FPUA2018
@Nagoya University 8th-9th, Jan. 2018

Relativistic calculations of parity and time reversal violation effects in molecules

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Outline

1. Electron EDM in molecules (paramagnetic)

   Improved value of
   effective electric field (E_{eff}) in YbF molecule

2. Nuclear EDM in molecules (diamagnetic)

   Molecular enhancement parameter (X)
   for the nuclear Schiff moment
   in diamagnetic molecules (TlF)

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Why CP violation?

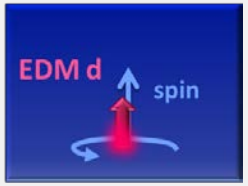
Particles and anti-particles were created after the Big-Ban as same numbers, but the present universe contains only particles.
Why anti-particles disappeared?

CP（Charge-Parity) Symmetry violation

A Sakharov's condition

The standard model is not sufficient to explain the present universe

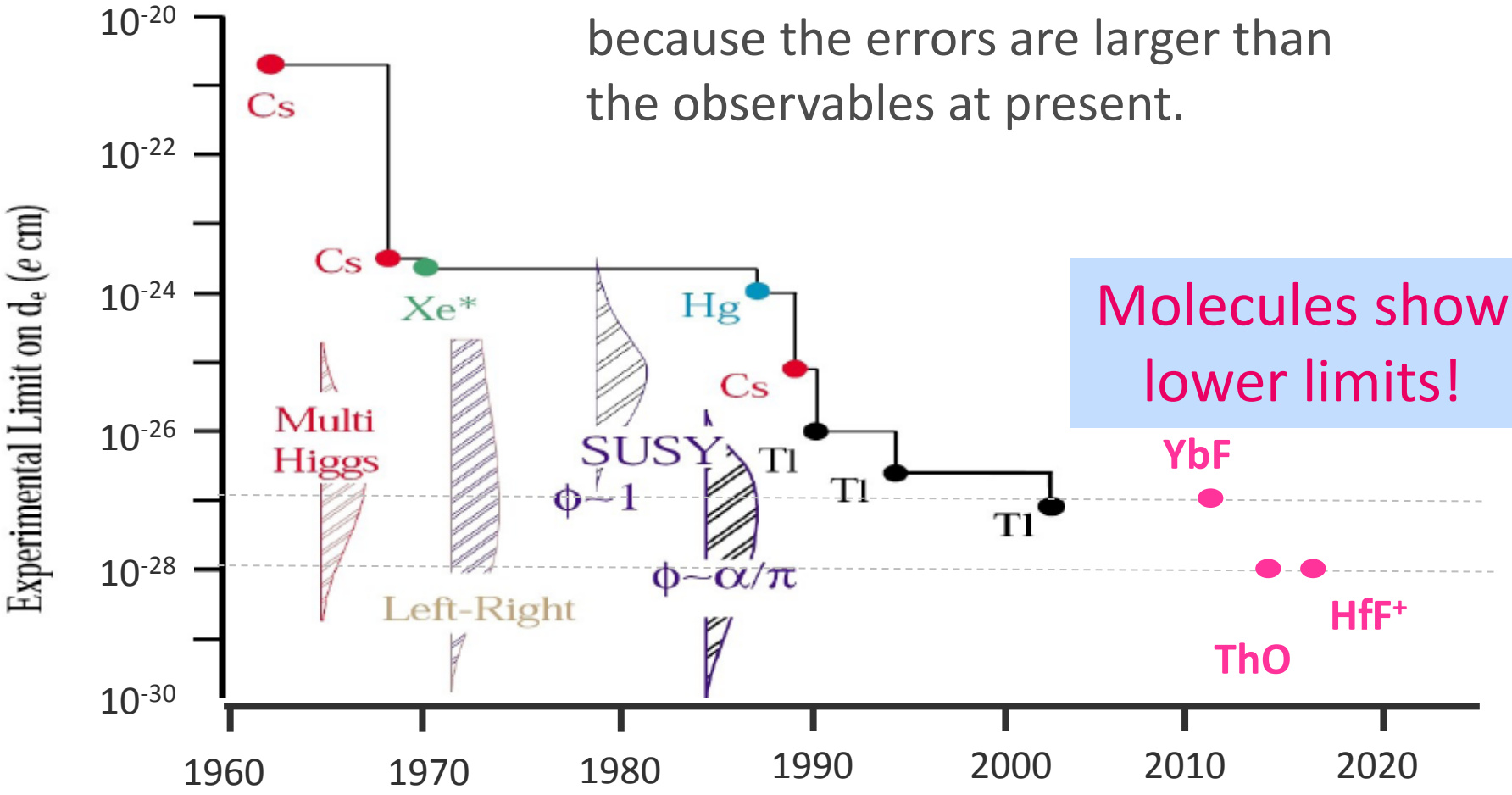
New theory and New CP violation experiment is desired



