

EDM of the electron in diatomic molecules

Mikhail Kozlov

Permanent address:

Petersburg Nuclear Physics Institute, Russia

Current address:

University of New South Wales, Australia

Spin-rotational Hamiltonian for $\Sigma_{1/2}$ state (BaF, YbF, & HgF)

$$\begin{aligned} H_{sr} = & BN^2 + \gamma \mathbf{S} \cdot \mathbf{N} + \mathbf{S} \hat{\mathbf{A}} \mathbf{I} + \mathbf{S} \hat{\mathbf{A}}' \mathbf{I}' \\ & + \mu_0 \mathbf{S} \hat{\mathbf{G}} \mathbf{B} - D \mathbf{n} \cdot \mathbf{E} \\ & + W_A k_A \mathbf{n} \times \mathbf{S} \cdot \mathbf{I} + (W_S k_S + W_d d_e) \mathbf{S} \cdot \mathbf{n} \end{aligned}$$

In this expression \mathbf{I} and \mathbf{I}' are the spins of heavy metal and F nuclei; \mathbf{N} is the rotational angular momentum; B and γ are the rotational and the spin-doubling constants. Tensors $\hat{\mathbf{A}}$ and $\hat{\mathbf{A}}'$ correspond to the hyperfine structures on two nuclei. μ_0 is the Bohr magneton; \mathbf{n} is the molecular axis unit vector directed from metal (Ba, Yb, or Hg) to F. \mathbf{B} and \mathbf{E} are the external fields.

The P -odd term is due to the anapole moment of the nucleus, k_A being the anapole moment constant. Two P, T -odd terms correspond

to the scalar electron-nucleus neutral current with the coupling constant k_S & EDM of the electron d_e .

Semi-empirical wave function

The main assumption of the method is that the WF of the molecule can be written as follows

$$|\Lambda, \Omega\rangle = |\lambda = \Lambda, \omega = \Omega\rangle_{\text{unpaired}} |\Lambda_c = 0, \Omega_c = 0\rangle_{\text{coupled}}$$

In the vicinity of the heavy nucleus (Ba, Yb, or Hg) the WF can be expanded in spherical waves

$$|\lambda, \omega\rangle = \sum_k C_k |l, j, \omega\rangle, \\ k = (l - j)(2j + 1)$$

Here $|l, j, \omega\rangle$ are normalized four-component spherical waves:

$$|l, j, \omega\rangle = \begin{pmatrix} f_{l,j} Y_{j,\omega}^l \\ i g_{l,j} Y_{j,\omega}^{l'} \end{pmatrix}$$

f and g are radial functions, $Y_{j,\omega}^l$ is the spherical spinor, $l' = 2j - l$.

At the small distances solutions of the Dirac equation are:

$$\begin{pmatrix} f_{l,j} \\ g_{l,j} \end{pmatrix} = \frac{k}{|k|} \frac{a_l}{Z^{1/2}r} \begin{pmatrix} (\gamma + k)J_{2\gamma}(x) - \frac{x}{2}J_{2\gamma-1}(x) \\ \alpha Z J_{2\gamma}(x) \end{pmatrix}$$

$$x = \sqrt{8Zr}$$

$$\gamma = \sqrt{(j + 1/2)^2 - \alpha^2 Z^2}$$

For each $l \neq 0$ a pair of functions with $j = l - 1/2$ and $j = l + 1/2$ on the large distances have to form nonrelativistic function

$|l, m_l = \lambda, \omega\rangle$. It means, that

$$p\text{-wave} : C_{-2} = -\sqrt{2}C_1,$$

$$d\text{-wave} : C_{-3} = -\sqrt{3/2}C_2, \dots$$

For small r molecular WF is defined by the products

$$\sigma_s = C_{0,1/2}a_0, \sigma_p = C_{1,1/2}a_1, \dots$$

The hyperfine axial tensor $\hat{\mathbf{A}}$:

