Theoretical study of ThO for the electron electric dipole moment search

Leonid V. Skripnikov

A.N. Petrov, A.V. Titov
http://qchem.pnpi.spb.ru

PETERSBURG NUCLEAR PHYSICS INSTITUTE
and
St.-Petersburg State University,
St.-Petersburg, RUSSIA

Why diatomics?

- **Fundamental experiments to search for an electron electric dipole moment:**

actual systems: YbF, HfF^+, ThF^+, WC, ThO*, PbF, PbO*; new candidates are of interest

- **Nuclear EDM / Schiff moment:**

RaO (Flambaum 2008: 500 times enhancement compared to TlF)

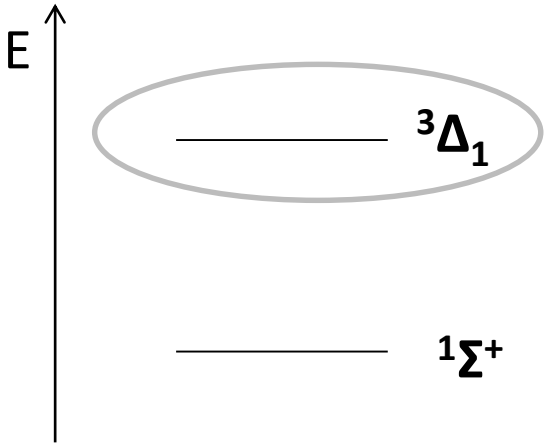
- **Search for variation of "fundamental constants" α; m_p/m_e in laboratory experiments (PbF, HfF^+ etc.);**

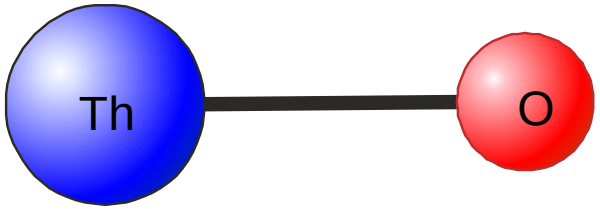
- **Studying the chemical properties of synthesized superheavy atoms**

in JINR (Dubna), GSI (Darmstadt) & LBNL (Berkeley) from «island of stability», dimers and other compounds of elements (111) – (122) etc.

- Cooling, trapping, Bose-condensation of molecules (spectroscopy, dipole moments, cross-sections, hyperfine constants, *g*-factors etc. are of interest for many ***exotic*** systems, e.g., *metal – alkaline-earth cations* like **$RbBa^+$**);

ThO molecule

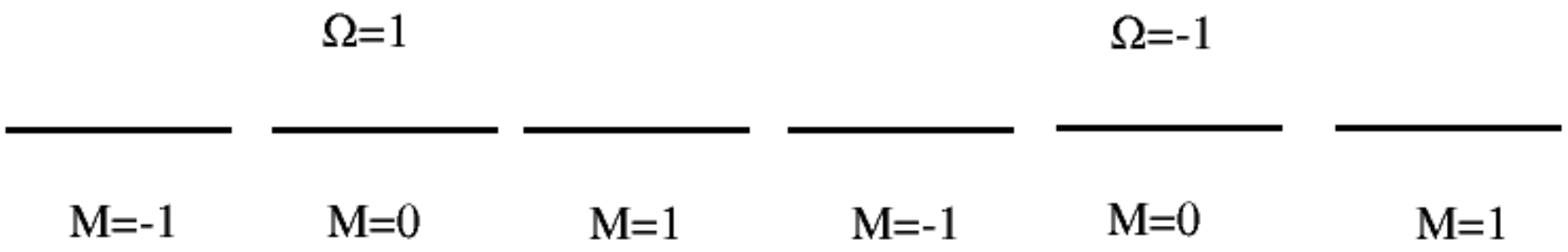




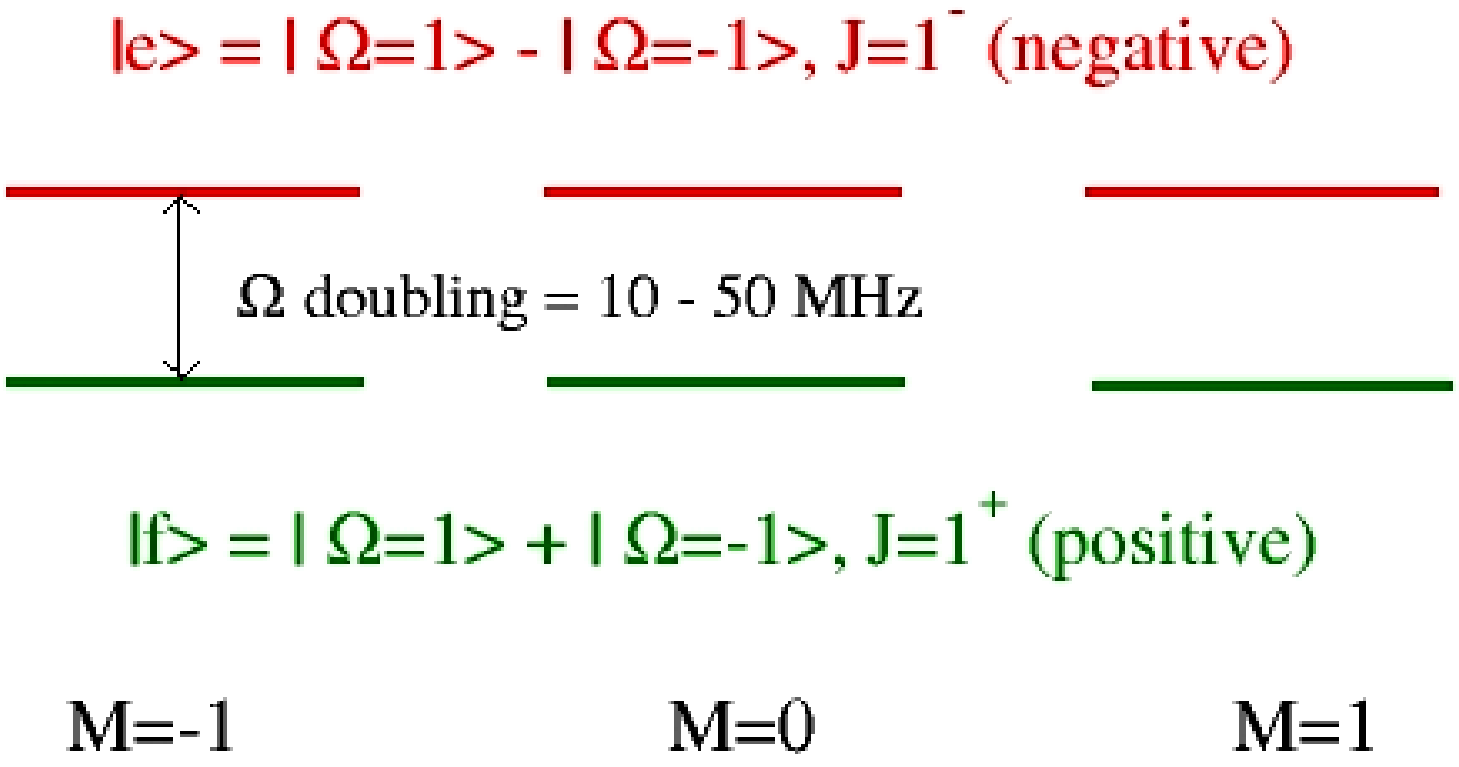
Working state $^3\Delta_1$:

