

## LETTER TO THE EDITOR

**Enhancement of the electric dipole moment of the electron in the YbF molecule**

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**Abstract.** We calculate an effective electric field on the unpaired electron in the YbF molecule. This field determines the sensitivity of the molecular experiment to the electric dipole moment of the electron. We use experimental values of the spin-doubling constant  $\gamma$  to estimate the admixture of the configuration with the hole in the 4f shell of ytterbium to the ground state of the molecule. This admixture reduces the field by 7%. Our value for the effective field is  $5.1 \text{ au} = 2.5 \times 10^{10} \text{ V cm}^{-1}$ .

It is well known that effects caused by an electric dipole moment (EDM) of the electron  $d_e$  are strongly enhanced in heavy diatomic radicals (for a review see, for example, [1]). An experimental search for the EDM of the electron is now underway at Sussex University on the YbF molecule [2]. For this reason reliable calculations for this molecule are necessary. The existence of a shallow 4f shell adds complexity to such calculations. Here we extend the semiempirical approach suggested in [3, 4] to account for a possible admixture of the configuration with the hole in the 4f shell of ytterbium. The idea that the f hole can explain the small value of the spin-doubling constant  $\gamma$  is due to Khriplovich [5].

The EDM experiments with radicals are performed on the spin-rotational levels of the electronic ground state. The spin-rotational degrees of freedom of the molecule are described by the following spin-rotational Hamiltonian [6–9]:

$$H_{\text{sr}} = BN^2 + \gamma \mathbf{S} \mathbf{N} + \underline{\underline{\mathbf{S} \mathbf{A} \mathbf{I}}} + W_d d_e \mathbf{S} \mathbf{n}. \quad (1)$$

In this expression  $\mathbf{N}$  is the rotational angular momentum,  $B$  is the rotational constant,  $\mathbf{S}$  is the spin of the electron and  $\mathbf{I}$  is the spin of the Yb nucleus,  $\mathbf{n}$  is the unit vector directed along the molecular axis from Yb to F. The spin-doubling constant  $\gamma$  characterizes the spin-rotational interaction. The axial tensor  $\underline{\underline{\mathbf{A}}}$  describes magnetic hyperfine structure. It can be determined by two parameters:  $A = (A_{\parallel} + 2A_{\perp})/3$  and  $A_d = (A_{\parallel} - A_{\perp})/3$ . The last term in (1) corresponds to the interaction of the EDM of the electron  $d_e$  with the molecular field, where  $\frac{1}{2}W_d$  is the effective electric field on the electron.

The parameters  $B$ ,  $\gamma$ ,  $A$  and  $A_d$  are known from experiment [10–12]:

$$B = 7237 \text{ MHz} \quad \gamma = 13 \text{ MHz} \quad A = 7617 \text{ MHz} \quad A_d = 102 \text{ MHz} \quad (2)$$

while  $W_d$  have to be calculated. There are three calculations of this parameter [4, 13, 14]. In earlier calculations [4, 13] the 4f shell of ytterbium was frozen. In [14] f electrons are included in the valence space, but details of this calculation have not yet been published. Here we allow the admixture of the f hole to the ground state of the molecule.

The ground state of the YbF molecule is known to be  $\Sigma_{1/2}$  [10]. The large hyperfine constants  $A$  and  $A_d$  indicate that an unpaired electron occupies the molecular orbital  $\sigma_s$  with a dominant contribution from the  $6s$  orbital and a significant contribution from the  $6p_0$  orbital of the Yb ion. But a simple one-configurational wavefunction cannot explain an exceptionally small value of the constant  $\gamma$ . Following Khriplovich we will assume that there is small admixture of the f hole:

$$|\Sigma, \omega\rangle = |\sigma_s, \omega\rangle + \delta_f \overline{|\sigma_f, -\omega\rangle} \quad (3)$$

where  $\omega = \pm \frac{1}{2}$  is the projection of the total electronic angular momentum on the molecular axis and the bar over the orbital corresponds to the hole. More explicitly (3) means that the many-electron wavefunction reads

$$|\Sigma, \omega\rangle = [\dots] \left( |\sigma_f, -\frac{1}{2}\rangle |\sigma_f, \frac{1}{2}\rangle |\sigma_s, \omega\rangle + \delta_f |\sigma_f, \omega\rangle |\sigma_s, -\frac{1}{2}\rangle |\sigma_s, \frac{1}{2}\rangle \right) \quad (4)$$

where  $[\dots]$  denotes the closed core. The spin-orbit interaction for the f hole is large and has the opposite sign. This can explain the small value of  $\gamma$  (see below).

