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Relativistic molecular orbital theory for CP violation

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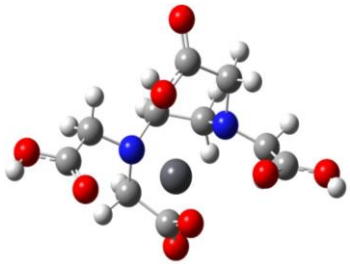

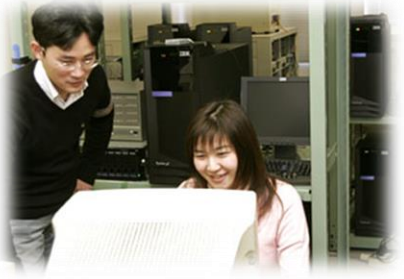

Topics of my talk

- My research works
  Related with Fundamental Physics
- Electron EDM in molecule
- Recent progresses based on our method

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Relativistic quantum chemistry

Schrödinger equation (Non relativistic)

$$i\hbar\frac{\partial\psi}{\partial t}=\left(\frac{\hat{p}^2}{2m}+V\right)\psi$$

Applicable to the molecules only containing light atoms

Dirac equation (Relativistic)

$$i\hbar\frac{\partial}{\partial t}\psi=\left(c\alpha\cdot\hat{p}+\beta mc^2\right)\psi$$

Important for the molecules containing heavy atoms

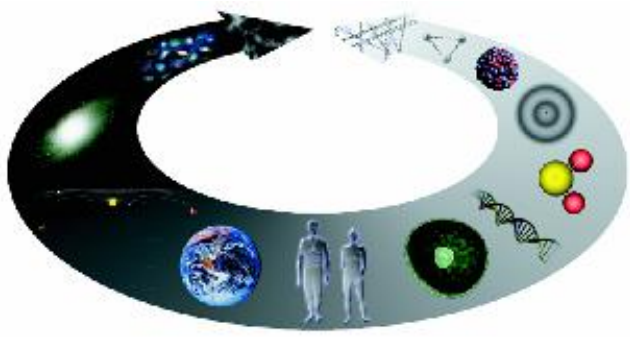
$$\begin{pmatrix} E-mc^2 & 0 & -ic\hbar\frac{\partial}{\partial z} & -ic\hbar\left(\frac{\partial}{\partial x}-i\frac{\partial}{\partial y}\right) \\ 0 & E-mc^2 & -ic\hbar\left(\frac{\partial}{\partial x}+i\frac{\partial}{\partial y}\right) & ic\hbar\frac{\partial}{\partial z} \\ & & & \end{pmatrix}\begin{pmatrix}\varphi_1\\ \varphi_2\end{pmatrix}=\begin{pmatrix}0\\0\end{pmatrix}$$

Four components and complicated!

My research work is mainly based on solving Dirac equation for molecular electronic states.

Collaborated works with Fundamental Physics using relativistic quantum chemistry

- **electron EDM for CP violation**
  (The operator is purely relativistic.)
- Born-Oppenheimer approximation correction for gravity correction in Yb_2
  (Yb is heavy atom)
- Double beta decay detection



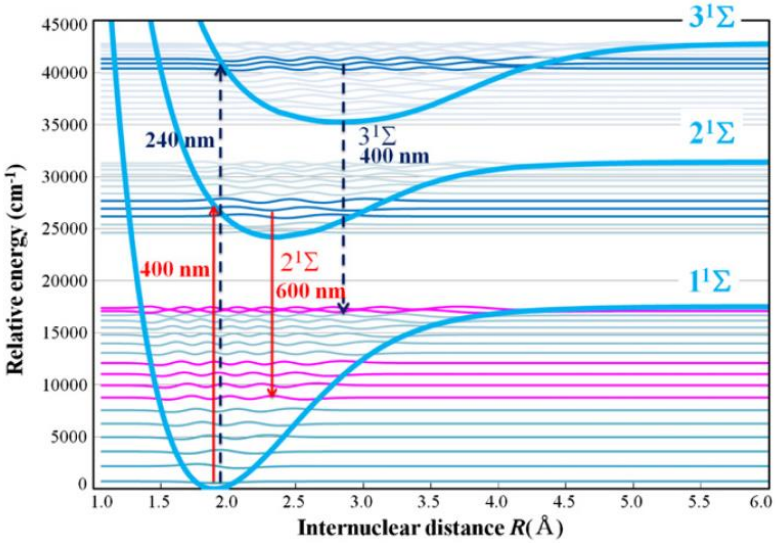
$$^{136}_{54}\mathrm{Xe} \rightarrow {}^{136}_{56}\mathrm{Ba}^{2+} + 2e^{-} + 2\bar{\nu}$$