Electric dipole moment(EDM) of elementary particle

Upper limit of electron EDM observed in atoms and molecules

Why upper limit
because the errors are larger than the observables at present.



Molecules show lower limits!

arXiv:1712.02868v1 [physics.atom-ph] 7 Dec 2017

Ultracold molecules for measuring the electron's electric dipole moment

J. Lim, J. R. Almond, M. A. Trigatzis, J. A. Devlin, N. J. Fitch, B. E. Sauer, M. R. Tarbutt,∗ and E. A. Hinds

The linewidth of such an eEDM measurement, or any spectroscopic measurement, cannot exceed the inverse of the coherence time, which for a molecular beam is limited by the thermal expansion of the cloud to $\tau_{max} \cong \sigma_{max}\sqrt{m/(kBT)}$. Here, m is the molecular mass, T is the translational temperature, and σmax is the useable size of the molecular cloud, limited by the detection area or other geometric constraints. So far, eEDM measurements using molecular beams produced at **T ≈ 4 K** by supersonic expansion or buffer gas cooling have been limited to **τmax ≈ 1 ms** [10, 11].

…

Here, we advance towards an eEDM experiment using **ultracold molecules by cooling a beam of YbF below 100 μK**, so that a coherence time exceeding **150 ms** is feasible in a beam, a fountain [40, 43] or a trap [44]

Better sensitivity with a factor of two

Collaborations of three fields are very important!

Particle Physics

(Theory)

$$-d_e \sum_i \langle \Psi | \beta \sigma_i \cdot \mathbf{E}_{\text{int}} | \Psi \rangle$$

Atomic, Molecular, and Optical Physics

(Experiment)

Relativistic Quantum Chemistry

to calculate E_{eff}

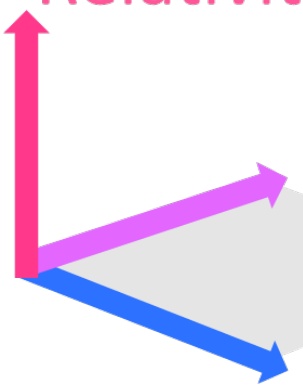
Computational methods

	Relativity	Basis set	Electron correlation
Titov et al.	2 comp. (spin-free)	GRECP	CCSDT
Berger et al.	2 comp. (ZORA)	All-electron	DFT (B3LYP)
Nayak & Fleig	4 component	All-electron	GASCI
Our methods	4 component	All-electron	CCSD, CASPT2

Relativity (**Dirac-Coulomb**)

Basis sets (Dyall QZ)

Electron correlation (**CCSD, CASPT2**)



$$|\Psi_{CCSD}\rangle \equiv \exp\left(\hat{T}_1 + \hat{T}_2\right)|DF\rangle$$

Dirac-Fock wave function

1e and 2e excitation operators

Expectation calculations at CCSD

1. Linear expectation approximation (LECC)

- ✓ Expand as a Taylor series and truncate at linear terms

$$\left\langle \hat{O} \right\rangle = \left\langle DF \left| \exp\left(\hat{T}_1 + \hat{T}_2 \right)^{\dagger} \hat{O}_N \exp\left(\hat{T}_1 + \hat{T}_2 \right) \right| DF \right\rangle_C + \left\langle DF \left| \hat{O} \right| DF \right\rangle$$

$$\approx \left\langle DF \left| \left(1 + \hat{T}_1^{\dagger} + \hat{T}_2^{\dagger} \right) \hat{O}_N \left(1 + \hat{T}_1 + \hat{T}_2 \right) \right| DF \right\rangle_C + \left\langle DF \left| \hat{O} \right| DF \right\rangle$$

