of the heavier atom is dominant. $W_{\mathrm{s},A}$ is a measure of the shift in energy due to the S-PS interaction between the electrons and the nucleus of atom A.

The electronic wave function used in our work is based on the Dirac−Coulomb (DC) Hamiltonian,

$$\hat{H}_{DC} = \sum_{i}^{N_{\mathrm{e}}} \left[c\boldsymbol{\alpha}\cdot\mathbf{p}_i + \beta c^2 - \sum_{A}^{N_{\mathrm{n}}} V_A(\mathbf{r}_i;\mathbf{R}_A) \right] + \sum_{i<j}^{N_{\mathrm{e}}} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}, \quad (6)$$

where c is the speed of light, $\boldsymbol{\alpha}$ is the Dirac matrix, $\mathbf{p}$ is the momentum operator, $\mathbf{r}$ and $\mathbf{R}$ are the position vectors of the electrons and nuclei, respectively. A is a label for nuclei and i and j are labels for electrons. The third term in Eq. (6) is the nuclear interaction potential and we used the Gaussian-type finite-size nuclear model.

Using the DC Hamiltonian, we obtained the molecular electronic wave function by the relativistic coupled cluster (CC) method, considered to be the current gold standard for the electronic structure of heavy atoms and molecules [14]. The CC method treats correlation effects to all orders in the residual Coulomb interaction for hole−particle excitations at any level. The method is size extensive unlike the truncated configuration interaction (CI) method [15]. The coupled cluster wave function $|\psi\rangle$ can be written as

$$|\psi\rangle = e^{\hat{T}}|\psi_0\rangle, \quad (7)$$

where $|\psi_0\rangle$ is the reference state function, which is taken to be a single determinant corresponding to an open-shell doublet at the Dirac−Fock (DF) level. $\hat{T}$ is the cluster operator, which is defined as

$$\begin{aligned}\hat{T} &= \hat{T}_1 + \hat{T}_2 + \cdots \hat{T}_{N_{\mathrm{e}}} \\ &= \sum_{i,a} t_i^a \hat{a}_i \hat{a}_a^\dagger + \frac{1}{4}\sum_{i>j,a>b} t_{ij}^{ab} \hat{a}_i \hat{a}_j \hat{a}_a^\dagger \hat{a}_b^\dagger + \cdots, \end{aligned} \quad (8)$$

where t_i^a and t_{ij}^{ab} are called as the cluster amplitudes, and i, and j (a and b) represent the orbitals which are occupied (unoccupied) in the reference function $|\psi_0\rangle$. $\hat{a}$ is the annihilation operator and $\hat{a}^\dagger$ is the creation operator. For practical reasons, it is common to discard the terms beyond the double excitations in the cluster operator in Eq. (8). This approximation is referred to as the coupled cluster singles and doubles (CCSD) method.

By using $|\psi\rangle$ in Eq. (7), the expectation value of an operator $\hat{O}$ can be exactly described as follows [16,17]

$$\left\langle \hat{O} \right\rangle = \frac{\langle \psi | \hat{O} | \psi \rangle}{\langle \psi | \psi \rangle} = \frac{\langle \psi_0 | e^{\hat{T}^\dagger} \hat{O} e^{\hat{T}} | \psi_0 \rangle}{\langle \psi_0 | e^{\hat{T}^\dagger} e^{\hat{T}} | \psi_0 \rangle}. \tag{9}$$

Here we introduce the normal-order operator $\hat{O}_N$,

$$\hat{O}_N = \hat{O} - O_0, \tag{10}$$

where O_0 is the expectation value of the operator $\hat{O}$ at the reference level (i.e. DF level in the present case). Combing Eq. (10) with Eq. (9), we can write $\langle \hat{O} \rangle$ as

$$\left\langle \hat{O} \right\rangle = \frac{\langle \psi_0 | e^{\hat{T}^\dagger} \hat{O}_N e^{\hat{T}} | \psi_0 \rangle}{\langle \psi_0 | e^{\hat{T}^\dagger} e^{\hat{T}} | \psi_0 \rangle} + O_0 = \langle \psi_0 | e^{\hat{T}^\dagger} \hat{O}_N e^{\hat{T}} | \psi_0 \rangle_C + O_0. \tag{11}$$