$$\begin{aligned}
A &= \frac{A_{\parallel} + 2A_{\perp}}{3} \\
&= \frac{4}{3}C_{-1}^2 h_{-1,-1} + \frac{4}{9}C_1^2 h_{1,1} + \frac{8}{9}C_{-2}^2 h_{-2,-2} \\
&\quad + \frac{8}{15}C_2^2 h_{2,2} + \frac{4}{5}C_{-3}^2 h_{-3,-3} \\
&\quad - \frac{8\sqrt{2}}{9}C_1 C_{-2} h_{1,-2} - \frac{8\sqrt{6}}{15}C_2 C_{-3} h_{2,-3} + \dots
\end{aligned}$$

$$\begin{aligned}
A_d &= \frac{A_{\parallel} - A_{\perp}}{3} \\
&= -\frac{8}{9}C_1^2 h_{1,1} - \frac{8}{45}C_{-2}^2 h_{-2,-2} \\
&\quad - \frac{8}{15}C_2^2 h_{2,2} - \frac{8}{35}C_{-3}^2 h_{-3,-3} \\
&\quad - \frac{2\sqrt{2}}{9}C_1 C_{-2} h_{1,-2} - \frac{2\sqrt{6}}{15}C_2 C_{-3} h_{2,-3} + \dots
\end{aligned}$$

$$h_{k,k'} = -\frac{g_n \alpha}{2m_p} \int_0^{\infty} (f_k g_{k'} + g_k f_{k'}) dr,$$

where g_n is G -factor of the nucleus and m_p is the proton mass.

Using experimental values for A and A_d , we obtain equations for parameters σ_i . For YbF molecule these equations have the form:

$$\begin{cases} A = 31170\sigma_s^2 - 1330\sigma_p^2 - 50\sigma_d^2 + \dots = 7617 \\ A_d = 5510\sigma_p^2 + 370\sigma_d^2 + \dots = 102 \end{cases}$$

The right hand side correspond to the experimental values for A and A_d in MHz measured by Van Zee *et al.*

Coefficients C_k are normalized to unity. The semi-classical analysis gives $a_l^2 \approx 0.3$, and approximate normalization condition for parameters σ_l reads:

$$\sigma_s^2 + 3\sigma_p^2 + \frac{5}{2}\sigma_d^2 \leq 0.3 \sum_k C_k^2 = 0.3$$

The solution which meets this condition correspond to the negligible contribution of the d -wave (less then 5%).

$$\begin{cases} \sigma_s^2 = 0.24 \\ \sigma_p^2 = 0.019 \end{cases} \Rightarrow \sigma_s \sigma_p = -0.067,$$

where the sign corresponds to the polarization in the field of negatively charged F ion.

***P*- and *P, T*-odd interactions**

Interaction of the EDM of the electron d_e with the molecular electric field ($-\nabla\phi$):

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

$$\langle \lambda, \omega | H_d | \lambda, \omega \rangle = W_d d_e \omega$$

$$\begin{aligned} W_d &= 8 \sum_i C_{-i} C_i \int_0^\infty g_{-i} g_i \frac{d\phi}{dr} r^2 dr \\ &= 16\alpha^2 Z^3 \left(\frac{\sigma_s \sigma_p}{\gamma_{1/2}(4\gamma_{1/2}^2 - 1)} - \frac{\sqrt{2}\sigma_p \sigma_d}{\gamma_{3/2}(4\gamma_{3/2}^2 - 1)} \right) \end{aligned}$$

For YbF molecule this expression gives

$$W_d = 174\sigma_s \sigma_p - 15\sigma_p \sigma_d + \dots = -11.7$$

P, T -odd electron–nuclear scalar interaction and P -odd interaction of the electron with the anapole moment of the nucleus have the form:

$$H_S = i \frac{G\alpha}{\sqrt{2}} Z k_S \gamma_0 \gamma_5 n(\mathbf{r})$$

$$H_A = \frac{G\alpha}{\sqrt{2}} k_A \mathbf{I} \gamma_0 \boldsymbol{\gamma} n(\mathbf{r})$$

G is the Fermi constant; γ_i are the Dirac matrices; $n(\mathbf{r})$ is the nuclear density normalized to unity. Dimensionless scalar coupling constant k_S is defined by: $Zk_S = Zk_{S,p} + Nk_{S,n}$, and k_A is the anapole moment constant of the nucleus (Flambaum & Khriplovich).