- lifetime~ 2 ms
- g-factor~ 0
- Fully polarization at ~ 10 V/cm
- Large effective electric field

Ground rotational level J=1 for diatomics with $\Omega=1$

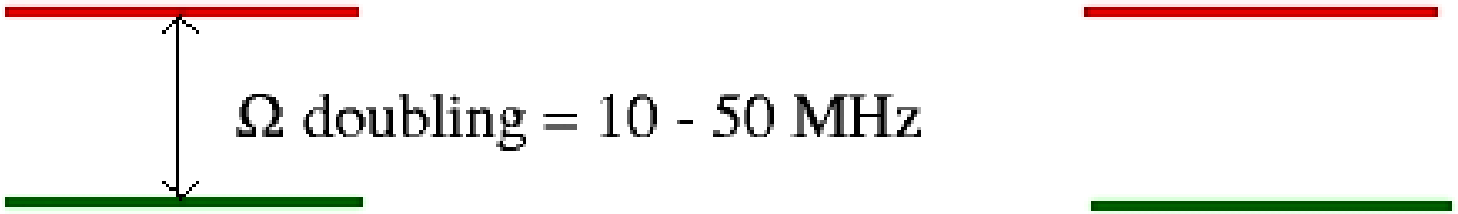


Ground rotational level J=1 for diatomics with Ω=1



Ground rotational level J=1 for diatomics with Ω=1

$|e\rangle = |\Omega=1\rangle - |\Omega=-1\rangle$, $J=1^-$ (negative)

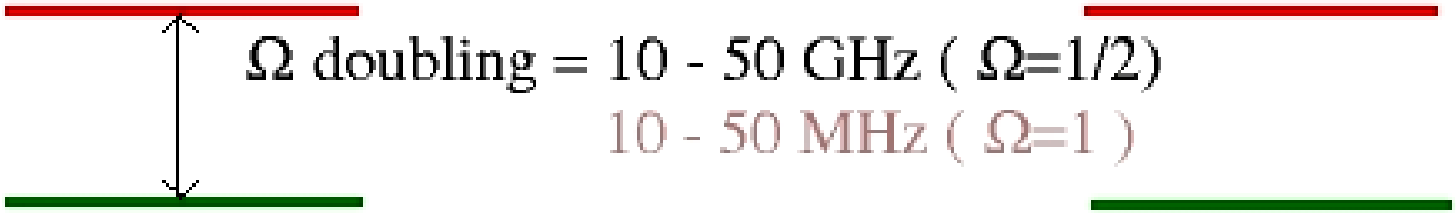


$|f\rangle = |\Omega=1\rangle + |\Omega=-1\rangle$, $J=1^+$ (positive)

M=-1 M=1

Ground rotational level J=1/2 for diatomics with Ω=1/2

$|e\rangle = |\Omega=1/2\rangle - |\Omega=-1/2\rangle$, $J=1/2^-$ (negative)