The subscript C refers to connected terms [16]. Using the amplitudes determined by the RCCSD method, and retaining only the linear terms in the exponential wave function given in Eq. (7), we calculated the expectation values as follows

$$\left\langle \psi_0 \left| \left(1 + \hat{T}_1 + \hat{T}_2\right)^\dagger \hat{O}_N \left(1 + \hat{T}_1 + \hat{T}_2\right) \right| \psi_0 \right\rangle_C + O_0. \tag{12}$$

The present method takes into account the dominant part of the contribution given by the electron correlation for the one-body expectation values for single reference systems with feasible computational cost. Using this expression, we calculated $W_{s,A}$, E_{eff}, the molecular electric dipole moments (DM) and the parallel components of hyperfine coupling constant (HFCC) $A_{//}$.

Using the electron EDM interaction Hamiltonian given by Salpeter [18], E_{eff} can be written as

$$E_{\mathrm{eff}} = \langle \Psi | \sum_i^{N_e} \beta \sigma_i \cdot \mathbf{E}_{\mathrm{int}} | \Psi \rangle, \tag{13}$$

The above expression can be rewritten specifically for molecules using the alternate one-body Hamiltonian [13, 19]

$$E_{\mathrm{eff}} = 2ic \langle \Psi | \sum_i^{N_e} \beta \gamma_5 \mathbf{p}_i^{\,2} | \Psi \rangle. \tag{14}$$

Eq. (13) and (14) are equivalent when the wave function $|\Psi\rangle$ is the exact eigenstate of the Eq. (6). The effective electron EDM interaction Hamiltonian for an atom has the same form as that for a molecule [20-22], even though the effective electric fields for the two cases are different. DM was calculated using the expression

$$\mathrm{DM} = -\left\langle \Psi \left| \sum_i^{N_e} \mathbf{r}_i \right| \Psi \right\rangle + \sum_A^{N_n} Z_A \mathbf{R}_A. \tag{15}$$

$A_{//}$ was calculated using Quiney's notation [23] as follows,

$$A_{\|} = \frac{g_N}{m_p} \left\langle \Psi \left| \sum_i^{N_e} t_0^1 \right| \Psi \right\rangle. \tag{16}$$

Here g_N is the nuclear g factor and m_p is proton mass. t_0^1 is an one-center component of the magnetic dipole hyperfine tensor interaction and the matrix element of the operator with the atomic orbital χ, χ' is calculated as follows,

$$\begin{aligned} \langle \chi | t_0^1 | \chi' \rangle &= -\alpha(\kappa + \kappa')(-1)^{m-1/2} \times \sqrt{(2j+1)(2j'+1)} \\ &\times \begin{pmatrix} j & 1 & j' \\ -\frac{1}{2} & 0 & \frac{1}{2} \end{pmatrix} \times \begin{pmatrix} j & 1 & j' \\ -m & 0 & m' \end{pmatrix} \\ &\times \int_0^\infty r^{-2} \left(P_\kappa(r) Q_{\kappa'}(r) + Q_\kappa(r) P_{\kappa'}(r) \right) dr . \end{aligned} \tag{17}$$

Here, κ, j, m are the relativistic quantum numbers of the atomic orbitals and the primed values indicate the quantum numbers for ket component. The six numbers in the parenthesis represent 6-j symbols. $P(r)$ and $Q(r)$ are the radial functions of large and small component of the atomic wave function. We calculate the expectation value of $A_{//}$ only taking the ytterbium atomic orbital components.

III. COMPUTATIONAL DETAILS

We used Dyall's four-component valence double-zeta (DZ), triple-zeta (TZ), and quadruple-zeta (QZ) basis sets for ytterbium [24], and Watanabe's four-component basis sets for fluorine [25]. In addition, we employed some diffuse and polarization functions from the Dyall and the Sapporo basis sets [24,26]. Those basis sets are used in uncontracted form. The natures of the basis sets and the total number of the basis spinors are given in Table I. The details are in the supplementary file [27]. The present basis sets are the same as those used in the previous calculations by Abe *et al.* for E_{eff} [13]. In the CCSD calculations, we cut off the virtual spinors with the orbital energy above 80 a.u.