All constants of the Hamiltonian (1) except for the constant  $B$  depend only on the electron spin density in the vicinity of the heavy nucleus. For this reason we can expand molecular orbitals in spherical waves with the origin at the Yb nucleus:

$$|\sigma_s, \omega\rangle = (x_s |\tilde{6s}\rangle + x_p |\tilde{6p}_0\rangle + x_d |\tilde{5d}_0\rangle + \dots) |\omega\rangle \quad (5)$$

$$|\sigma_f, \omega\rangle = (|\tilde{4f}_0\rangle + \varepsilon_d |\tilde{5d}_0\rangle + \dots) |\omega\rangle \quad (6)$$

where  $|\omega\rangle$  denotes the spin function. The radial functions in this expansion can be considered as distorted orbitals of the  $\text{Yb}^+$  ion. Corresponding principal quantum numbers are marked with a tilde. Dots in (5) and (6) stand for higher spherical waves and orbitals centred on the fluorine. The latter are very important for the formation of the chemical bond, but their contribution to the constants  $\gamma$ ,  $\underline{A}$  and  $W_d$  is negligible because of the strong  $Z$  dependence of the corresponding matrix elements [1, 4].

The wavefunction (3) is written in a pure nonrelativistic coupling case. The spin-orbit interaction  $H_{so}$  mixes state (3) with the  $\Pi_{1/2}$  states. One can expect that the largest admixtures correspond to the molecular orbitals  $\pi_p$  and  $\pi_f$  (the spin-orbit interaction for the 5d shell is much smaller):

$$|\pi_p, \omega\rangle = (a_p |\tilde{6p}_{2\omega}\rangle + \dots) |-\omega\rangle \quad (7)$$

$$|\pi_f, \omega\rangle = (|\tilde{4f}_{2\omega}\rangle + \dots) |-\omega\rangle. \quad (8)$$

Then, the wavefunction of the ground state has the form

$$|\Sigma, \omega\rangle = |\sigma_s, \omega\rangle + c_p |\pi_p, \omega\rangle + \delta_f \overline{|\sigma_f, -\omega\rangle} + c_f \overline{|\pi_f, -\omega\rangle}. \quad (9)$$

The operator of the hyperfine interaction in atomic units has the form

$$H_{hf} = \frac{g_n \alpha}{2m_p} (\boldsymbol{\alpha} \times \mathbf{r} \cdot \mathbf{I}) \frac{1}{r^3} \quad (10)$$

where  $g_n$  is the nuclear  $g$ -factor,  $\alpha$  is the fine-structure constant,  $m_p$  is the proton mass and  $\boldsymbol{\alpha}$  is the vector of Dirac matrices. This operator is known to be almost diagonal in quantum number  $l$  and in the following calculations we neglect nondiagonal terms.

Let us start with the nonrelativistic expressions for a spherical wave  $l \neq 0$ . It is not difficult to derive that for the  $\sigma$ -type state  $|l, 0\rangle$

$$A = 0 \quad A_d = \frac{g_n \alpha^2}{2m_p} \frac{l(l+1)}{(2l-1)(2l+3)} \langle n, l | \frac{1}{r^3} | n, l \rangle. \quad (11)$$

So, in the nonrelativistic approximation only the s-wave contributes to the isotropic constant  $A$ . Note that the radial integral in (11) is rapidly decreasing with  $l$ , while the coefficient in front of it is a weak function of  $l$ .