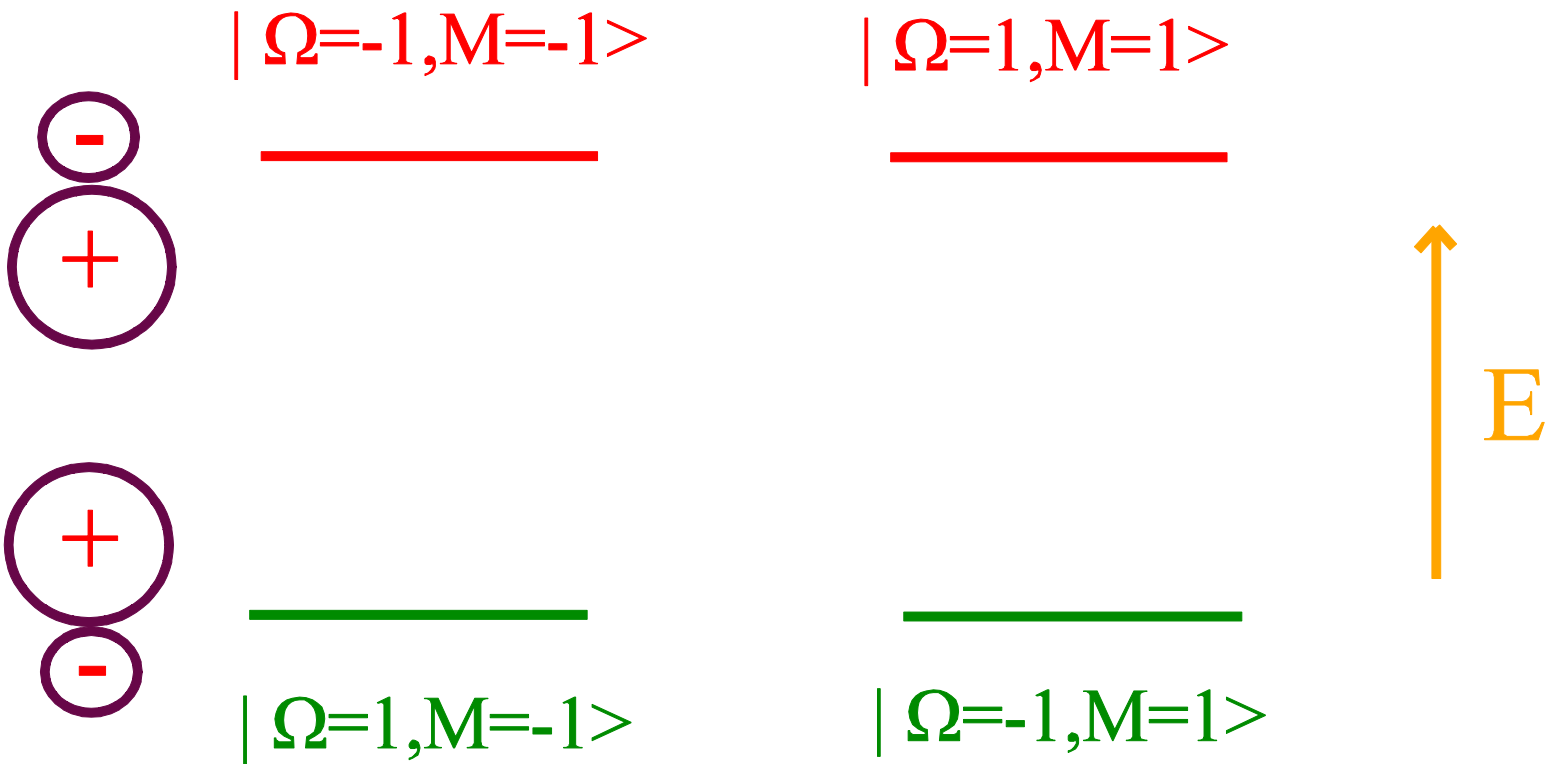


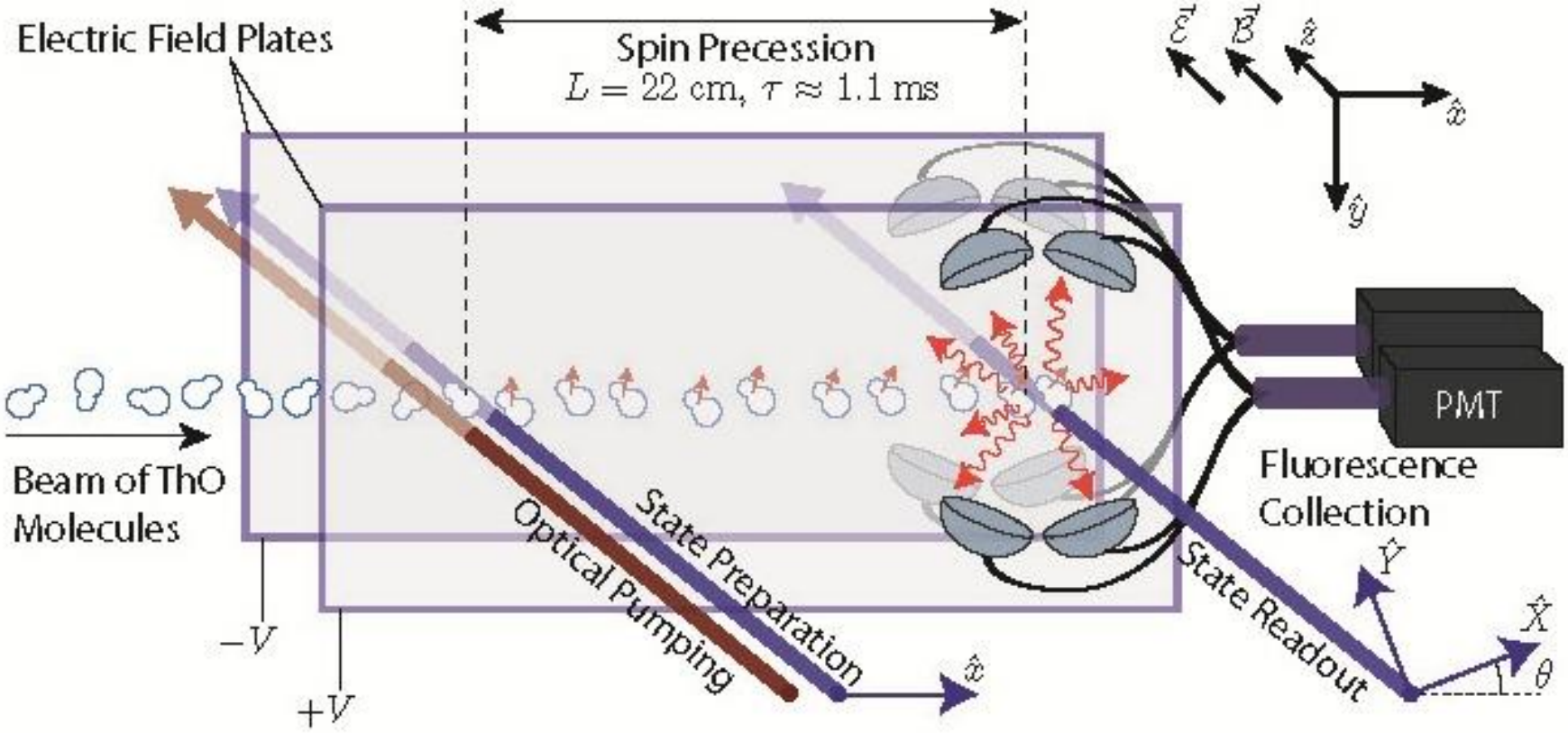
$|f\rangle = |\Omega=1/2\rangle + |\Omega=-1/2\rangle$, $J=1/2^+$ (positive)

