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Ω -doubling and a limit for the enhancement of the
electron EDM effect in diatomic molecules

D.V. Chubukov and L.N. Labzowsky

I. A short history of a problem.

1950 E.M. Purcell and N.F. Ramsey:

First proposal for the search of the neutron EDM by observation of a linear Stark effect in electric and magnetic fields via the magnetic resonance.

1958 E.E. Salpeter:

A proposal to observe an electron EDM in atoms.

1963 L.I. Schiff:

Schiff Theorem (ST): charged particle EDM effect in a closed system is absent due to the electrostatic equilibrium. ST is violated by strong interactions (nuclear size effect), then nuclear EDM effect in atoms arises but still is suppressed compared to the free nucleus effect.

I. A short history of a problem.

1965 P.G.H. Sandars:

ST is violated also by the magnetic interactions, i.e. relativistic effects, then in heavy atoms and molecules the electron EDM effect can be even enhanced compared to the free electron due to the strong relativity.

1967 P.G.H. Sandars:

Nuclear EDM in heavy diatomic molecules can be strongly ($\sim 10^5$ times compared to atoms) enhanced. The reason is that even with the finite nuclear size taken into account, the nuclear EDM effect in any atom or molecule vanishes if the inversion symmetry is not violated (Schiff 1963). This symmetry is violated when the system is polarized in an external electric field. The diatomic molecules are $\sim 10^5$ times easier polarized than atoms, what explains the enhancement. More explicitly this enhancement can be explained by the mixing of the closely lying rotational levels of opposite parity (O.P. Sushkov, V.V. Flambaum and I.B. Khriplovich 1984).

I. A short history of a problem.

1978 L.N. Labzowsky:

P-odd effect in heavy heteronuclear diatomic molecules with open electron shells.
What is Λ -doubling?

$$\text{Rotational level} \begin{cases} \text{—————} & \psi^- = \psi(\mathbf{1}) - \psi(-\mathbf{1}) \\ \text{—————} & \psi^+ = \psi(\mathbf{1}) + \psi(-\mathbf{1}) \end{cases}$$

Λ is the projection of the electron orbital angular momentum on the molecular axis,

\pm denote the parity.

In heavy molecules the projection of the total electron momentum (including spin) Ω should be used.

I. A short history of a problem.

Ω -splitting:

$$\Delta E_{\Omega} \sim (V_{er})^{2\Omega}$$

$V_{er} \sim B$ is the interaction of the electron motion inside molecule with rotation of the molecule,

B is rotational constant.

For closed electron shells there is no $\Lambda(\Omega)$ -doubling ($\Lambda = \Omega = 0$).

Effective P-odd electron-nucleus interaction operator

$$V^P = V_1^P + V_2^P$$

V_1^P is the electron axial - nuclear vector interaction,

V_2^P is the electron vector - nuclear axial interaction.

$V_1^P \sim A$ (atomic number), $V_2^P \sim I$ (nuclear spin).

V_2^P is approximately Z times smaller than V_1^P .

I. A short history of a problem.

Later **V.V. Flambaum** and **I.B. Khriplovich** (1980) demonstrated that actually the V_2^P interaction will be mainly represented by the anapole moment of the nucleus. Anapole moment is a P-odd, T-even moment introduced by **Ya. Zeldovich** (1957).

In diatomic molecules the V_1^P interaction does not contribute to the P-odd effects since it violates also T-invariance. So the observation of P-odd effect in these molecules would give directly the value of the nuclear anapole moment, which up to now was observable only as a small correction to the P-odd effect due to V_1^P in atomic experiment.

Note that the enhancement of the P-odd effects in diatomic molecules due to the Λ -doubling was first discussed by **V.A. Onishuk** in 1967, when the neutral currents were not yet introduced. This discussion was based on the 4-fermion weak interaction and gave very small value for the P-odd effect.

I. A short history of a problem.

1978 O.P. Sushkov and V.V. Flambaum:

Extension of the idea to employ the Ω -doubling effect in diatomic molecules to the observation of the electron Electric Dipole Moment (EDM). The enhancement of the electron EDM effect is the same as for the P-odd effect.

1979 V.G. Gorshkov, L.N. Labzowsky and A.N. Moskalev :

Extension of the idea to employ the Ω -doubling effect in diatomic molecules to the observation of the P,T-odd scalar electron-nucleus interaction. The enhancement in this case is again the same as for the P-odd effect, even Z times stronger since the neutral current operator $V_1^{P,T}$ which corresponds to V_1^P , contributes to the effect (T-noninvariance is assumed).

It was also shown that this effect cannot be distinguished from the electron EDM effect in any experiment with any particular atom or molecule (see, however, report by D.V. Chubukov). One of the favorite molecules for P,T-violation search PbF ($^2\Pi_{1/2}$ state, notation $^{2S+1}\Lambda_\Omega$) was first mentioned.