For YbF the values of the constants W_i are:

$$W_S = -48 \text{ kHz}$$

$$W_A = 0.73 \text{ kHz}$$

SO & f-hole corrections to the wave function of YbF molecule.

We assume that wave function of the ground state of YbF has the form:

$$|\Sigma, \omega\rangle = |\sigma_s, \omega\rangle + \delta_f \overline{|\sigma_f, -\omega\rangle}, \quad \omega = \pm \frac{1}{2}$$

where the bar over the orbital corresponds to the hole. When spin-orbit interaction is taken into account, this wave function becomes:

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

We can expand molecular orbitals in spherical waves with the origin at the Yb nucleus:

$$\begin{aligned} |\sigma_s, \omega\rangle &= (x_s |\tilde{6}s\rangle + x_p |\tilde{6}p_0\rangle + x_d |\tilde{5}d_0\rangle + \dots) |\omega\rangle \\ |\sigma_f, \omega\rangle &= (|\tilde{4}f_0\rangle + \varepsilon_d |\tilde{5}d_0 + \dots\rangle) |\omega\rangle \\ |\pi_p, \omega\rangle &= (a_p |\tilde{6}p_{2\omega}\rangle + \dots) |-\omega\rangle \\ |\pi_f, \omega\rangle &= (|\tilde{4}f_{2\omega}\rangle + \dots) |-\omega\rangle \end{aligned}$$

We can estimate SO-mixing coefficients c_p and c_f :

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

$$c_f = \delta_f \frac{\langle \pi_f, -\omega | H_{so} | \sigma_f, -\omega \rangle}{E_X - E_F} \approx \frac{-\sqrt{3}\delta_f \bar{\xi}_{4,3}}{E_X - E_F},$$

where $\xi_{n,l}$ denotes SO constant for the shell n, l of Yb⁺ ion:

$$\xi_{6,1} = 1900 \text{ cm}^{-1}, \quad \bar{\xi}_{4,3} = -3665 \text{ cm}^{-1}$$

We can use experimental data on the spin-doubling constant to find the f-hole correction δ_f .

$$\gamma = 2B \left(1 - \langle \Sigma(X), \frac{1}{2} | J_{e,+} | \Sigma(X), -\frac{1}{2} \rangle \right) = 13 \text{ MHz},$$

where $\mathbf{J}_e = \mathbf{L} + \mathbf{S}$ is the total angular momentum of the electrons. For the pure Σ state $\langle \mathbf{J}_e \rangle = 1$ and $\gamma = 0$. This is no longer true, when SO corrections are taken into account. One can calculate γ :

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

Equation for γ gives the following relation between x_p and δ_f :

$$2100x_p^2 - 11150\delta_f^2 = 13, \quad \Rightarrow \quad \delta_f^2 \approx 0.19x_p^2$$

We can now calculate f-hole corrections to the HFS constants:

$$\begin{aligned}\delta A &= -11x_p^2 \text{ MHz} \\ \delta A_d &= 64x_p^2 \text{ MHz}\end{aligned}$$

With these corrections HFS equations have the form:

$$\begin{aligned}A &= (11850x_s^2 - 102x_p^2 - 5x_d^2) \text{ MHz} = 7617 \text{ MHz} \\ A_d &= (486x_p^2 + 36x_d^2) \text{ MHz} = 102 \text{ MHz}\end{aligned}$$

Solution of these equations is:

$$x_s = 0.80, \quad x_p = 0.45, \quad x_d \leq 0.4$$

Now we can use these numbers to calculate parameter W_d :

$$\begin{aligned}W_d &= (-29.7x_sx_p + 1.3x_px_d + \dots) \text{ au} \\ &= -10.2 \text{ au} = -1.26 \cdot 10^{25} \text{ Hz}/(\text{e cm}).\end{aligned}$$

(Without f-hole correction was: $W_d = -11.7 \text{ au}$)

Hyperfine constants, spin-doubling constant γ , and P, T -odd constant W_d for BaF molecule

Methods used: Semiempirical method (SE); relativistic effective core potential method (RECP); restricted active space method (RAS); Dirac-Hartree-Fock (DHF) and unrestricted Dirac-Hartree-Fock methods (UDHF); many-body perturbation theory (MBPT).