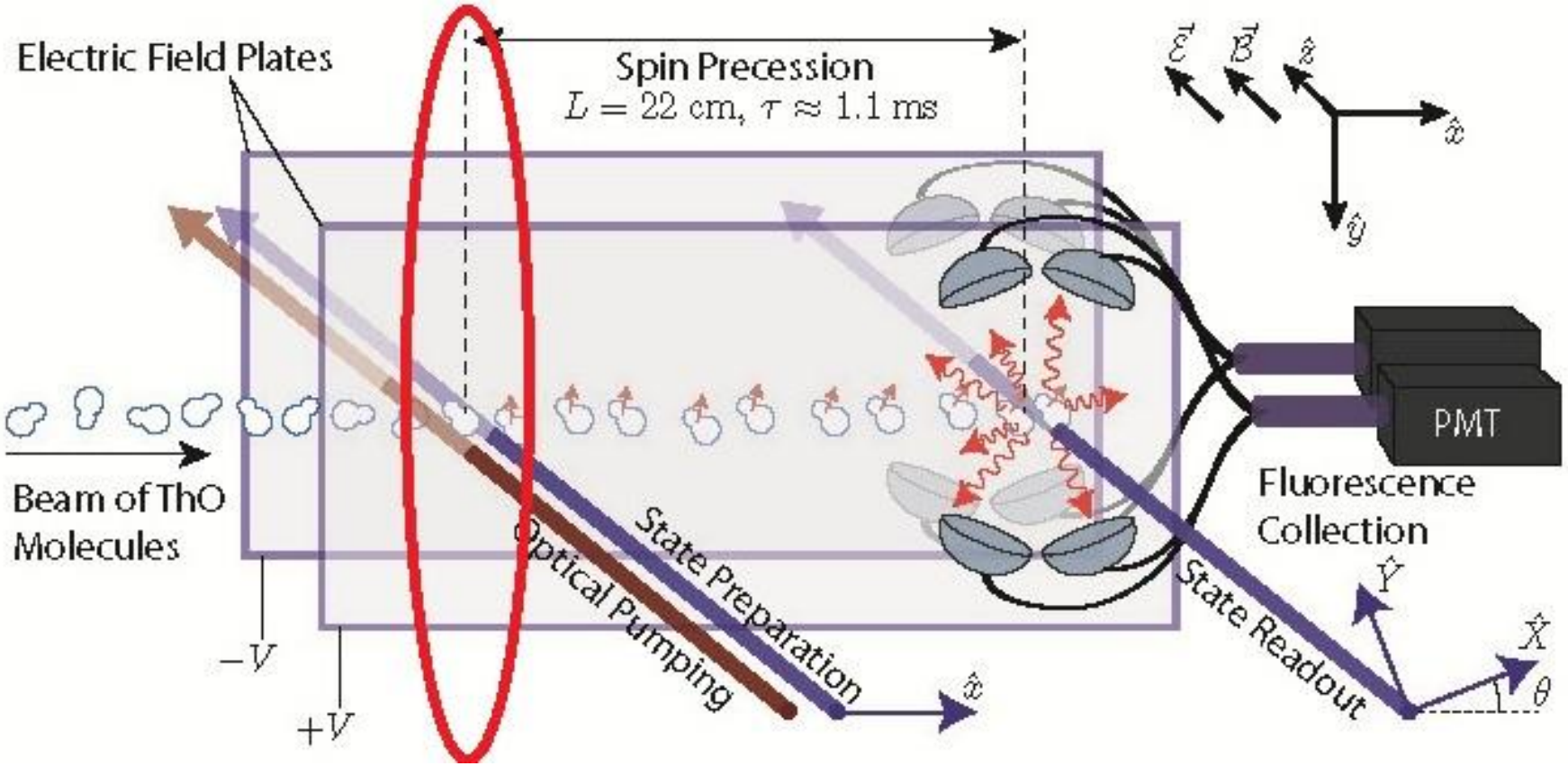
M=-1/2 M=1/2

Ground rotational level J=1 for diatomics with Ω=1

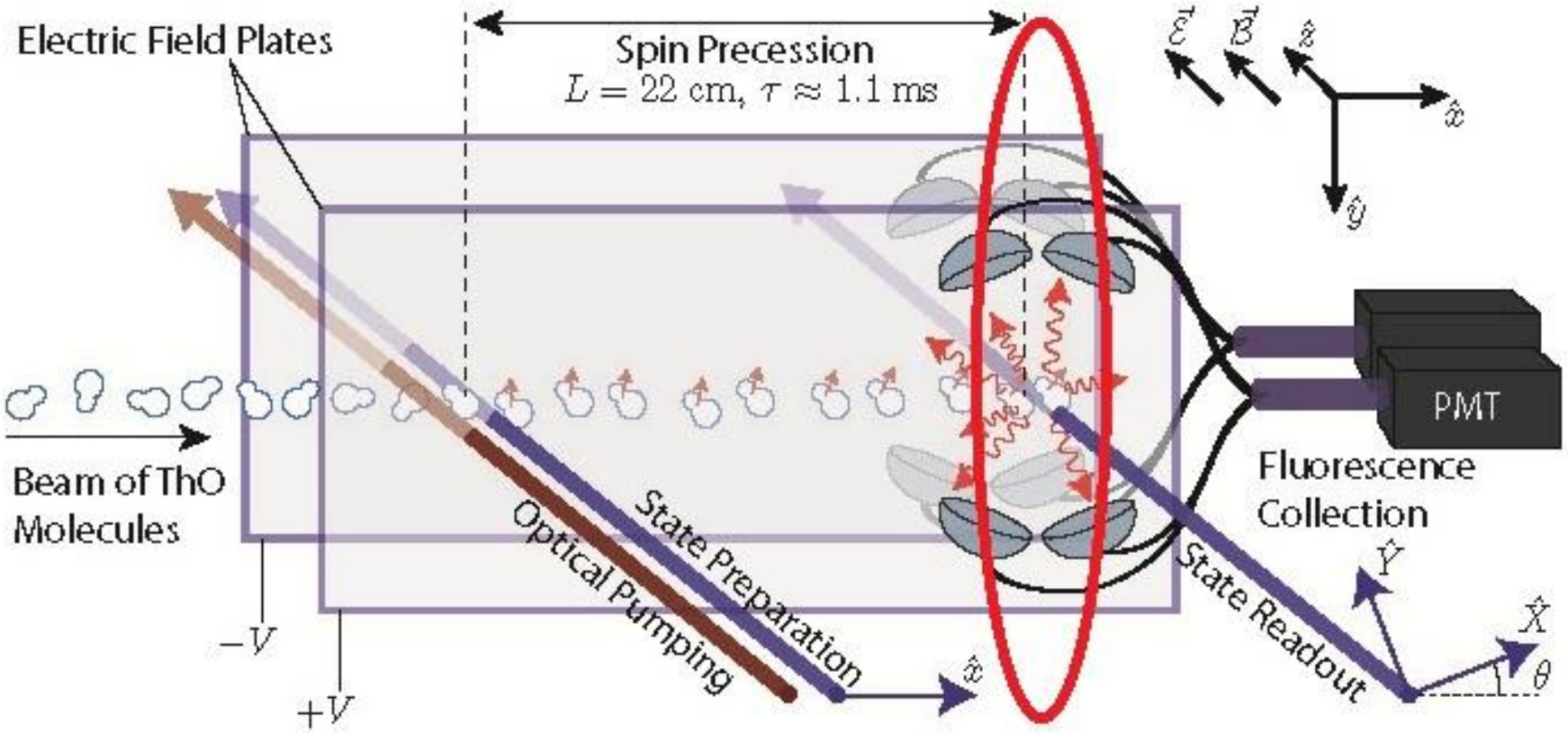
in the presence of Electric field




Electric Field Plates
Spin Precession
$L = 22$ cm, $\tau \approx 1.1$ ms
$\vec{\mathcal{E}}$
$\vec{\mathcal{B}}$
$\hat{z}$
$\hat{x}$
$\hat{y}$
PMT
Fluorescence Collection
Beam of ThO Molecules
State Preparation
Optical Pumping
State Readout
$-V$
$+V$
$\hat{x}$
$\hat{Y}$
$\hat{X}$
θ



$$\psi = \left(\left| M = 1 \right\rangle + \left| M = -1 \right\rangle \right) / \sqrt{2}$$



$$\psi = \left(e^{-i\varphi}\left|M=1\right\rangle + e^{i\varphi}\left|M=-1\right\rangle\right)/\sqrt{2}$$

$$\varphi \sim \tau E_{eff} d_e$$

Goals of theoretical calculations

- ✓ Scheme of energy levels. What is the ground state, etc.?
- ✓ Transition probabilities.
- ✓ Parameters of P,T-odd interactions

for interpretation of experimental measurements