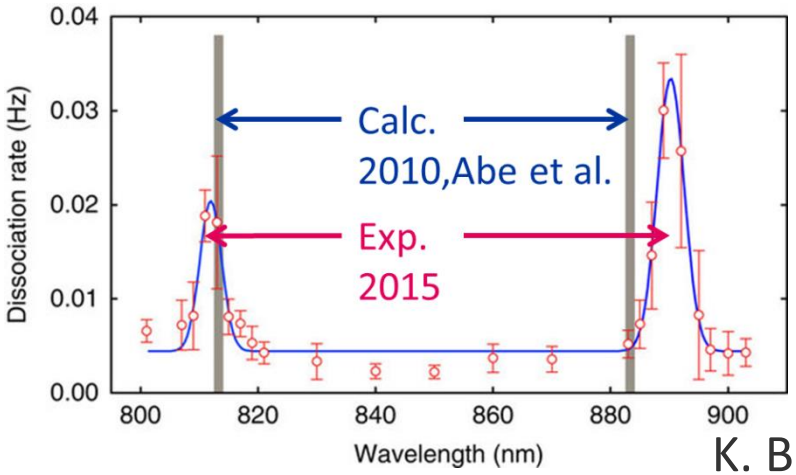
(BaO electronic states, Ba is heavy atom)

etc.

Potential energy curve calculations for diatomic molecules

CaH^+ toward the detection of m_p/m_e variation





K. Brown
(Observation)

v=0-v=9, 10 overtones

"Observation of vibrational overtones by single-molecule resonant photodissociation"
Kenneth R. Brown et al.
Nature Communications 6, 7825, 2015.

Dr. Kajita
(m_p/m_e variation proposal)

M. Abe
(Calculations)

Potential energy curve calculations for diatomic molecules

Other published works for PECs

TlH, Tl_2 (Four-component relativistic CASPT2)

XH^+ (X=Mg, Ca, Sr, Cd, Ba, Hg)

SrLi, CaLi, YbLi, BaLi, MgLi,…

Unpublished works

BaO, BiO, FrSr, etc… (on going)

Theoretical estimation is sometimes important to plan the molecular spectroscopic experiments for the survey of fundamental physics.

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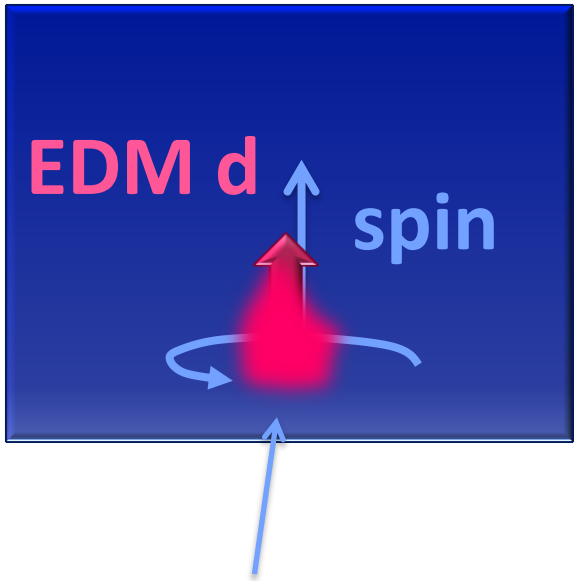
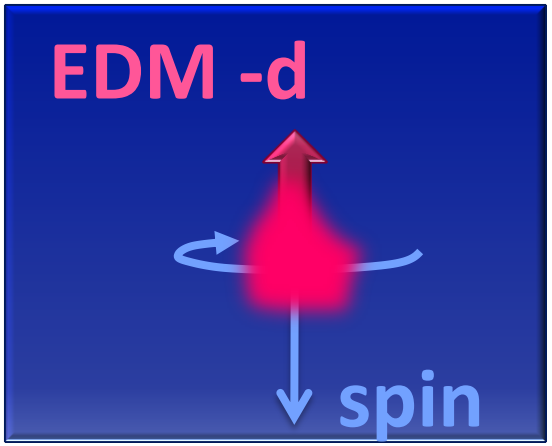
Electric dipole moment (EDM) of an elementary particle



Time reversal
(t → -t)