2. Finite field perturbation approach (FFCC)

- ✓ Apply finite field perturbations from the correlation calculations

$$\hat{H}_N(\lambda) = \hat{H}_N + \lambda \hat{O}_N$$

$$E_{corr}(\lambda) = \left\langle \Phi_0 \left| \left(\hat{H}_N(\lambda) e^{\hat{T}(\lambda)} \right)_C \right| \Phi_0 \right\rangle$$

$$\left. \frac{dE_{corr}(\lambda)}{d\lambda} \right|_{\lambda=0} \approx \frac{E_{corr}(\lambda) - E_{corr}(-\lambda)}{2\lambda}$$

Detailed comparisons between LECC and FFCC

Mr. Prasannaa

	PDM (Debye)				E_{eff} (GV/cm)			
	DF	LECC	FFCC	Diff (%)	DF	LECC	FFCC	Diff (%)
BeF (DZ)	1.32	0.93	1.01	-7.9	0.002	0.003	0.003	0.0
BeF (TZ)	1.31	1.06	1.12	-5.4	0.002	0.004	0.004	0.0
BeF (QZ)	1.30	1.10	1.15	-4.3	0.003	0.005	0.005	0.0
MgF (DZ)	3.21	2.84	2.91	-2.4	0.04	0.06	0.06	0.0
MgF (TZ)	3.21	3.02	3.08	-1.9	0.05	0.06	0.06	0.0
MgF (QZ)	3.16	3.07	3.13	-1.9	0.05	0.07	0.07	0.0
CaF (DZ)	2.89	3.01	3.07	-2.0	0.16	0.23	0.23	0.0
CaF (TZ)	2.82	3.13	3.17	-1.3	0.18	0.27	0.27	0.0
CaF (QZ)	2.77	3.16	3.19	-0.9	0.19	0.28	0.28	0.0
SrF (DZ)	2.83	2.95	3.02	-2.3	1.33	1.91	1.99	-4.0
SrF (TZ)	2.95	3.42	3.46	-1.2	1.51	2.14	2.12	0.9
SrF (QZ)	3.01	3.60	3.62	-0.6	1.54	2.17	2.16	0.5
BaF (DZ)	2.42	2.69	2.77	-2.9	4.58	6.48	6.42	0.9
BaF (TZ)	2.28	3.00	2.96	1.4	4.83	6.65	6.60	0.8
BaF (QZ)	2.65	3.40	3.41	-0.3	4.80	6.50	6.46	0.6

LECC results agree with FFCC results in E_{eff} of Alkali-Earth Fluorides.

Detailed comparisons between LECC and FFCC

Mr. Prasannaa

	PDM (Debye)				E_{eff} (GV/cm)			
	DF	LECC	FFCC	Diff (%)	DF	LECC	FFCC	Diff (%)
HgF	3.96	2.61	2.92	-10.6	104.25	115.42	116.37	-0.8
HgCl	4.23	2.72	2.96	-8.1	103.57	113.56	114.31	-0.7
HgBr	4.40	2.36	2.71	-12.9	97.89	109.29	109.56	-0.2
HgI	3.91	1.64	2.06	-20.4	96.85	109.30	109.56	-0.2
PbF	4.42	3.72	3.88	-4.1	40.20	37.24	37.91	-1.8

Dyall-DZ

- LECC results agree with FFCC results in E_{eff} of Mercury halides and PbF.
- PDMs show large differences but they can be due to using the poor basis set (DZ).