in terms of fundamental quantities such as the electron EDM

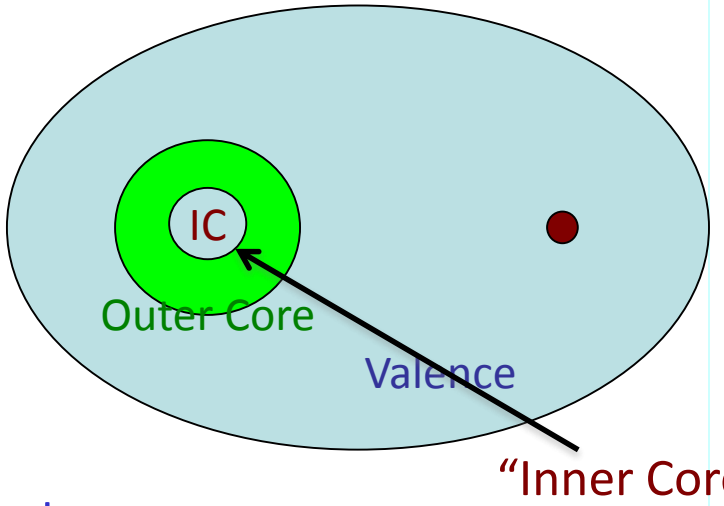
- ✓ Hyperfine structure constants,
- ✓ oscillation frequency, g-factors, etc.

Th: …$5s^2\ 5p^6\ 5d^{10}\ 6s^2\ 6p^6\ 7s^2\ 6d^2\ 5f^0$
O: $1s^2\ 2s^2\ 2p^4$

Th – actinide => strong correlation and spin-orbit effects

Methods outline

Generalized relativistic effective core potential (GRECP) as Hamiltonian

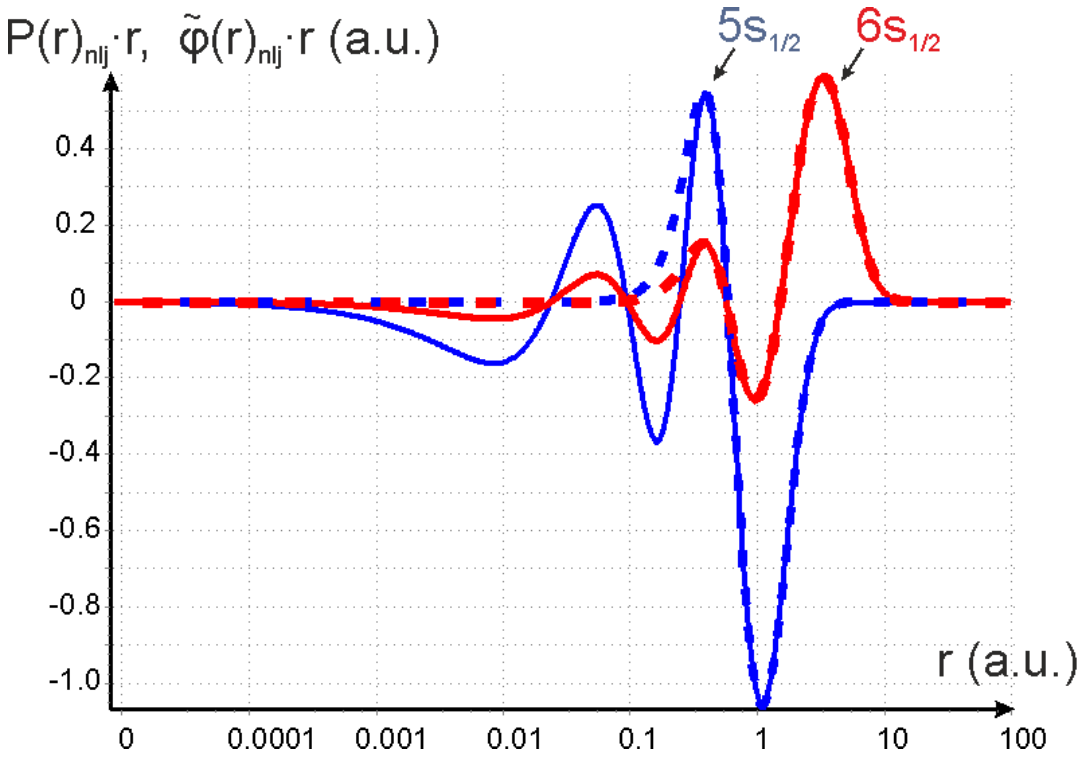


- ✓ Exclusion of inactive inner core electrons
- ✓ Due to smoothed behavior in a core region a small basis set can be used
- ✓ Possibility to perform calculation within scalar-relativistic approximation for valence electrons (while, effectively, 4-component description for inner core electrons)
- ✓ For scalar-relativistic GRECP calculations the most of popular quantum-chemical packages can be used **including solid-state codes**