(p→-p) (r→r)
L→-L d→d



Assume that
EDM is parallel to spin axis

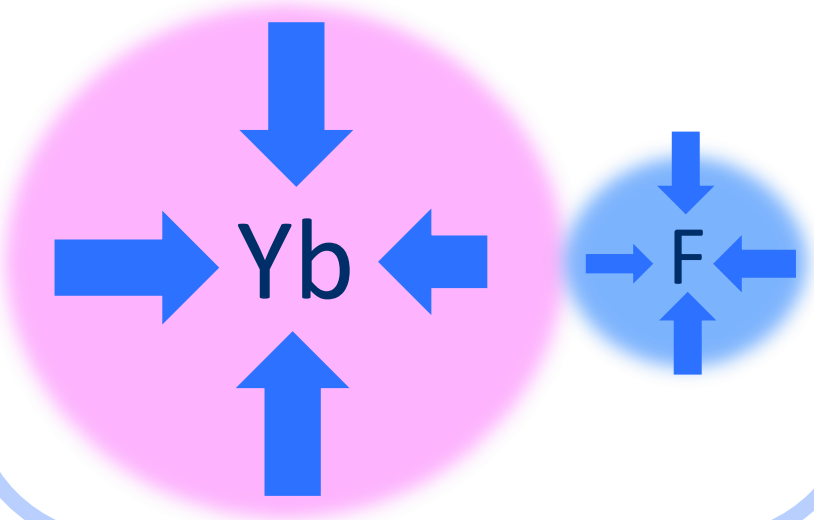
EDM becomes anti-parallel to spin axis

Non-zero value of EDM = T symmetry violation
= CP symmetry violation (under CPT theorem)

What is observed in molecules for EDM

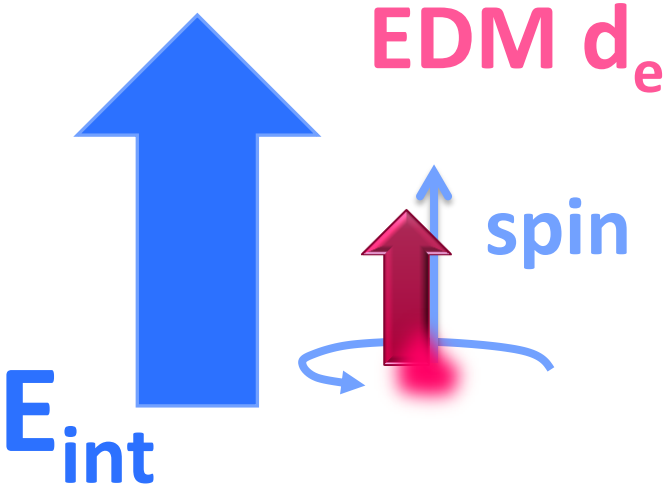
Internal electric field in a molecule

E_{int}



Interaction energy between E_{int} and d_e

$$\Delta E = \mathbf{d}_e \cdot \mathbf{E}_{int}$$



More precisely・・・

$$\Delta E = \sum_{i}^{N_{elec}} \left\langle \Psi_{DC} \left| d_e \beta \sigma_i \cdot \mathbf{E}_{\text{int}} \right| \Psi_{DC} \right\rangle$$

β matrix in EDM operator appears from relativistic correction

$$\Delta E = d_e E_{eff}$$

$$\beta = \begin{pmatrix} 1_{2\times2} & 0_{2\times2} \\ 0_{2\times2} & -1_{2\times2} \end{pmatrix}$$

Effective electric field (E_{eff}) can be non-zero only from relativistic calculations. (Schiff, Sandars)

Moreover, it is never determined from experiments!

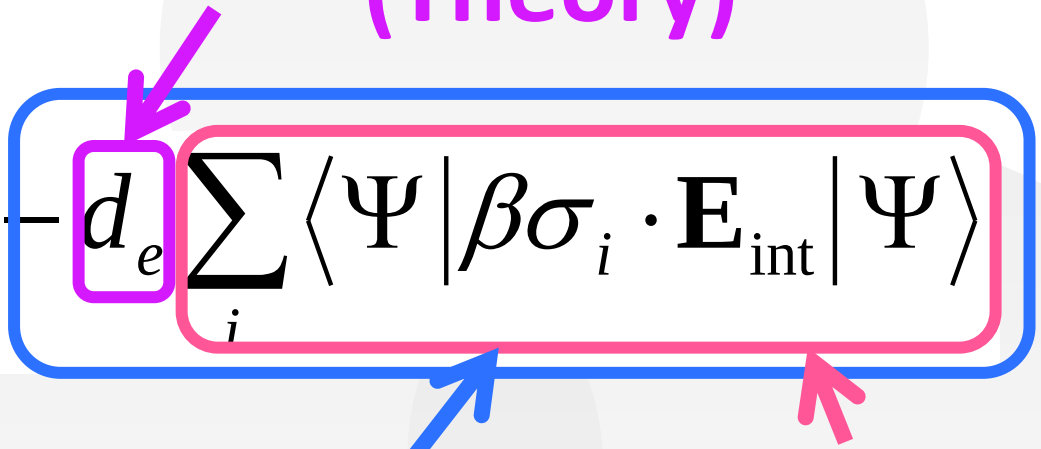
Four-component Dirac-Coulomb Hamiltonian

$$\hat{H}_{DC} = \sum_{i}^{N_{elec}} \left[c\alpha p_i + \beta mc^2 - \sum_{A}^{N_{nuc}} \frac{Z_A}{\left|\mathbf{r}_i - \mathbf{R}_A\right|} \right] + \sum_{i<j}^{N_{elec}} \frac{1}{\left|\mathbf{r}_i - \mathbf{r}_j\right|} \qquad \Psi_{DC} = \begin{pmatrix} \psi_\alpha^L \\ \psi_\beta^L \\ \psi_\alpha^S \\ \psi_\beta^S \end{pmatrix}$$

Collaborations of three fields are very important!