Interaction of the EDM of the electron with the molecular electric field  $-\nabla\phi$  is also singular at the nucleus [15]. The most convenient form of this operator is [16]

$$H_d = 2d_e \begin{pmatrix} 0 & 0 \\ 0 & \sigma \end{pmatrix} (-\nabla\phi). \quad (12)$$

Relativistic expressions for  $A$ ,  $A_d$  and  $W_d$  can be found in [1, 3, 4]. In [4] these constants were calculated for the wavefunction (9) with  $c_p = \delta_f = c_f = 0$ :

$$A = (11\,850x_s^2 - 102x_p^2 - 5x_d^2 + \dots) \text{ MHz} \quad (13)$$

$$A_d = (422x_p^2 + 36x_d^2 + \dots) \text{ MHz} \quad (14)$$

$$W_d = (-29.7x_sx_p + 1.3x_px_d + \dots) \text{ au.} \quad (15)$$

If we neglect the d-wave terms and use the experimental values (2) for  $A$  and  $A_d$ , we can solve (13)–(15) for  $x_s$ ,  $x_p$  and  $W_d$ :

$$x_s = 0.803 \quad x_p = 0.492 \quad (16)$$

$$W_d = -11.7 \text{ au} = -1.45 \times 10^{25} \text{ Hz (e cm)}^{-1} \quad (17)$$

where the signs of  $x_s$  and  $x_p$  are chosen to account for the repulsion of the unpaired electron from the  $F^-$  ion.

Result (17) is more accurate than one can expect from (13)–(15). It follows from the proportionality between  $W_d$  and  $\sqrt{AA_d}$ :

$$W_d = -1.69 \times 10^{16} \sqrt{AA_d} \text{ (e cm)}^{-1} \quad (18)$$

which is based on the behaviour of s- and p-waves in the vicinity of the nucleus where the molecular potential is close to that of the nucleus. In contrast to that, results (16) depend on the assumption that spherical waves in (5) correspond to the orbitals of  $Yb^+$ .

Below we calculate several corrections to (17) and (18), which mostly account for contributions of the higher spherical waves. If we use the normalization condition  $x_s^2 + x_p^2 + x_d^2 \approx 1$ , we can solve equations (13)–(15) with the d-wave included:

$$x_s = 0.803 \quad x_p = 0.481 \quad x_d = 0.356 \quad W_d = -11.2 \text{ au.} \quad (19)$$

Comparison of (17) and (19) gives the following correction coefficient for the d-wave contribution to  $W_d$ :

$$k_d = 0.96. \quad (20)$$

Note that the normalization condition gives the upper bound for the coefficient  $x_d$ . So, it is likely, that (19) and (20) somewhat overestimate the d-wave contribution.

Let us estimate the mixing coefficient  $c_p$  in (9):

$$c_p = \frac{\langle \Pi(A_1) | H_{so} | \Sigma(X) \rangle}{E_X - E_A} = \frac{\langle \pi_p, \omega | H_{so} | \sigma_s, \omega \rangle}{E_X - E_A} \approx \frac{x_p a_p \xi_{6,1}}{\sqrt{2}(E_X - E_A)} \quad (21)$$

where we use (5) and (7) to calculate the numerator:

$$\langle \pi_p, \omega | H_{so} | \sigma_s, \omega \rangle \approx x_p a_p \langle \tilde{6}p_1, -\frac{1}{2} | H_{so} | \tilde{6}p_0, \frac{1}{2} \rangle \approx x_p a_p \langle 6p_1, -\frac{1}{2} | H_{so} | 6p_0, \frac{1}{2} \rangle \quad (22)$$

$$\langle n, l, 1, -\frac{1}{2} | H_{so} | n, l, 0, \frac{1}{2} \rangle \equiv -\xi_{n,l} \langle l, 1 | l_1 | l, 0 \rangle \langle -\frac{1}{2} | s_{-1} | \frac{1}{2} \rangle = \frac{1}{2} \xi_{n,l} \sqrt{l(l+1)} \quad (23)$$

and  $\xi_{n,l}$  is the atomic spin-orbit constant for the  $(n, l)$  shell. It is proportional to the radial integral which enters (11). For the  $Yb^+$  ion  $\xi_{6,1} = 1900 \text{ cm}^{-1}$ .