The QZ basis set is the most accurate basis set among the ones we considered. Gomes *et al.* [24] already reported its accuracy in spectroscopic parameters: The bond length and harmonic frequency of YbF were obtained as 2.0196 Å and 503.2 cm^{-1}, respectively, with the Dyall-QZ basis set at the CCSD level. The corresponding experimental values are 2.0161 Å [28] and 506.6674 cm^{-1} [29]. The results using the QZ basis set are also close to the extrapolated values, 2.0174 Å and 507.6 cm^{-1}, obtained from the results of DZ, TZ, and QZ basis sets.

We modified the REL4D code, which is the relativistic part in UTCHEM [30], to calculate $W_{\mathrm{s,A}}$. Our calculations were performed using the UTCHEM and Dirac08 codes [31] modified and combined by Abe *et al*. [13]. UTCHEM was used for the generation of Dirac−Fock orbitals and the molecular orbital integral transformation [32], and DIRAC08 was used for the RCCSD calculations [33].

Similar to our previous work, three kinds of the RCCSD calculations were performed with different numbers of active electrons (49, 69, and 79 electrons). The information of the frozen-core orbitals in each calculation is presented in Table II. We fixed the bond length as 2.0161 Å, experimentally reported. We used the root-mean-squared nuclear charge radius (R^A_{rms}) as 5.305 fm for Ytterbium (^{174}Yb) [34] and 2.90 fm for Fluorine (^{19}F) [35], experimentally determined.

IV. RESULTS AND DISUCUSSION

Table III shows a summary of our calculated results, both at the DF and the CCSD levels. In addition to W_{s} coefficients, E_{eff}, DM, and $A_{//}$ are presented. Some of these values were also reported in our previous paper [13], but show slightly different values because we recalculated them using slightly different numbers of the virtual spinors.

Both $W_{\mathrm{s,Yb}}$ and $W_{\mathrm{s,F}}$ do not depend on the size of basis set at the DF level, but they depend on it at the CCSD level. This trend is also found in the other properties; E_{eff}, DM, and HFCC. Hence, the choice of the basis set is important when we incorporate electron correlation. The TZ basis set at the CCSD level lowers the value of W_{s} compared to its values that were obtained using the DZ and QZ basis sets. This is because of the instability of the CCSD calculations using the TZ basis set, which shows large values of T_1 diagnostic (T_1 diag.). The instability of the TZ basis set was also previously discussed by Gomes *et al*. [24] and Abe *et al*. [13].

For all the basis sets, the values of W_{s} and E_{eff} at CCSD(69e) and CCSD(79e) are very close. The difference between the CCSD(49e) and CCSD(79e) results is rather large; it is about 2~3% for all the properties except for $W_{\mathrm{s,F}}$ and DM. Hence, the 3*s*, 3*p*, and 3*d* orbitals of Yb should be included in the electron correlation calculations to obtain $W_{\mathrm{s,Yb}}$, E_{eff} and HFCC accurately. (Naively, the 1*s* orbital of F is also included in the CCSD(69e) calculation, but the effect is expected to be small because it is the core orbital of the light atom.)

When we compare $W_{\mathrm{s,Yb}}$ and $W_{\mathrm{s,F}}$ in all the calculations, we confirm that $W_{\mathrm{s,Yb}}$ is much larger than $W_{\mathrm{s,F}}$ as expected. Hence, the dominant contribution to the experimental energy shift due to the S-PS interaction comes from $k_{\mathrm{s,Yb}}W_{\mathrm{s,Yb}}$. Since the contribution of Yb is significantly larger than that of F, we have decomposed the value of $W_{\mathrm{s,Yb}}$ at the level of CCSD(79e) with the QZ basis set in order to illustrate the contribution of the correlation effects for $W_{\mathrm{s,Yb}}$.

From Eq. (7), we expand $W_{\mathrm{s,Yb,}}$ which is an expectation value, in terms of combinations involving DF, singly excited (*S*), and doubly excited (*D*) terms in between bra and ket states. Table IV and V show the decomposed nine terms of $W_{\mathrm{s,Yb}}$ and E_{eff}. The largest contribution comes from the DF−DF, and the DF−*S* and *S*−DF terms are the next largest for both $W_{\mathrm{s,Yb}}$ and E_{eff}.

