

P, T-Odd Spin-Rotational Hamiltonian for YbF Molecule

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An *ab initio* relativistic effective core potential calculation of electronic wave function for the ground state ($^2\Sigma$) of a YbF molecule is carried out followed by the restoration of molecular four-component spinor behavior in the core region of ytterbium in the framework of a nonvariational procedure. The constructed spinors are used to evaluate the spin-rotational Hamiltonian parameters including *P*- and *P, T*-odd terms of the molecule. [S0031-9007(96)01783-8]

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It is recognized now that the two-atomic molecules containing heavy atoms are very promising objects for the experimental search for the break of inversion symmetry (*P*) and time-reversal invariance (*T*). Such experiments are of fundamental importance in physics, and they were carried on for a series of atoms and for the TlF molecule [1,2]. The latest results in the experiments on the TlF molecule were obtained at Yale University [3]. The next generation of experiments is in progress now at Brighton University (Hinds and co-workers) on the YbF molecule [4] and is in preparation in Petersburg Nuclear Physics Institute on TlF molecule [5]. However, the calculation of *P*- and *P, T*-odd interaction constants, as well as the matrix elements of other operators singular on nuclei, from them is impossible without knowledge of electronic wave function (WF) of the molecules.

The first calculation of *P, T*-odd interaction constants [describing the interaction of the electric dipole moment (EDM) of nucleons with the electric field on the Tl nucleus] was carried out in 1980 [6] for the TlF molecule with the use of a "relativistic matching" of nonrelativistic one-configurational WF. Then *ab initio* method based on the relativistic effective core potential (RECP) calculation of the molecular WF [7,8] and a semiempirical scheme [9,10] were developed for the calculation of *P, T*-odd interactions in molecules.

Modern electronic structure calculations of molecules with the "nodeless" RECP are rather good for potential curves (surfaces) of ground and low-lying excited states and their chemical properties [11] because the RECP method allows one to treat satisfactorily the correlation structure and relativistic effects in the valence region of a molecule. However, the valence molecular orbitals (spinors) are smoothed in the core region of heavy elements and, as a result, direct calculation of such properties as electronic density near heavy nuclei, hyperfine structure (HFS) and *P, T*-odd interaction constants is impossible.

On the contrary, the all-electron relativistic Dirac-Fock (DF) calculations (e.g., see [12] and references) that give the correct shape of four-component spinors near heavy nuclei are much more expensive than the RECP ones, and they will hardly be used in the near future for accurate

calculation of the correlation structure of many-electron molecules with low symmetry.

It seems to us that the best way to overcome the above mentioned difficulties is to perform the RECP calculation of molecular pseudowave function (PWF) that is good for the electronic density in the valence region and then to restore the proper behavior of the molecular spinors in the core region of the heavy atom.

The first RECP-based calculations of the *P, T*-odd spin-rotational Hamiltonian parameters for PbF and HgF molecules were carried out in the framework of the one-configurational approximation [7,8] with minimal atomic basis sets; i.e., the correlation structure was not taken into account. In the present calculation, we used more flexible atomic basis sets and considered the correlation effects within the restricted active space self-consistent field (RASSCF) method [13,14] that is a variant of the multi-configurational self-consistent field (MC SCF) approach.

Electronic wave function.—The scheme of the one-configurational calculation is described in [7,8], and below we will focus only on specific features of the present calculations.

Following the procedure described in [15], different shape-consistent RECP variants for Yb atom were generated (see Table I). In order to compare these RECPs by accuracy, calculations of transitions energies (TE) between the states of Yb atom with different occupation numbers of *6s, 6p* shells and with closed *4f* shell were implemented taking into account that *4f* electrons are chemically inactive in the ground state $^2\Sigma$ of YbF. The absolute errors of TE reproduction in the RECP calculations (as compared to the TE from all-electron DF calculation), the shells involved in the procedure of the RECP generation, and the number of electrons explicitly included in the calculations with RECP are presented in Table I. The GRECP-(1) (generalized RECP) (see [15] for details) was chosen for molecular calculations because this RECP variant provides sufficient accuracy with small computational expenses.