The level (7) is identified as  $A_1$  ( $E_{A_1} = 18\,090\text{ cm}^{-1}$ ). Its fine-structure splitting with the level  $A_2$  ( $\Pi_{3/2}$ ) is  $1370\text{ cm}^{-1}$  [10]. Within the same approximation we can link this splitting to the constant  $\xi_{6,1}$  and find parameter  $a_p$ :

$$E_{A_2} - E_{A_1} \approx a_p^2 \xi_{6,1} \Rightarrow a_p^2 \approx 0.72. \quad (24)$$

In the same manner we can calculate the coefficient  $c_f$  in (9). In this case the spin-orbit interaction mixes the  $\sigma_f$  hole with the  $\pi_f$  hole:

$$c_f = \frac{\langle \Pi(F) | H_{so} | \Sigma(X) \rangle}{E_X - E_F} \approx \delta_f \frac{\langle \pi_f, -\omega | H_{so} | \sigma_f, -\omega \rangle}{E_X - E_F} \approx \frac{-\sqrt{3} \delta_f \bar{\xi}_{4,3}}{E_X - E_F}. \quad (25)$$

The only problem here is that the molecular state with the  $\pi_f$  hole, which we define as  $\Pi(F)$ , is not known, and thus we do not know the energy denominator. The spin-orbit constant for the f hole has the opposite sign to normal:  $\bar{\xi}_{4,3} = -3665\text{ cm}^{-1}$ .

Equations (21), (24) and (25) reduce the number of independent parameters in the wavefunction (9). Still, it has two extra parameters  $\delta_f$  and  $\varepsilon_d$  compared to the wavefunction (5) which was used in (13)–(15). Below we eliminate parameter  $\delta_f$  using the experimental value of the spin-doubling constant  $\gamma$ .

The spin-doubling term in the effective Hamiltonian (1) arises from the spin-orbit interaction. It was shown in [9] that

$$\gamma = 2B \left( 1 - \langle \Sigma(X), \frac{1}{2} | J_{e,+} | \Sigma(X), -\frac{1}{2} \rangle \right) \quad (26)$$

where  $J_e = L + S$  is the total angular momentum of the electrons. For the pure  $\Sigma$  state  $\langle J_e \rangle = \langle S \rangle$  and (26) gives  $\gamma = 0$ . This is no longer true when the spin-orbit corrections are taken into account. With the help of (26), (21) and (25) it is easy to calculate  $\gamma$  for the state (9):

$$\gamma = 2B \left( 2(x_p a_p)^2 \frac{\xi_{6,1}}{E_X - E_A} + 12\delta_f^2 \frac{\bar{\xi}_{4,3}}{E_X - E_F} \right). \quad (27)$$

Note that numerical factors in parentheses are equal to  $l(l+1)$ .

As we have already pointed out, the second denominator in (27) is unknown. If we use the corresponding energy interval for the  $\text{Yb}^+$  ion, we find the following relation between  $x_p$  and  $\delta_f$ :

$$2100x_p^2 - 11\,150\delta_f^2 = 13 \Rightarrow \delta_f^2 \approx 0.19x_p^2. \quad (28)$$

This equation shows that the experimental value of  $\gamma$  corresponds to an almost complete cancellation between p- and f-wave contributions. To obtain this relation between  $\delta_f$  and  $x_p$  we used ionic spin-orbit constants  $\xi_{n,l}$  and the ionic denominator in (27). So, we cannot expect it to be much better than an order of magnitude estimate.

It follows from (11), (27) and (28) that for the molecular state (9) the f-wave contribution to the constant  $A_d$  should be approximately six times smaller than that of the p-wave. Indeed, the two contributions to the constant  $\gamma$  cancel each other, but in (27) there is the factor  $l(l+1)$  which is not present in (11).

A straightforward relativistic calculation results in the following f-hole correction to the hyperfine tensor

$$\delta A = -\frac{g_n \alpha}{2m_p} \delta_f^2 \left( \frac{12}{49} h_{5/2,5/2} + \frac{32}{49} h_{5/2,7/2} + \frac{64}{147} h_{7/2,7/2} \right) \text{ au} \quad (29)$$

$$\delta A_d = \frac{g_n \alpha}{2m_p} \delta_f^2 \left( \frac{48}{245} h_{5/2,5/2} - \frac{8}{49} h_{5/2,7/2} + \frac{64}{441} h_{7/2,7/2} \right) \text{ au}. \quad (30)$$

The radial integrals  $h_{j,j'}$  here have the form  $h_{j,j'} = \int_0^\infty dr (f_j g_{j'} + g_j f_{j'})$ , where  $f_j$  and  $g_j$  are the upper and lower components of the radial Dirac wavefunction. Again we take radial integrals for the  $\text{Yb}^+$  ion and use (28) to arrive at

$$\delta A = -11x_p^2 \text{ MHz} \quad \delta A_d = 64x_p^2 \text{ MHz}. \quad (31)$$

It is clear, that the correction (31) to isotropic constant  $A$  (13) is negligible, while the correction to the dipole constant  $A_d$  (14) is about 15% for a given  $x_p$ , which is in a good agreement with our nonrelativistic estimate  $\frac{1}{6}$ .