I. A short history of a problem.

1987-1992 M.G. Kozlov, Y.I. Fomichev, Yu.Yu. Dmitriev,
L.N. Labzowsky, A.V. Titov (1987);
Yu.Yu. Dmitriev, Yu.G. Khait, M.G. Kozlov, L.N. Labzowsky,
A.O. Mitrushenkov, A.V. Titov (1992):

First ab initio calculations of P,T-odd effects in heavy diatomics (PbF).

1994 M.G. Kozlov and V.F. Ezhov:

First introduction of YbF ($^2\Sigma_{1/2}$) molecule as a candidate for the experiments.

1995 M.G. Kozlov and L.N. Labzowsky:

First review on P- and P,T-odd effects in diatomics. Formulation of the semi-empirical approach for the evaluation of P,T-odd effects.

I. A short history of a problem.

1996-2014 Accurate calculations of the P,T-odd effects in diatomics by A.V. Titov group (PNPI):

A.V. Titov, N.S. Mosyagin, V.F. Ezhov 1996 (YbF);

T.A. Isaev, A.N. Petrov, N.S. Mosyagin, A.V. Titov, E. Eliav,

U. Kaldor 2004 (PbO $^3\Sigma_1$);

A.N. Petrov, L.V. Skripnikov, A.V. Titov and R. J. Mawhorter 2013 (PbF);

L.V. Skripnikov, A.N. Petrov and A.V. Titov 2014 (ThO $^3\Delta_1$).

2011 J.J. Hudson, D.M. Kara, I. J. Smallman, B. E. Sauer,
M. R. Tarbutt, E. A. Hinds:

First molecular experiment (on YbF) which established the upper bound for the electron EDM lower than in atomic experiments.

2014 ACME collaboration, USA:

Molecular experiment (ThO) that established the lowest bound for the electron EDM $0.87 \cdot 10^{-28}$ e cm.

II. Enhancement coefficient.

A. In case of diatomic molecule with closed electron shells:

$$\mathcal{K} = \frac{\Delta E_e}{B}$$

ΔE_e - normal atomic spacing between the electronic levels in atoms ~ 1 a.u.

B - rotational constant $\sim 10^{-6}$ a.u. for heavy molecules.

B. In diatomics with open electron shells

$$\mathcal{K} = \frac{\Delta E_e}{\Delta E_\Lambda}$$

ΔE_Λ - spacing between Λ -doublets.

II. Enhancement coefficient.

Table I

State	Splitting ΔE_{Λ}
${}^2\Pi_{1/2}$	$B (A/\Delta E_e) (J + 1/2)$
${}^2\Pi_{3/2}$	$B (B/A) (B/\Delta E_e) (J - 1/2) (J + 1/2) (J + 3/2)$
${}^3\Pi_1$	$B (B/\Delta E_e) J (J + 1)$
${}^3\Pi_2$	$B (B/\Delta E_e) (A/\Delta E_e)^2 (J - 1) J (J + 1) (J + 2)$
${}^3\Delta_1$	$B (B/\Delta E_e) (A/\Delta E_e)^2 J (J + 1)$
${}^3\Delta_2$	$B (B/\Delta E_e)^3 (J - 1) J (J + 1) (J + 2)$
${}^3\Delta_3$	$B (B/\Delta E_e)^3 (B/A)^2 (J - 2) (J - 1) J (J + 1) (J + 2) (J + 3)$

However this definition does not take into account the effect of saturation.

III. Interpretation of the EDM experiment.

The results of the EDM experiments are usually presented in the form

$$\Delta S = -\vec{d}_e \vec{\mathcal{E}}.$$

ΔS is the linear Stark shift (or equivalent quantity - electron spin precession angle in an external electric field),

\vec{d}_e - EDM, $\vec{\mathcal{E}}$ - electric field.

Two ways to attribute enhancement:

- A) to d_e , than we understand d_e as molecular EDM d_e^{mol} , \mathcal{E} - external field \mathcal{E}_{ext} ;
- B) to \mathcal{E} , than d_e is free electron EDM d_e^{free} , \mathcal{E} is effective field \mathcal{E}_{eff} (nonreal).

The second way is most popular. \mathcal{E}_{eff} cannot be measured, only evaluated.