The RASSCF calculations of the molecular WF were carried on with the spin-averaged part of the RECP (AREP), and contribution of the spin-orbit interaction (i.e., effective spin-orbit potential or ESOP as a part of the

TABLE I. The transitions between the states of Yb atom averaged upon the nonrelativistic configuration.

| DF | Val. | | Ion. | | | |
|---------------------------------|-----------|-----------------------------------|-------|------|--------|-------|
| | RECP | RECP | GRECP | RECP | GRECP | GRECP |
| | (1) | (1) | (1) | (2) | (2) | (2) |
| | 6s6p | 5s5p | 5s5p | 4f | 4f5s5p | |
| | | | 6s6p | 6s6p | 6s6p | |
| All | 2 | 10 | 10 | 16 | 24 | |
| Conf. | TE (a.u.) | Absolute errors (10^{-5} a.u.) | | | | |
| 6s ² | 0.00000 | 0 | 0 | 0 | 0 | 0 |
| 6s ¹ 6p ¹ | 0.06996 | -90 | 190 | -5 | -66 | 0 |
| 6s ¹ 5d ¹ | 0.10544 | -26 | 474 | 8 | -154 | -6 |
| 6s ¹ | 0.18928 | 6 | 283 | -5 | -57 | 1 |
| 6p ¹ | 0.31137 | 62 | 556 | 4 | 31 | 6 |
| 5d ¹ | 0.29809 | 138 | 968 | 27 | -144 | -6 |

RECP) was estimated in the framework of the perturbation theory.

For fluorine we used the basis set of Duijneveldt from the ANO-I library [14].

As it was suggested earlier (see [1,8]), the hybridization of valence s and p orbitals of the heavy atom for the unpaired electron in molecules similar to YbF and HgF with the ground state $^2\Sigma$ is mainly of interest when studying the P, T -odd interactions. To examine this assumption and evaluate the P, T -odd spin-rotational Hamiltonian parameters for YbF, we used in the present molecular calculations the following s and p pseudo-orbitals of ytterbium derived from numerical Hartree-Fock calculations with the AREP:

$\tilde{\varphi}_1^s$ is $5s$ orbital and $\tilde{\varphi}_1^p$ is $5p$ orbital from the ionic state (Yb⁺) with the configuration $[Pd4f^{14}5s^2]5p^66s^1$ (in the following atomic calculations, all the orbitals were kept as frozen except $6s$ and $6p$ ones);

$\tilde{\varphi}_2^s$ is $6s$ orbital from $[\dots]5p^56s^1$ (Yb⁺⁺);

$\tilde{\varphi}_3^s$ is $6s$ orbital from $[\dots]5p^66s^1$ (Yb⁺);

$\tilde{\varphi}_4^s$ is $6s$ orbital from $[\dots]5p^66s^2$ (Yb);

$\tilde{\varphi}_5^s$ is $7s$ orbital from $[\dots]5p^66s^07s^1$ (Yb⁺);

$\tilde{\varphi}_2^p$ is $6p$ orbital from $[\dots]5p^56p^1$ (Yb⁺⁺);

$\tilde{\varphi}_3^p$ is $6p$ orbital from $[\dots]5p^66p^1$ (Yb⁺);

$\tilde{\varphi}_4^p$ is $6p$ orbital from $[\dots]5p^66s^16p^1$ (Yb).

For molecular calculation, these basis functions were approximated by linear combinations of ten Gaussian functions in a general contraction scheme to provide reproduction of the numerical pseudo-orbitals with high accuracy.

All the other atomic orbitals (d, f polarization functions for ytterbium, s, p , and polarization d functions for fluo-

rine) were used in the RECP calculations of YbF as contracted combinations of Gaussians {basis set contraction for Yb, (10, 10, 6, 6) \rightarrow [5, 4, 6, 4], and for F, (14, 9, 4) \rightarrow [5, 4, 2]} in order to provide reproduction of spectroscopic constants with good accuracy (see below).