The contribution of singly excited terms, estimated by the summation of DF-*S*, *S*-DF and *S*-*S*, is −8.82 (kHz) and its ratio from the total W_{s} value (−40.5kHz) is 22%. The contribution of doubly excited terms, similarly estimated by the summation of *S*-*D*, *D*-*S* and *D*-*D* is 0.02(kHz), and its ratio is 0.05%. Because the contribution of *D* is much smaller than *S*, the contribution of the higher excitations such as triples would be much smaller in the case of W_{s} of YbF (and similarly it also hold in E_{eff}). Since the excitation effect from the semi-core orbitals of Yb (3*s*, 3*p*, and 3*d*) is about 2% as already discussed, the semi-core excitation effect seems to be more important than the triple cluster excitations.

Since E_{eff} and W_{s} are calculated quantities and their experimental values do not exist, we estimate their error from other related observable quantities, such as HFCC [36] and DM. To justify the validity of our error estimation, we summarize below the similarities and differences in the operators used in the calculations of E_{eff}, W_{s}, HFCC, and DM.

First, the Hamiltonians associated with E_{eff} and W_{s} contain $\beta\gamma^5$ matrix, which provide the off-diagonal coupling between the large and small components of the orbitals. It is similar for HFCC (see in Eq. (17)), but not for DM; which involves diagonal couplings, i.e. large-large and small-small components of the orbitals.

Besides, the Hamiltonian used in the calculation of W_{s}, which contains the nuclear charge density, ρ_{N}. Therefore, the electronic wave function that penetrates the nucleus (femtometer region around the center of the nucleus) mainly determines the size of W_s. Similarly, in the case of E_{eff}, the Hamiltonian in Eq. (13) contains the internal electric field ($\mathbf{E}_{\mathrm{int}}$), which must be significantly large in the region close to the nucleus. Hence E_{eff} would be large when the electrons are distributed close to the heavy nucleus. Similarly, for HFCC, which is associated with a magnetic interaction between the electron and the nuclear spin, the electron density near the target nucleus is also important.

For the three Hamiltonians associated with E_{eff}, W_s, and HFCC, there is one more similarity; the dependence on the electron spin. If we consider the restricted open-shell Dirac−Fock (RODF) method and Kramers restricted molecular orbitals at the DF level, molecular orbital integrals of these three operators obey the following equation.

$$\left\langle \phi_i \middle| \hat{O} \middle| \phi_i \right\rangle = -\left\langle \bar{\phi}_i \middle| \hat{O} \middle| \bar{\phi}_i \right\rangle \tag{18}$$

Here $|\phi\rangle$ and $|\bar{\phi}\rangle$ refer to a particular molecular orbital and its Kramers pair, respectively. Hence at the DF level, the contributions of all the Kramers paired electrons always cancel each other. Only the molecular orbital integrals for the unpaired electrons contribute to the final value at the DF level. In particular for a doublet sigma system such as the YbF molecule, only the contribution from the singly occupied molecular orbital (SOMO) survives.

In summary, E_{eff}, W_s, and HFCC, have the following similarities: (i) They involve the couplings between the large and small components of the single particle wave functions. (ii) Their magnitudes depend on the density of the unpaired electrons in the region close to the nucleus. (iii) Only the SOMO contributes to the DF results.

Finally, we mention the similarity between E_{eff}, W_s, and DM. Since the Hamiltonians used in the evaluation of these quantities are parity odd operators, the mixing of atomic orbitals with different parities is important. In particular for E_{eff} and W_s, as already mentioned, the contribution comes only from the SOMO at the DF level. Hence, the mixing of atomic orbitals of opposite parities in the SOMO is needed to have values of E_{eff} and W_s. Moreover, the s and $p_{1/2}$ orbitals belonging to the heavy atom contribute to large electron densities near the heavy nucleus and hence the mixing of s and $p_{1/2}$ orbitals in SOMO provides large values of E_{eff} and W_s. In contrast, there are no such restrictions for DM. This means that not only the s−$p_{1/2}$ mixing in SOMO, but also other mixings involving opposite-parity occupied orbitals could contribute to the value of DM.