✓"Core properties" (HFS, E_{eff}, etc.) can be calculated using nonvariational restoration method

Two-step method

$5s_{1/2}$ and $6s_{1/2}$ spinors and pseudospinors of Yb^+



[qchem.pnpi.spb.ru]

1. Molecular GRECP calculation
2. Smoothed spinors are replaced by true four-component spinors

$$\tilde{\phi}_i(\mathbf{x}) \approx \sum_{l=0}^{L_{max}} \sum_{j=|l-1/2|}^{j=|l+1/2|} \sum_{n,m} c^i_{nljm} \tilde{f}_{nlj}(r) \chi_{ljm}$$

$$\phi_i(\mathbf{x}) \approx \sum_{l=0}^{L_{\max}} \sum_{j=|l-1/2|}^{j=|l+1/2|} \sum_{n,m} c^i_{nljm} \begin{pmatrix} f_{nlj}(r)\chi_{ljm} \\ g_{nlj}(r)\chi_{l'jm} \end{pmatrix}$$

The coupled clusters method

Accounting for correlation effects

$$\Psi = e^{\hat{T}}\Phi_0$$

$$e^{\hat{T}} = 1 + \hat{T} + \frac{\hat{T}^2}{2!} + \frac{\hat{T}^3}{3!} + \cdots$$

$$\hat{T} = \hat{T}_1 + \hat{T}_2 \quad \rightarrow \boldsymbol{CCSD}$$

$$\hat{T} = \hat{T}_1 + \hat{T}_2 + \hat{T}_3 \quad \rightarrow \boldsymbol{CCSDT}$$

$$\hat{T}_1 = \sum_i \hat{t}_i = \sum_{i,a} t_i^a \, a_a^+ a_i$$

$$\hat{T}_2 = \frac{1}{2}\sum_{ij} \hat{t}_{ij} = \frac{1}{4}\sum_{ijab} t_{ij}^{ab} \, a_a^+ a_b^+ a_j a_i$$

- more effective than CI: t(CISD) ~ t(CCSD)

Ab initio calculation of $H^3\Delta_1$ state of ThO

[L.V. Skripnikov, A.N.Petrov, A.V. Titov, J. Chem. Phys. **139**, 221103 (2013)
L.V. Skripnikov, A.V. Titov http://arxiv.org/abs/1410.2485 (2014)]

Method	T_e, cm^{-1}	Dipole, D	E_{eff}, GV/cm	
scalar-relativistic CCSD	6321	4.30	72.9	
scalar-relativistic CCSD(T)	6698	4.23	71.0	
relativistic CCSD	5210	4.28	83.2	0.003
relativistic CCSD(T)	5525	4.21	81.7	0.006
CCSDT(Q)-CCSD(T) & basis set corrections	-122	-0.10	-0.2	
Final (RCCSD(T)+basis corr.+correlation corr.)	5403	4.19	81.5	
Experiment	5337	4.24 ± 0.1	-	

Experiment: [Vutha et al., PRA 84, 034502 (2011)]

Estimation of theoretical uncertainty

[T. Fleig and M. K. Nayak, Journal of Molecular Spectroscopy 300, 16 (2014)]:
Eeff=75.2 GV/cm with 3% uncertainty

[L.V. Skripnikov, A.V. Titov arxiv.1410.2485 (2014)]:

										F leig and Nayak [30] 4-comp.		CBas basis set , 1-comp.		
#	# of act. els.	Reference space	Excitation types 1v, 2v	1o, 2o, 1o1v	1o2v, 2o1v,	2o2v	3o, 3o1v	4o	Method	$E_{\rm eff}$, GV/cm	$A_{\|\|}$, $\frac{\mu_{\rm Th}}{\mu_{\rm N}}$·MHz	$E_{\rm eff}$, GV/cm	$A_{\|\|}$, $\frac{\mu_{\rm Th}}{\mu_{\rm N}}$·MHz	Energy, Hartree
1	2	Single ref. [a]	+	-	-	-	-	-	CISD	0.0 (68.5)	0 (-2809)	0.0 (59.4 [b])	0 (-3001)	0
2	18	3 OS (s, $6d_\delta$)	+	+	-	-	-	-	MR(3)-CISD	12.5	-62	12.5	-58	-0.329
3	18	3 OS+9 virt.	+	+	±	±	-	-	MR(12)-CISD [c]	6.7	-167			
4	18	3 OS+all virt.	+	+	+	+	-	-	MR(∞)-CISD			7.8	-129	-0.335
5	18	3 OS+all virt.	+	+	+	+	+	-	$(MR(\infty)\text{-CISDT})_4$			11.3	-129	-0.356
6	18	Single ref.	+	+	+	+	+	+	CISDTQ			12.1	-83	-0.381
7	18	3 OS+all occ.							MR_3^{+T}-CISD[f]	12.3[d,e]	-36[d,e]			
8	18	3 OS+all occ.							MR_3^{+TQ}-CISD[g]			13.0	-49	-0.331
9	18	3 OS	+	+	+	-	-	-	MR_3-CISDT	6.1[d]	-189[d]			
10	18	3 OS	+	+	+	-	+,-	-	MR(3)-CISDT			13.3	-104	-0.346
6a	18	Single ref.	+	+	-	-	-	-	CISD			12.4	-48	-0.329
6b	18	Single ref.	+	+	+	-	+,-	-	CISDT			14.5	-117	-0.342
6	18	Single ref.	+	+	+	+	+	+	CISDTQ			12.1	-83	-0.381
11	18	Single ref.	+	+	(+)	(+)	(+)	(+)	CCSD			12.8	-115	-0.368
12	18	Single ref.	+	+	+	(+)	+,(+)	(+)	CCSD(T)			11.0	-103	-0.387
13	18	Single ref.	+	+	+	(+)	+,(+)	(+)	CCSDT			10.6	-96	-0.387
14	18	Single ref.	+	+	+	+	+	+	CCSDTQ			10.4	-93	-0.388
15	18	3 OS+all virt.	+	+	+	+	(+)	(+)	MR(∞)-CCSD			10.0	-98	-0.374
16	18	3 OS+all virt.	+	+	+	+	+	(+)	$(MR(\infty)\text{-CCSDT})_4$			10.3	-91	-0.388