		A_{\parallel}	$A_{\parallel} - A_{\perp}$	γ	W_d
		MHz	MHz	MHz	$10^{24} \frac{\text{Hz}}{e \text{ cm}}$
Experiment	[1]	2376	75	83.3	
Experiment	[2]	2453	52	81.03	
SE	[3]	2376	75		-4.1
RECP	[4]	1479	33		-2.3
RAS+RECP	[4]	1488	33		-2.2
RAS+MBPT	[4]	2272	72		-3.6

- 1 Knight L B, Easley W C and Weltner W 1971 *J.Phys.Chem.* **54** 322
- 2 Ryzlewicz C *et al* 1982 *Chem.Phys.* **71** 389
- 3 Kozlov M G 1985 *Zh.Eksp.Teor.Fiz.* **89** 1933
- 4 Kozlov M G, Titov A V, Mosyagin N S, and Souchko P V 1997 *Phys.Rev.A* **56** R3326

Hyperfine constants, spin-doubling constant γ , and P, T -odd constant W_d for YbF molecule

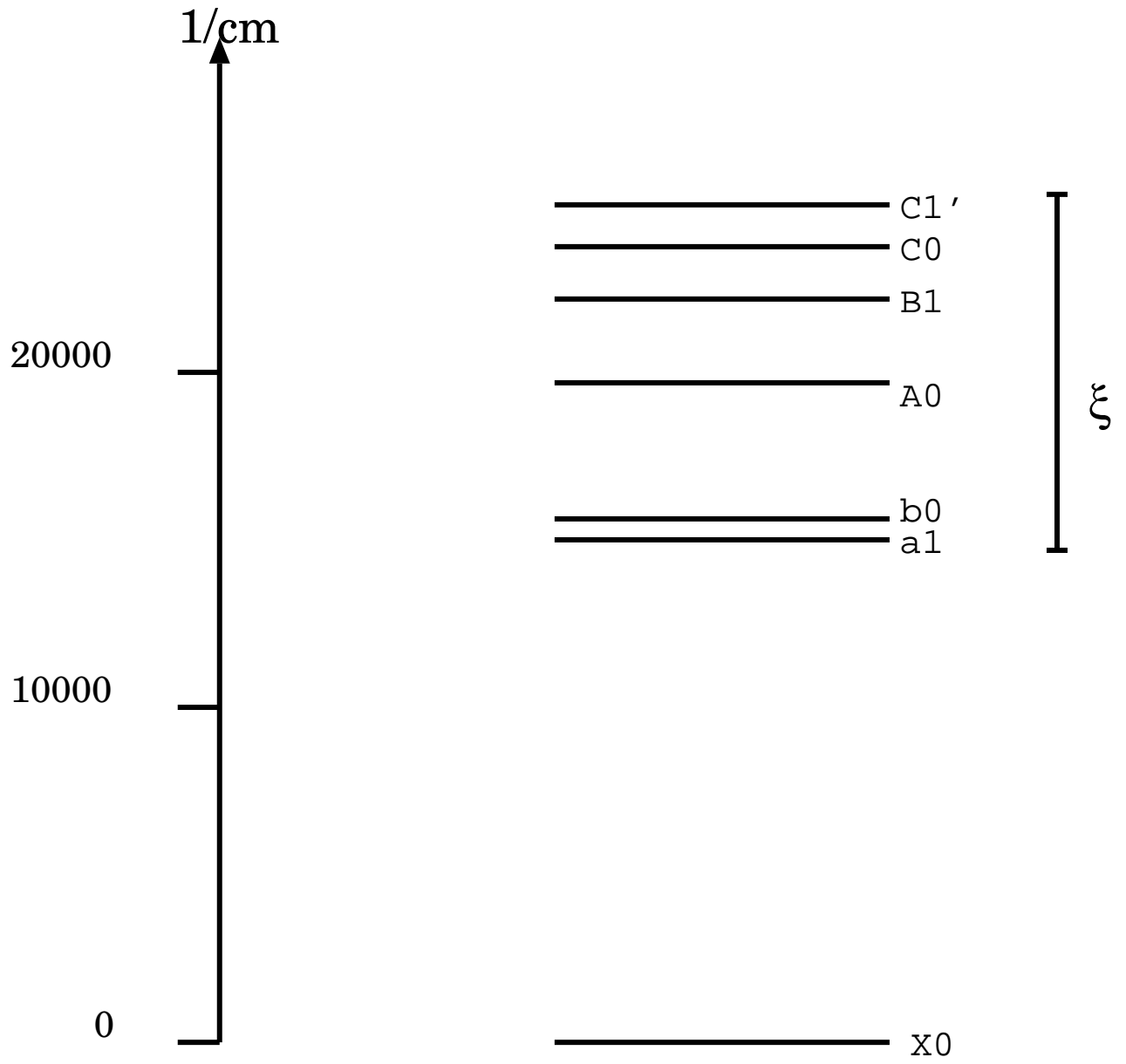
		A_{\parallel}	$A_{\parallel} - A_{\perp}$	γ	W_d
		MHz	MHz	MHz	$10^{24} \frac{\text{Hz}}{\text{e cm}}$
Experiment	[1,2]	7822	309	13	
SE	[3]	"	"	500	-15
SE (f-hole)	[4]	"	"	13	-12.6
RECP+RAS	[5]	4975	181		-9.1
DHF+CP	[6]	7985	180		-6.0($\times 2$)?
UDHF	[7]				-12.0
RECP+MBPT	[8]	7801	312		-13.05