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P and T symmetry violations in a diamagnetic molecule

Nuclear spin operator

$$H_{\mathrm{eff}} = -d\sigma_N \cdot \lambda$$

Unit vector in the direction of the molecular axis

Coupling constants d

Four different d

- A proton EDM — ① d^V : volume effect, ② d^M : magnetic effect
- A weak neutral current interaction — ③ d^T : weak-neutral current effect
- An nuclear EDM induced by *P,T*-odd nuclear forces — ④ d^Q : Schiff moment effect

P and T symmetry violations in a diamagnetic molecule

Coupling constants *d*

Four different d

- A proton EDM — ① d^V : volume effect, ② d^M : magnetic effect
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$$d^V = d_p X R \qquad d^M = -2d_p\left(\frac{1}{2M_N c} + \frac{g_N}{2Z m_p c}\right)\sum_j \left\langle \psi_j \left| \left(\frac{\alpha \times l}{r^3}\right)_j \right| \psi_j \right\rangle_\lambda$$

$$d^T = \sqrt{2} i C_T \sum_j \langle \psi_j | \varrho_p(r_j)(\gamma_0 \alpha)_{j,\lambda} | \psi_j \rangle$$

$$d^Q = -6QX$$

These parameters are calculated from the electronic wave function.

P and T symmetry violations in a diamagnetic molecule

Coupling constants *d*

Four sources

- A proton EDM — ① d^V : volume effect, ② d^M : magnetic effect
- A weak neutral current interaction — ③ d^T : weak-neutral current effect
- An nuclear EDM induced by *PT*-odd nuclear forces — ④ d^Q : Schiff moment effect

$$d^V = d_p X R \qquad d^Q = -6 Q X$$

We have developed the program to calculate the quantity of X.

$$X = \sum_{j=1}^{N_{occ}} X_j \qquad X_j = \frac{2\pi}{3} \left[\nabla \left((\psi_j^\dagger(0) \psi_j(0)) \right) \right]_\lambda$$

The derivative of the electron density at the nucleus along with the molecular axis

http://meetings.aps.org/link/BAPS.2016.DAMOP.K1.192

47th Annual Meeting of the APS Division of Atomic, Molecular and Optical Physics Volume 61, Number 8

A cold, slow beam of TlF molecules for an improved probe for the nuclear Schiff moment

Daniel McCarron et al. (Yale University)

We present a new experimental effort to search for the nuclear Schiff moment (SM) using thallium fluoride (TlF) molecules. Our approach capitalizes on the strong internal electric field present in a polarized molecule to amplify the effect of the SM. We project a 25-fold improvement over the current state of the art sensitivity to certain underlying mechanisms such as the CP-violating QCD θ-parameter [1]. Our recent measurements indicate that optical cycling is possible on the $X_1\Sigma_+ \longrightarrow B_3\Pi_1$ electronic transition of TlF [2]. Here a single laser will enable 100 photons to be scattered before an excited vibrational level is populated. This is sufficient for unit-efficiency fluorescence detection, rotational cooling, and state preparation. With a single repump laser, ¥textasciitilde 10$_4$ photons could be scattered, sufficient for transverse laser cooling that could substantially increase the brightness of the molecular beam. We report on the production of a cold and slow beam of TlF molecules from a cryogenic buffer gas beam source and present flux measurements for a range of TlF vaporization techniques. We also present our progress towards understanding the hyperfine structure in the $B_3\Pi_1$ state and its role in optical cycling. [1] B. Graner, Y. Chen, E. G. Lindahl, and B.R. Heckel, Reduced limit on the Permanent Electric Dipole Moment of ^{199}Hg, arXiv:1601.04339. [2] L. R. Hunter, S. K. Peck, A. S. Greenspon, S. Saad Alam, and D. DeMille, Prospects for laser cooling TlF, ¥textit{Phys. Rev. A}, ¥textbf{85}, 012511 (2012).

Summary

We established the programs to calculate E_{eff} and X parameter at the relativistic CCSD level.

1. E_{eff} in YbF molecule

- LECC is a good approximation of FFCC for E_{eff} but may not be for PDM with DZ basis sets.
- Calculated PDM and HFC values show better agreement with experiments by using FFCC method.

2. X parameter in TlF molecule

- The first application of Dirac-CCSD.
- X values heavily depend on the choice of basis sets.
- Correlation effects decrease the value of X about 23 %.