The AREP/RASSCF calculations of the pseudowave function were performed for the ground state $^2\Sigma$ of YbF with the help of the MOLGEP program [16]. We made calculations for the parameters of the P, T -odd part of the spin-rotational Hamiltonian at the experimental equilibrium internuclear distance [17]. The active space in the RASSCF wave function was varied from 1 to 80 000 configurations in order to study first the change of the state of unpaired valence electron caused by correlation effects.

The following results for the unpaired electron of YbF in the ground state are obtained.

(i) The MO LCAO coefficients for $6s$ and $6p_0$ atomic orbitals are very stable in all our calculations.

(ii) The MO LCAO coefficients of d and f orbitals of ytterbium are about 20 times smaller and the MO LCAO coefficients of s and p orbitals of fluorine are about 5 times smaller than that for the $6p_0$ orbital of ytterbium, therefore they are negligible in the calculation of the P, T -odd spin-rotational Hamiltonian parameters.

(iii) The sp -hybridized molecular orbital of an unpaired electron is a rather diffuse one; its "average radius" is about 2 times larger than the internuclear distance and the "center" is shifted from ytterbium to the opposite direction with respect to the fluorine atom.

(iv) Spin-orbit mixing for the $6p$ orbitals of Yb (which give contribution to the state of unpaired electron when correlations are taken into account) leads to the MO LCAO coefficients for $6p_{\pm 1}$ orbitals at least 30 times smaller as compared to the $6p_0$ orbital coefficients and, therefore, may be neglected for the accuracy required by the experiment.

As a summary of these results, one can write the molecular pseudo-orbital of the unpaired electron in the form

$$\tilde{\varphi}_u^M = \sum_i C_i^s \tilde{\varphi}_i^s + \sum_i C_i^p \tilde{\varphi}_i^{p, m_i=0} + \dots, \quad (1)$$

where $\tilde{\varphi}_i^{s,p}$ are the pseudo-orbitals of ytterbium (as described before) with the MO LCAO coefficients C_i^s, C_i^p for SCF and RASSCF calculations listed in Table II and contributions of fluorine orbitals are neglected.

The results of our AREP/RASSCF calculations with 21 520 configurations [in C_{2v} point group with (a_1, b_1, b_2, a_2) irreps and with distribution of 19 electrons on active orbitals within RAS 1 = (4, 2, 2, 0), RAS 2 = (3, 0, 0, 0), and RAS 3 = (4, 2, 2, 2) subspaces] for the equilibrium distance, vibration constant, and dipole moment ($R_e = 2.050$ Å, $\omega_e = 489$ cm⁻¹, $D_e = 3.58D$) are in a good agreement with the experimental data ($R_e = 2.016$ Å [17], $\omega_e = 502$ cm⁻¹ [17], $D_e = 3.9D$ [18])

TABLE II. MO LCAO coefficients for the unpaired electron in YbF.

| | SCF | RASSCF | SCF | RASSCF |
|---------|---------|---------|---------|---------|
| C_1^s | 0.0081 | 0.0083 | C_1^p | -0.0262 |
| C_2^s | 0.1100 | 0.1263 | C_2^p | -0.0115 |
| C_3^s | -0.0259 | 0.0011 | C_3^p | -0.3578 |
| C_4^s | -0.9970 | -1.0413 | C_4^p | -0.0137 |
| C_5^s | -0.0096 | -0.0180 | | |

and with results of RECP calculations of Dolg *et al.* [19] ($R_e = 2.045 \text{ \AA}$, $\omega_e = 492 \text{ cm}^{-1}$, $D_e = 3.55D$).