- 1 van Zee R J, Seely M L, de Vore T C , Weltner W Jr. 1978 *J. Phys. Chem* **82** 1192
- 2 Sauer B, Wang J, and Hinds E A 1995 *Phys. Rev. Lett.* **74** 1554
- 3 Kozlov M G and Labzowsky L N 1996 *J. Phys. B: At. Mol. Opt Phys* **28** 1933
- 4 Kozlov M G 1997 *J. Phys. B: At. Mol. Opt Phys* **30** L607
- 5 Titov A V , Mosyagin N S, Ezhov V F 1996 *Phys. Rev. Lett.* **77** 5346
- 6 Quiney H M, Skaane H, Grant I P 1997 *J. Phys. B: At. Mol. Opt Phys* **30**
- 7 Parpia F A 1998 *J. Phys. B: At. Mol. Opt Phys* **31** 1409
- 8 Mosyagin N S *et al* 2001 (unpublished)

Calculated values of P, T -odd constant W_d for diatomic radicals BaF, YbF, PbF, & HgF

Molecule	Ground state	$W_d \left(10^{24} \frac{\text{Hz}}{\text{e cm}}\right)$
BaF	$\Sigma_{1/2}$	-4
YbF	$\Sigma_{1/2}$	-13
PbF	$\Pi_{1/2}$	-14
HgF	$\Sigma_{1/2}$	-48

Spectrum of PbO



SO interaction between the levels a_1 and B_1 leads to the mixing:

$$\begin{aligned} |a_1\rangle &\Rightarrow c_1|a_1\rangle + s_1|B_1\rangle \\ s_1 &= 0.53 P_1 S_p \end{aligned}$$

The final form of the model wave function of the state a_1 is:

$$\begin{aligned} |a_1\rangle &= \frac{c_1}{\sqrt{2}}|\pi_{1,3/2}\tilde{\pi}_{2,-1/2}\rangle + \frac{s_1}{\sqrt{2}}|\sigma_{1/2}\pi_{2,1/2}\rangle \\ &+ \frac{1}{\sqrt{2}}|\tilde{\pi}_{1,-1/2}\pi_{2,3/2}\rangle, \end{aligned}$$

where

$$|\tilde{\pi}_{i,\omega}\rangle = c_i|\pi_{i,\omega}\rangle + s_i|\sigma_\omega\rangle$$