Estimation of theoretical uncertainty

[T. Fleig and M. K. Nayak, Journal of Molecular Spectroscopy 300, 16 (2014)]:
Eeff=75.2 GV/cm with 3% uncertainty

[L.V. Skripnikov, A.V. Titov arxiv.1410.2485 (2014)]:

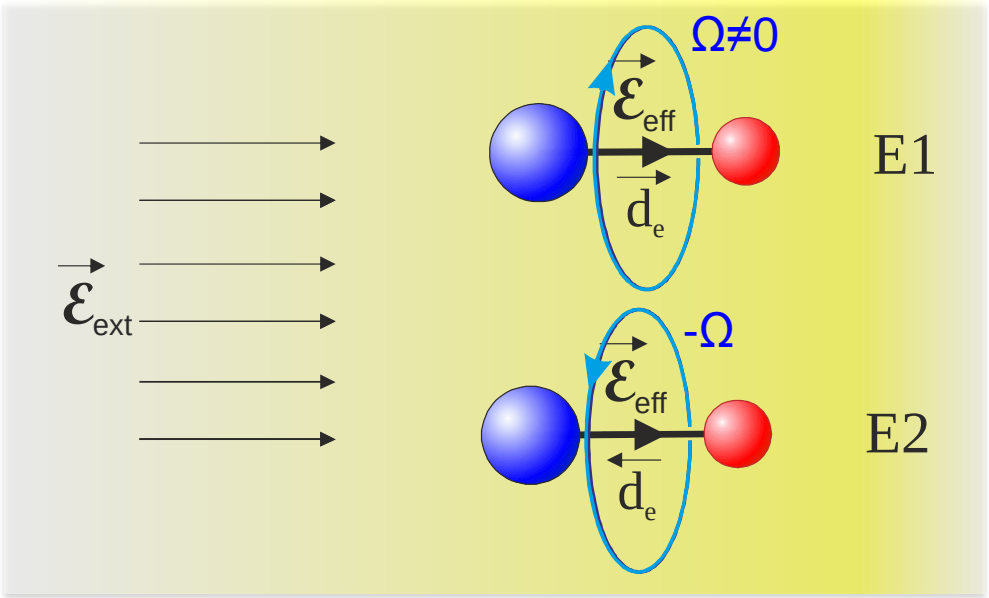
OC

Th: …$5s^2\ 5p^6\ 5d^{10}\ 6s^2\ 6p^6\ 7s^2\ 6d^2$

O: $1s^2\ 2s^2\ 2p^4$

	Fleig & Nayak	This work
Method	18e-MR(12)-CISD	38e-CCSD(T) + 18e-CCSDT(Q) correction
Correlation	7%	< 1%
OC contribution	5%	-
Basis set	<4%	< 1%
one-electron spinors	7%	< 1%
Other uncertainty	???	5%

ThO results



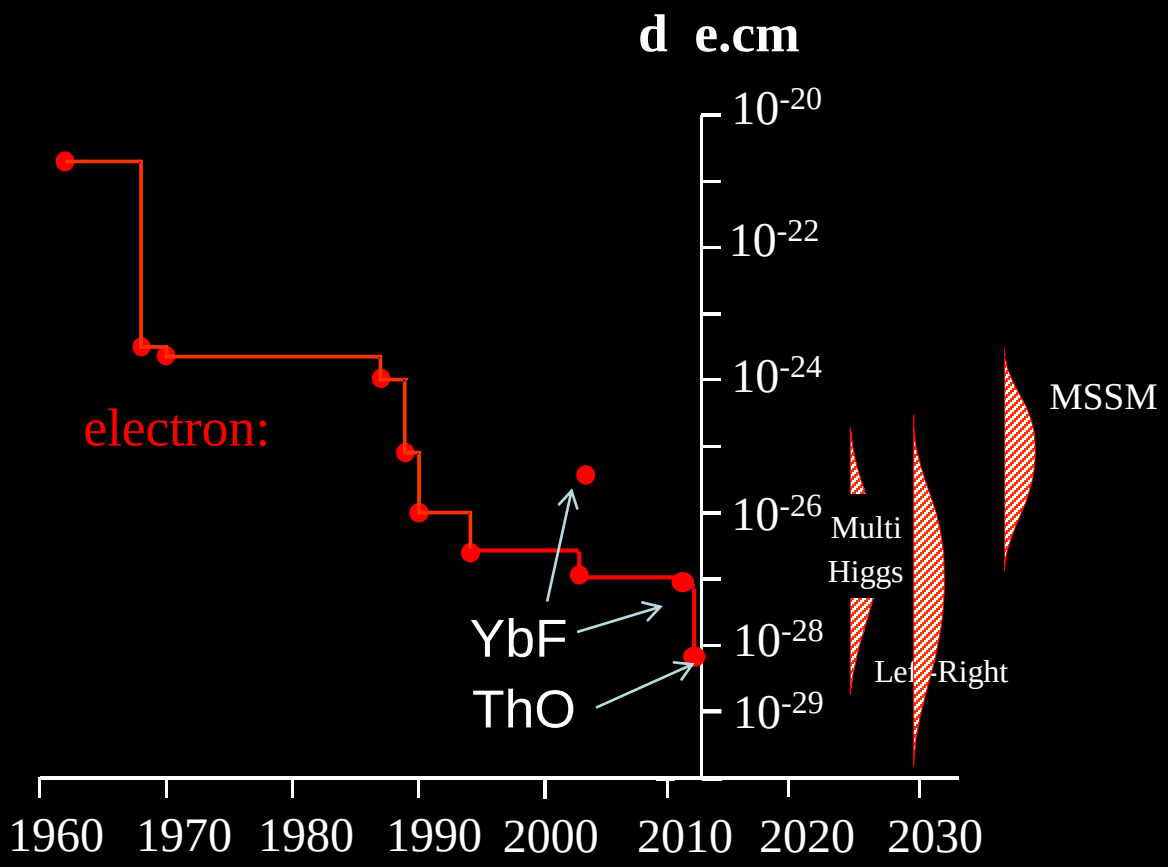
$$\Delta E = E1 - E2$$

[ACME Collaboration, Science. **343** 269. (2014)]:

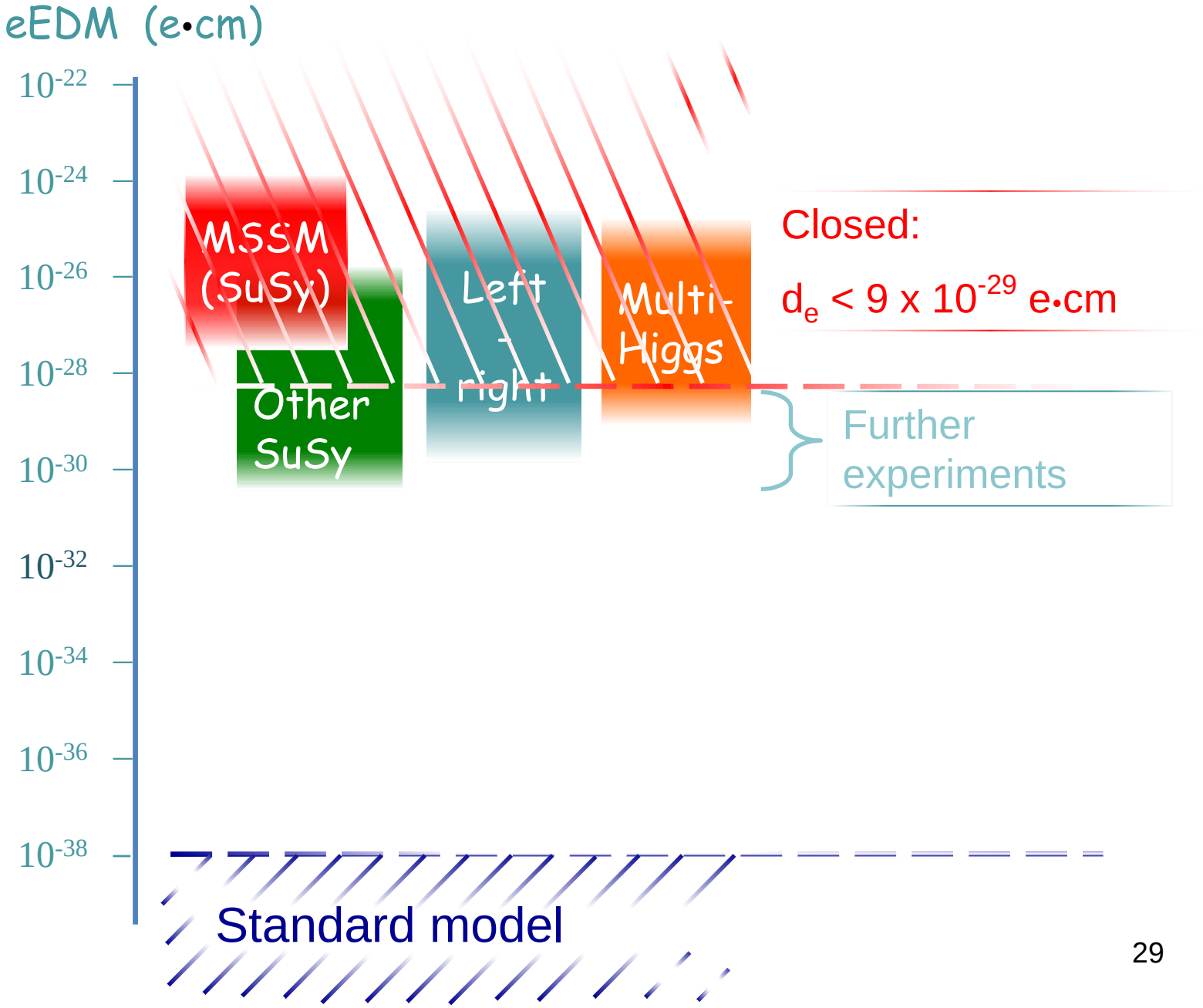
$$d_e < \frac{\Delta E}{81.5} = 9 \cdot 10^{-29}\, e \cdot cm$$

[L.V. Skripnikov, A.N.Petrov, A.V. Titov, J. Chem. Phys. **139**, 221103 (2013)
L.V. Skripnikov, A.V. Titov http://arxiv.org/abs/1410.2485 (2014)]

Electron EDM status



Prediction of SM and its extensions



Other T,P-odd experiments

Atoms: $|d_e| < 1.6\times10^{-27}$ *e*·cm

[Regan et. al. *PRL* **88,** 071805 (2002)]

Molecules: $|d_e| < 9\times10^{-29}$ *e*·cm

[ACME Collaboration, arXiv:1310.7534 (2013)]

Crystals: $|d_e| < 6.05\times10^{-25}$ *e*·cm

Молекулы:

- ✓ ThO* beam (ACME collaboration: D.DeMille:Yale Uni.; J.Doyle & G.Gabrielse: Harvard);
  $|d_e| < 9\times10^{-29}$ e·cm (2014)
- ✓ YbF-radical beam (E.Hinds: Imperial college, London,UK);
  $|d_e| < 1.0\times10^{-27}$ e·cm (2011)
- ✓ HfF^+ (& ThF^+, PtH^+ …) trapped cations (E.Cornell: JILA, Boulder);
- ✓ WC ($^3\Delta_1$ – ground state) molecular beam (A.E.Leanhard: Michigan U.)
- ✓ PbO ($^3\Sigma^+$) (Eckel, DeMille et al Yale Uni)
  $|d_e| < 1.7\times10^{-26}$ e·cm (2013)

Твёрдые тела:

- ✓ $Eu_{0.5}Ba_{0.5}TiO_3$ (ferroelectric structure) (S. Eckel, A.O.Sushkov, S. Lamoreaux: Yale Uni).
  $|d_e| < 6.05\times10^{-25}$ e·cm (2011)
- ✓ Gd-Ga Garnet (S. Lamoreaux: LANL ; C.-Y. Liu: Indiana)
- ✓ Gd-Iron Garnet (L. Hunter: Amherst),

Thank you!