Spin-rotational Hamiltonian.—The spin-rotational structure for the $^2\Sigma$ state of diatomics may be described by the Hamiltonian operator \hat{H}_{sr} in terms of the effective electronic spin \mathbf{S}_e ($S_e = \frac{1}{2}$) [8–10],

$$\begin{aligned} \hat{H}_{sr} = & BN^\dagger \mathbf{N} + \gamma \mathbf{S}_e^\dagger \mathbf{N} + \mathbf{S}_e^\dagger \hat{\mathbf{A}} \mathbf{I} \\ & + \mu_0 \mathbf{S}^\dagger \hat{\mathbf{G}} \mathbf{B} - D_e \mathbf{n}^\dagger \mathbf{E} \\ & + W_{PKP} [\mathbf{n} \times \mathbf{S}_e]^\dagger \mathbf{I} + (W_{PTKP} + W_d d_e) \mathbf{S}_e^\dagger \mathbf{n} \\ & - W_M \frac{M}{2I(2I-1)} \mathbf{S}_e^\dagger \hat{\mathbf{T}} \mathbf{n}. \end{aligned} \quad (2)$$

The first line of this expression describes the rotational structure with the spin doubling (γ is the spin-doubling constant) and the hyperfine interaction of the electron spin with the nuclear spins \mathbf{I} of ytterbium. The parameter B is the rotational constant, and \mathbf{N} is rotational angular momentum.

The second line presents the interaction of the molecule with the external magnetic (\mathbf{B}) and electric (\mathbf{E}) fields. The unit vector \mathbf{n} is directed from the heavy nucleus to the light one.

The remaining terms in Eq. (2) correspond to P - and P, T -odd weak interactions of an electron with the heavy nucleus and to the interactions caused by the P - and P, T -forbidden electromagnetic moments of an electron and the nucleus. The anapole moment of nucleus κ_P and the constant of the scalar electron-nucleus neutral currents interaction κ_{PT} are the dimensionless constants on the contrary to the EDM of an electron d_e and the nuclear magnetic quadrupole moment M . Components of tensor $\hat{\mathbf{T}}$ are defined by the equation

$$T_{m,n} = I_m I_n + I_n I_m - \frac{2}{3} I(I+1).$$

The γ , W_i , and molecular dipole moment D_e constants, $\hat{\mathbf{A}}$ and $\hat{\mathbf{G}}$ tensors are matrix elements (MEs) of the corresponding operators that are important to know for interpretation of the experiments on the search for the break of inversion symmetry and time-reversal invariance in a molecule like YbF. For a more detailed description of these MEs, P - and P, T -odd properties, see papers [1,8,10].

With the exception of the B and D_e constants, all the other one-electron operators in Eq. (2) are spin dependent,

therefore their evaluation is reduced to the calculation of MEs with the molecular orbital (1) of the unpaired electron when neglecting the spin-correlation effects of this electron with the other ones.

Results.—In order to evaluate the matrix elements of the operators singular near nucleus of ytterbium, the molecular relativistic spinor for the unpaired electron is constructed from the molecular pseudo-orbital (1) so that the atomic s - and p -pseudo-orbitals of Yb in (1) are replaced by the original unsmoothed four-component spinors derived for the same nonrelativistically averaged atomic configurations as were used in the generation of basis s, p pseudo-orbitals (see the section on electronic wave function). The MO LCAO coefficients (Table II) are preserved after the RECP calculations. This technique was proposed in [7] and in slightly different form in [20] for the shape-consistent pseudo-orbital formalism. A more advanced variational two-step technique suggested in [21] and based on the generalized RECP method [15] is in progress now.

As the spin-orbit interaction for the unpaired electron is small, the “spin-averaged” unpaired atomic p pseudo-orbital was replaced by the linear combination of the corresponding spinors with $j = l \pm 1/2$,

$$\begin{aligned} \tilde{\varphi}_i^{l=1, m_l=0} \chi^{m_s=1/2} \rightarrow & \sqrt{\frac{1}{3}} \psi_i^{l=1, j=1/2, m=1/2} \\ & + \sqrt{\frac{2}{3}} \psi_i^{l=1, j=3/2, m=1/2}, \end{aligned} \quad (3)$$

where $\sqrt{1/3}$, $\sqrt{2/3}$ are Clebsch-Gordan coefficients.