Resent measurement of G -factor gives equation for mixing angles:

$$\begin{aligned} G_{\parallel} &= \langle a_1|L_0 + 2S_0|a_1\rangle \\ &= 2 - s_1^2 - \frac{1}{2}s_2^2 = 1.86(3) \\ &\Rightarrow 2s_1^2 + s_2^2 = 0.28(6) \end{aligned}$$

Another equation follows from the measurement of HFS constant A_{\parallel} :

$$\begin{aligned} A_{\parallel}(\mathbf{I} \cdot \mathbf{n}) &= \langle a_1|H_{\text{hfs}}|a_1\rangle = -4.1 \text{ GHz} \\ &= \frac{c_1^2}{2} [\langle \pi_{1,3/2}|h_{\text{hfs}}|\pi_{1,3/2}\rangle - \langle \tilde{\pi}_{2,1/2}|h_{\text{hfs}}|\tilde{\pi}_{2,1/2}\rangle] \\ &+ \frac{s_1^2}{2} [\langle \sigma_{1/2}|h_{\text{hfs}}|\sigma_{1/2}\rangle - \langle \pi_{2,1/2}|h_{\text{hfs}}|\pi_{2,1/2}\rangle] \\ &+ \frac{1}{2} [\langle \pi_{2,3/2}|h_{\text{hfs}}|\pi_{2,3/2}\rangle - \langle \tilde{\pi}_{1,1/2}|h_{\text{hfs}}|\tilde{\pi}_{1,1/2}\rangle] . \end{aligned}$$

The model does not allow to determine all parameters of the wave function. However, there are number of features, which hold for the whole allowed domain:

1. The orbital $\tilde{\pi}_{1,1/2}$ is strongly shifted to oxygen, less than 10% of its weight is on lead. That is in agreement with naive picture that two electrons from lead move to oxygen to close its $2p$ -shell.
2. The orbital $\tilde{\pi}_{2,1/2}$ is by 50% of $6p$ -type.
3. The $\sigma_{1/2}$ orbital is predominantly of $6s$ -type with small admixture of $6p_z$, corresponding weights being ≥ 0.78 and ≤ 0.25 .
4. The mixing angles appear to be: $s_2 \approx 0.5$ and $s_1 \leq 0.17$, which is in agreement with the fact that the orbital $\tilde{\pi}_{2,1/2}$ is centered on lead and $\tilde{\pi}_{1,1/2}$ — on oxygen.
5. The number of electrons on lead for the ground state is: $2.2 \leq N_X \leq 2.8$, where we neglected small contribution from orbitals $\sigma_{1,2}$, which should be strongly shifted to oxygen. Therefore, the model predicts significant positive charge on lead (neutral lead has 4 electrons above the core). That is again in agreement with naive picture.

There are three contributions to W_d from three molecular orbitals:

$$W_d = -\frac{c_1^2}{2}W_d^{\tilde{\pi}_2} - \frac{1}{2}W_d^{\tilde{\pi}_1} + \frac{s_1^2}{2}W_d^\sigma$$

The first term here dominates; the second term is much smaller and its value significantly depends on free parameters of the model. The third term is proportional to the square of the small parameter s_1 and is always negligible.

The final prediction of the model is:

$$|W_d| = 19 \pm 6 \text{ a.u.} = (23 \pm 8) \cdot 10^{24} \frac{\text{Hz}}{e \text{ cm}}.$$

This value is 2.5 times smaller, than the largest known value for the ground state of HgF molecule, but is almost two times larger, than W_d for the ground states of the YbF molecule and PbF molecule. The model shows significant similarity between a_1 state of PbO and the ground state of PbF. The larger value of W_d here is mainly due to the larger SO mixing s_2 .