With the f-hole correction (31) included, equation (14) is changed to

$$A_d = (486x_p^2 + 36x_d^2) \text{ MHz} \quad (32)$$

and we obtain the following f-hole correction coefficient to  $W_d$

$$k_f = 0.93. \quad (33)$$

In deriving (33) we have ignored the direct f-wave contribution to the constant  $W_d$  (see equation (15)). Such a contribution is proportional to a small product  $x_d \delta_f \leq 0.1$  and is less than 1%.

The last correction to the constant  $W_d$  is associated with the admixture of the  $\pi_p$  state to (9). According to (21)  $c_p \approx -0.06x_p$ . This admixture changes the weights of the  $p_{1/2}$  and  $p_{3/2}$  waves in the wavefunction. That, in turn, slightly changes coefficients in (14) and (15) (note, that only the  $p_{1/2}$  wave contributes to  $W_d$ ). A simple calculation gives

$$k_{so} = 0.98. \quad (34)$$

Taking into account (20), (33) and (34), we obtain the total correction factor for  $W_d$  to be  $k_{\text{corr}} = k_d k_f k_{so} = 0.87$ . Applying it to (18), we arrive at

$$W_d = -10.2 \text{ au} = -1.26 \times 10^{25} \text{ Hz (e cm)}^{-1}. \quad (35)$$

We have calculated corrections to the semiempirical value of the constant  $W_d$  of the spin-rotational Hamiltonian (1) which can account for the  $P$ ,  $T$ -odd effects in the  $\text{YbF}$  molecule. The main correction is caused by the f-hole admixture to the ground state. Two other corrections account for the spin-orbit interaction and for the d-wave term in the wavefunction. Altogether they reduce the answer by almost 15%.

We think that the wavefunction (9) includes the two most important configurations. An admixture of other configurations will tend to decrease the constant  $W_d$ , so we can expect our value (35) to be slightly overestimated. It is unlikely that these corrections are significantly larger than the f-hole correction. So we estimate them to be less than 10–15%. Another possible source of error is the quasiclassical approximation, used here to calculate electronic matrix elements. It is known from atomic calculations that for  $Z \geq 50$  the corresponding error is also  $\sim 10$ –15%. Finally, we have not considered the contribution of the fluorine orbitals to  $W_d$ . It is suppressed by the factor  $(Z_F/Z_{\text{Yb}})^3 \approx 0.002$  and thus is negligible. Summing up, we conclude that the accuracy of our calculation is about 20%.

However, let us stress once again that wavefunction (9) with molecular orbitals (5)–(8) can be used only for matrix elements, which mostly depend on the spin density in the vicinity of the  $\text{Yb}$  nucleus.

*Ab initio* calculation [13] gave a smaller absolute value for  $W_d$ , but it also underestimated both  $A$  and  $A_d$ . It is more informative to compare the coefficient in equation (18) which corresponds to different calculations. Our final value for this coefficient is  $-1.47 \times 10^{16} \text{ (e cm)}^{-1}$ , while results of [13] correspond to  $-1.75 \times 10^{16} \text{ (e cm)}^{-1}$ . So, in this sense, our result is even smaller than that of [13].

In this paper we have not considered other possible sources of  $P$ ,  $T$ -violation, such as scalar neutral currents [7] and the magnetic quadrupole moment of the nucleus [17]. The corresponding constants  $W_S$  and  $W_M$  of the spin-rotational Hamiltonian can be calculated in a similar way to  $W_d$  [4]. Our value for the former constant is  $W_S = -43$  kHz. Because of the higher multipolarity of the electronic operator associated with the constant  $W_M$ , this interaction is much more sensitive to the higher terms of the spherical wave expansion of the molecular wavefunction. Thus, it is more difficult to make accurate calculation of this interaction within the semiempirical approach.

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