Based on our discussion in the previous sections, we assess the accuracy of our calculated results. Our most accurate calculation is based on the non-frozen-core CCSD method with QZ basis set. The values of W_s, E_{eff}, DM and $A_{//}$ for this method are −40.5 kHz, 23.2 GV/cm, 3.59 D and 7916 MHz, respectively. The discrepancies between the measured and the calculated values are 8.1% and 6.6%, for DM [37] and $A_{//}$ [38], respectively. From these results, we estimate that the errors for W_s and E_{eff} are 7~8%. The errors are likely to reduce if we use a larger basis set or include higher-order correlation effects.

Table VI shows the comparison of our present results of W_s with those of previous calculations. [23, 39−44] The results considering electron correlation and semi-empirical methods yield similar values around 40 kHz whereas the DF or quasi-relativistic Hartree−Fock results are smaller; around 30 kHz.

In Table VI, The DM calculations by Nayak *et al.* using restricted active space configuration interaction (RASCI) method [39-41] and by Parpia using unrestricted DF (UDF) method [42] are in better agreement with the measured value than our result. However, they did not use the experimental value for the bond length, but the ones they obtained from their calculations (R = 2.051 Å by Nayak *et al.* [40] and 2.074 Å by Parpia [42]). In our calculations, when we used a longer bond length, 2.073 Å, we also obtained a larger value of the DM (3.93 D) at the DF level with the basis sets used by Nayak *et al.* [39-41]. This DM value is closer to the experimental DM than our RCCSD result. Hence, the agreement of their calculated DMs with experiment is just fortuitous. From the point of view of the bond length, our method is arguably more accurate than theirs because the bond length optimized at the RCCSD method with the Dyall-QZ basis set was 2.0196 Å, reported by Gomes *et al.* [24]. This value is much closer to the experimental result (2.016 Å) than the values obtained by RASCI (2.051 Å) and UDF (2.073 Å). Since our expectation values were calculated using the experimental bond length and the estimated errors (7~8%) are small, our obtained W_s is more reliable than the previously reported ones.

In addition to the agreement with the experiment, our method is theoretically more rigorous than the other reported methods because of the following two reasons. Firstly, our method is based on the four-component relativistic method, which is of course superior to the quasi-relativistic methods. Secondly, unlike the four-component RASCI [39] and MBPT [41] by Nayak *et al.*, our method is based on the RCC method with much larger core and virtual spinors in the correlation calculation.

IV. CONCLUSION

The value of the S-PS coefficient, $W_{\mathrm{s,Yb}}$, that we obtained is −40.5kHz using the four-component RCCSD method for YbF molecule, a promising candidate for the observation of P and T violation arising from the S-PS interaction and the electron EDM. The error in the calculation of $W_{\mathrm{s,Yb}}$ is estimated as 7~8% by comparing our calculated values of $A_{//}$ and DM with the results of the measurements of these two quantities. From the comparison of our CCSD(49e), CCSD(69e), and CCSD(79e) results, the electron correlation from semi-core orbitals such as the 3*s*, 3*p*, and 3*d* of Yb is non-negligible for obtaining accurate values of $W_{\mathrm{s},A}$, E_{eff}, and $A_{//}$. The method we have used in the present work can be applied to other molecules that can be described by a single reference method. We intend to use it to find new candidates that are better suited for the experimental searches related to the S-PS interaction than the ones that are being currently investigated.

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TABLE I. Basis set information.

Basis set	Nature	Number of basis spinors
DZ (Yb)	24s19p13d8f1g	422
TZ (Yb)	30s24p18d14f3g2h	678
QZ (Yb)	35s30p19d13f5g3h2i	830
F	13s10p4d3f	168

TABLE II. Frozen orbital information in 49 and 69 active-electron calculations

# of active electrons	Frozen orbitals
49	Yb:3*s*, 3*p*, 3*d*, 2*s*, 2*p*, 1*s*. F:1*s*.
69	Yb:2*s*, 2*p*, 1*s*.

TABLE III. Summary of our calculation results at the DF and CCSD methods.