Particle Physics

(Theory)



Atomic, Molecular, and Optical Physics

(Experiment)

Relativistic Quantum Chemistry

to calculate E_{eff}

Previous works (E_{eff})

Atomic EDM:

Dirac-Coulomb + Coupled-Cluster Singles and Doubles(CCSD)

… etc

・Accurate calculations are reported for both relativity and electron correlations.

Molecular EDM (PbO,TlF,ThO,YbF…) :

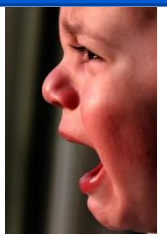
（One or two-component）GRECP＋CCSD, GRECP+SOCI

（Four-component） RASCI, GASCI, CCSD

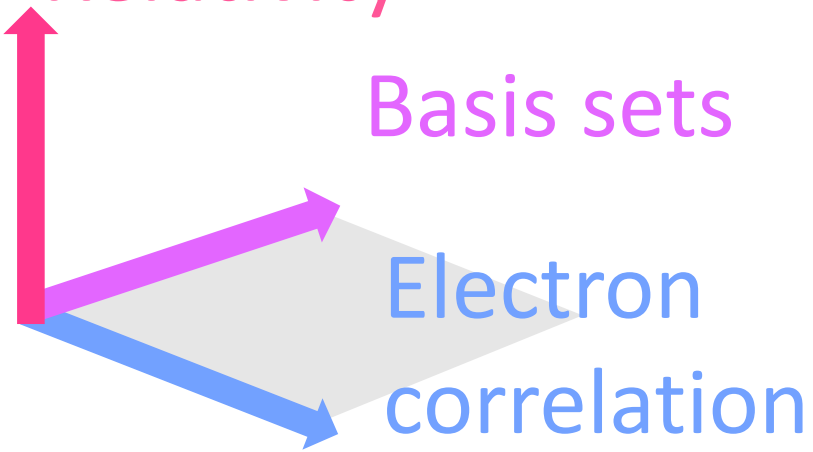
・Only a few works are reported, enough accurate in relativity, electron correlation, and basis set size.

Our motivation

Calculated E_{eff} ➔ cannot be compared with any experiments



We should calculate E_{eff} as precise as possible with the techniques of quantum chemistry and available computational resource!



4-cmp Dirac-Coulomb

Dyall QZ

primitive basis sets

CCSD

Computational details for YbF

Phys. Rev. A 90, 022501 (2014)

Wave function : Dirac-Fock, Dirac-CCSD

Program : UTChem + DIRAC08

Basis sets: Dyall's DZ, TZ, and QZ for Yb

+ Watanabe's basis for F

+ Sapporo (DK3) polarization

in uncontracted form

We approximate the expectation value with CCSD wave function as follows.

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

Measurable properties related with E_{eff}

- Hyperfine coupling constant (parallel) $A_{//}$:
  Interaction between electron spin and Yb nuclear spin
- Molecular dipole moment DM: s-p hybridization

	E_{eff} (GV/cm)	$A_{//}$ (MHz)	DM (D)
QZ 79e-CCSD(293)	23.1	7913	3.60
Experiments	-	7424	3.91
Error from experiments		7%	8%

A scheme of Relativistic CCSD for property calculations is now established!

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Parallelization (in CDAC super computer in India)

Mr. Kuwata
(Parallelization coding)

Nodes	Processes	Node Elapsed Time (minutes)
1	1	888
1	6	256
2	6	198
3	6	190
4	6	176

Mr. Prasannaa
(Bench mark calc.)

Bench mark calculations of SrF

6-core parallelization within one node

➔ 3～4 times faster

（Multi-node calculation is not effective.）

Conclusions and Prospect

- Relativistic CCSD (RCCSD) method is established for the calculation of effective electric field (E_{eff}), necessary for the detection of e-EDM.
- The method is applied to various diatomic systems such as, HgX (X= F, Cl, Br, I), XF (X=Sr, Cd, Ba, Yb, Hg, Ra), FrSr, BiO, etc. to find better candidates or support eEDM experiments.
- However, RCCSD is only applicable to the limited systems, so called single-reference electronic states. For more general systems, we are now developing Relativistic CASPT2 method for E_{eff} calculation.