The results of an experiment are presented as

$$d_e^{free} \leq \frac{\Delta S}{\mathcal{E}_{eff}}.$$

Then the enhancement coefficient can be defined as

$$\mathcal{K} = \frac{\mathcal{E}_{eff}}{\mathcal{E}_{ext}}.$$

IV. Saturation.

Expression for ΔS (**Flambaum 1976**)

$$\Delta S = d_e e \vec{\mathcal{E}}_{ext} \left[\sum_n \frac{\langle 0 | \vec{r} | n \rangle \langle n | (\gamma_0 - 1) \vec{\Sigma} \vec{\mathcal{E}}_c | 0 \rangle}{E_n - E_0} + \sum_n \frac{\langle 0 | (\gamma_0 - 1) \vec{\Sigma} \vec{\mathcal{E}}_c | n \rangle \langle n | \vec{r} | 0 \rangle}{E_n - E_0} \right],$$

$\gamma_0, \vec{\Sigma}$ - the Dirac matrices, $(\gamma_0 - 1)$ retains only lower Dirac wave function component, i.e. pure relativistic effect (Schiff theorem!),

$\vec{\mathcal{E}}_c$ is the Coulomb field of the nucleus, $|0\rangle$ is the ground (or metastable) state, summations extends over the entire spectrum of the electron states in molecule. If there is one closely lying to $|0\rangle$ level of opposite parity (as in diatomics) only this term $|n\rangle = |1\rangle$ in the sum should be retained.

If the mixing becomes too strong, these two levels $|0\rangle$ and $|1\rangle$ begin to repulse - saturation occurs.

Condition of saturation:

$$\langle 0 | e \vec{r} \vec{\mathcal{E}}_{sat} | 1 \rangle = E_1 - E_0.$$

IV. Saturation.

Enhancement coefficient should be redefined as

$$\mathcal{K} = \frac{\mathcal{E}_{eff}}{\mathcal{E}_{sat}}.$$

In atomic EDM experiments \mathcal{E}_{ext} never reaches \mathcal{E}_{sat} , but in molecular experiments $\mathcal{E}_{ext} = \mathcal{E}_{sat}$ can be easily reached.

The order-of-magnitude estimates for ΔS

$$\Delta S \approx d_e |\vec{\mathcal{E}}_{sat}| \frac{\Delta E_e}{\Delta E_\Omega} Z_{eff}^2,$$

Z_{eff} accounts for the screening of the valence electron by the core electrons in heavy atom in diatomic molecule.

From Table I for heavy molecules ($A \approx \Delta E_e$)

$$\Delta E_\Omega \approx B \left(\frac{B}{\Delta E_e} \right)^n$$

$n = 0$ for $\Omega = 1/2$ (PbF, YbF), $n = 1$ for $\Omega = 1$ (ThO),

$n = 2$ for ${}^3\Delta_2$ state (metastable, ThO).

IV. Saturation.

$$\mathcal{E}_{sat} \approx \mathcal{E}_{sat,at} \left(\frac{B}{\Delta E_e} \right)^{n+1}$$

$\mathcal{E}_{sat,at} \approx 10^9 \text{ V/cm}$ - atomic saturation field (for ground atomic state).

Finally,

$$\Delta S \approx d_e Z_{eff}^2 10^9 \text{ V/cm},$$

hence

$$\mathcal{E}_{eff} \approx 10^9 Z_{eff}^2 \text{ V/cm}$$

$$1 \leq Z_{eff} \leq 10.$$

This result holds for any heavy diatomic molecule in any electronic state $^{2S+1}\Lambda_{\Omega}$.
The effective field \mathcal{E}_{eff} is limited by the value 100 billions V/cm.

IV. Saturation.

Table II

Molecule, State	$\mathcal{E}_{eff},$ V/cm	$\mathcal{E}_{sat},$ V/cm	Reference
PbF $^2\Pi_{1/2},$ ground	$\approx 10^9$	$\approx 10^3$	Kozlov et al. (1987), Dmitriev et al. (1992)
YbF $^2\Sigma_{1/2},$ ground	$26 \cdot 10^9$	$\approx 10^3$	Kozlov and Ezhov (1994), Titov et al. (1996), Kozlov (1997)
PbO $^3\Sigma_1^+,$ metastable	$6 \cdot 10^9$	$\approx 10^{-3}$	De Mille et al. (2000)
WC $^3\Delta_1,$ ground	$54 \cdot 10^9$	$\approx 10^{-3}$	Lee et al. (2009)
ThO $^3\Delta_1,$ metastable	$84 \cdot 10^9$	$\approx 10^{-3}$	Skripnikov, Petrov and Titov (2014)

V. Conclusion.

- Even for the molecule with the ground or metastable state ${}^3\Delta_2$ (yet unknown) the value \mathcal{E}_{eff} cannot be higher than 100 billions V/cm.
- The enhancement coefficient $\mathcal{K} = \frac{\mathcal{E}_{eff}}{\mathcal{E}_{sat}}$ becomes 10^6 times higher but only due to the lower value of $\mathcal{E}_{sat} \sim 10^{-9}$ V/cm. This is, however of no use for the experiment.