Basis set and method	# of active electrons (# of virtual orbitals)	Total energy (a.u.)	T_1 diag.	$W_{s,Yb}$ (kHz)	$W_{s,F}$ (kHz)	E_{eff} (GV/cm)	DM[a] (D)	$A_{//}$ (MHz)
DZ-DF	–	−14167.289602	–	-29.9	-0.00126	17.9	3.20	6324
TZ-DF	–	−14167.321791	–	-31.6	-0.00125	18.2	3.21	6240
QZ-DF	–	−14167.323266	–	-31.8	-0.00125	18.2	3.20	6239
DZ-CCSD	49e(157)	−14169.344299	0.0403	-35.8	-0.00205	21.4	3.36	8153
DZ-CCSD	69e(157)	−14169.777915	0.0393	-36.6	-0.00222	21.9	3.37	8279
DZ-CCSD	79e(157)	−14169.807608	0.0393	-36.6	-0.00222	21.9	3.37	8293
TZ-CCSD	49e(248)	−14169.860116	0.0477	-36.3	-0.00464	20.9	3.44	6049
TZ-CCSD	69e(248)	−14170.323353	0.0469	-37.0	-0.00481	21.3	3.45	6234
TZ-CCSD	79e(248)	−14170.346980	0.0467	-37.0	-0.00480	21.3	3.45	6259
QZ-CCSD	49e(294)	−14170.031793	0.0316	-39.8	-0.00401	22.8	3.58	7755
QZ-CCSD	69e(294)	−14170.518440	0.0312	-40.5	-0.00416	23.2	3.59	7902
QZ-CCSD	79e(294)	−14170.541674	0.0311	-40.5	-0.00416	23.2	3.59	7916
Exp.	–	–	–	–	–	–	3.91(4)[b]	7424(81)[c]

[a] The direction of the dipole moment is taken as the molecular axis from the fluorine to the ytterbium atom.

[b] Ref. [37]

[c] Ref. [38]

TABLE IV. Contributions of the nine combination terms of W_s at the level of QZ-CCSD(79).

	DF	*S*	*D*
DF	-31.76	-5.54	0.00
S	-5.54	2.26	-0.16
D	0.00	-0.16	0.38

TABLE V. Contributions of the nine combination terms of E_{eff} at the level of QZ-CCSD(79e).

	DF	S	D
DF	18.16	3.19	0.00
S	3.19	−1.30	0.10
D	0.00	0.10	−0.21

TABLE VI. Calculated values of $W_{s,Yb}$, HFCC ($A_{//}$), and DM in the previous and present papers.

Method	Reference	Used bond length (Å)	$W_{s,Yb}$ (kHz)	HFCC ($A_{//}$) (MHz)	DM (D)
Semiempirical	Kozlov [43]	–	−43	–	–
GRECP and SCF	Titov *et al.* [44]	2.0161	−33.0	–	–
GRECP and RASSCF[a]	Titov *et al.* [44]	2.0161	−33.0	4975	–
DHF	Quiney *et al.* [23]	–	−22.0	–	–
DHF+CP	Quiney *et al.* [23]	–	−42.0	7985	–
UDF (unpaired electron)	Parpia [42]	2.074	−34.6	–	–
UDF (all electrons)	Parpia [42]	2.074	−44.0	–	4.00
DF	Nayak *et al.* [39]	2.051	−34.2	–	–
DF	Nayak *et al.* [40]	2.073	–	–	3.98
RASCI[b]	Nayak *et al.* [39]	2.051	−41.2	–	–
RASCI[b]	Nayak *et al.* [40]	2.051	–	–	3.90
MBPT	Nayak *et al.* [41]	2.051	−37.1	–	–
QZ-DF	Present paper	2.0161	−31.8	6239	3.20
QZ-CCSD(79e)	Present paper	2.0161	−40.5	7916	3.59
Experiment	[37,38]	2.0161	–	7424(81)	3.91(4)

[a] GRECP and RASSCF represents the generalized relativistic effective core potential-restricted-active-space self-consistent field.

[b] The numbers of active orbitals taken for RASCI are different in reference [39] and [40].