Calculations of the atomic four-component spinors and spin-rotational Hamiltonian parameters were done with the finite size of ^{173}Yb nucleus (in the model of uniformly charged ball) taken into account. The results for the P, T -odd spin-rotational Hamiltonian parameters calculated with the orbital (1) can be found in Table III.

Calculation of the HFS constants is important in the first turn in order to estimate the quality of above-mentioned parameters because the corresponding matrix elements are interlinked to each other [8,10]. The tensor $\hat{\mathbf{A}}$ is diagonal in the molecular frame of references, and two components perpendicular to the molecular axis are equal to each other ($I = 1/2$). The one-configurational (SCF) calculations of YbF leads to the following HFS constants, ($A_{\parallel} = 5049 \text{ MHz}$, $A_{\perp} = 4873 \text{ MHz}$), whereas the RASSCF calculations with 21 520 configurations gives ($A_{\parallel} = 4975 \text{ MHz}$, $A_{\perp} = 4794 \text{ MHz}$).

TABLE III. Results of the calculations for YbF molecule.

| | W^d ($10^{25} \frac{\text{Hz}}{e \text{ cm}}$) | $W_1^{P,T}$ (kHz) | W_2^P (Hz) | $W^{\mathcal{M}}$ ($10^{33} \frac{\text{Hz}}{e \text{ cm}^2}$) |
|----------------------------|---|----------------------|-----------------|---|
| Semiempirical ^a | -1.5 | -48 | 730 | -2.1 |
| SCF ^b | -0.91 | -33 | 484 | -1.3 |
| RASSCF ^b | -0.91 | -33 | 486 | -1.3 |

^aData are taken from the work of Ref. [10].

^bOur data.

These data can be compared with the experimental results [17] ($A_{\parallel} = 7822$ MHz, $A_{\perp} = 7513$ MHz), and one can see that both our SCF and RASSCF results are about 1.5 times smaller than the experimental data. Thus, correlations taken into account within our RASSCF calculations (in the valence region and in the $2p$ shell of fluorine mainly due to the basis set selection) are not responsible for the serious increase in HFS constants.

Analysis of results of all-electron four-component configuration interaction (CI) calculations for the ion Yb^+ with the leading configuration $[\dots]5p^66s^1$ (and with the core and core-valence correlations taken into account) shows the increase of more than 40% for the HFS constants as compared to the corresponding one-configuration calculation (see also MBPT analysis of this problem and results of atomic calculations in papers [2,22]). Thus, one can conclude that the spin-correlation effects of the unpaired electron occupying mainly the $6s, 6p$ hybridized orbital with outer core $5s, 5p$ electrons of ytterbium and correlations in the core shells of Yb should be taken into account in the first turn in order to perform precise calculations of HFS constants.

Despite the large deviation from the experimental HFS data, we estimate the quality of our SCF results both for the HFS constants and for P - and P, T -odd interaction parameters in YbF within (5–10)% of accuracy as could be compared with the corresponding DF calculations, and this is at least 3 times better than the accuracy of previous HgF and PbF calculation [8].

One of the most interesting objects for experimental investigation in YbF is the EDM of electron [1]. The W_d value in Table III can be compared with the corresponding semiempirical calculations of YbF [10], *ab initio* results for HgF [8] and with atomic data [1]. The value $W_d/2$ is the averaged electric field on the unpaired electron, that in the conventional units is 2×10^{10} V/cm. It is about 3–4 times smaller than the average field on the unpaired electron in HgF but approximately 3 orders larger than the electric fields in the case of atomic experiments. As was analyzed in [8–10], this molecular electric field can be directed along the molecular axis and oriented by the external field of order 10^4 V/cm. Taking into account experimental difficulties with detection of HgF molecules, the experiments on YbF seem to be quite promising.

It should be mentioned also that our results for the P, T -odd interaction parameters, the most likely, underestimate the real values while the results of [10] (see Table III) overestimate them. So one should expect the proper magnitudes for W_P, W_{PT}, W_d , and W_M within rather small intervals of these data. One more remark is that the obtained results are quite satisfactory for the experimental requirements.

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