Relativistic Quantum Chemical Calculations of Nuclear Electric Dipole Moments in Diamagnetic Molecules

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Outline

0. General introduction of CP violation and EDM

1. Electron EDM works by Ayaki Sunaga

2. Nuclear EDM in molecular systems
   ✓ Accurate determination of parameter X
   ✓ Accuracy about representation of X
0. General introduction of CP violation and EDM

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2. Nuclear EDM in molecular systems
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A mystery in Physics

Why anti-particles almost die out in our universe, even though the same number of particles and anti-particles are created in Big-Bang?
Disappearance of anti-particles ➔ particles and anti-particles obey different laws

Sakharov’s three necessity conditions

1. Charge symmetry and Charge-Parity (CP) symmetry violation
2. Baryon number violation
3. Interactions out of thermal equilibrium
The standard model predicts CP violation, but it is very weak and cannot explain the too small amount of anti-particles in the present universe.

We need a new theory and experimental evidences which explains much larger CP violation.
Electric dipole moment (EDM) of fundamental particle

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

Assume that EDM is parallel to spin axis

EDM becomes anti-parallel to spin axis
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!
There are various CP violation interactions. We need to determine electronic structure factors based on relativistic atomic/molecular orbital theories. Ex. Effective electric field ($E_{\text{eff}}$) for electron EDM
Collaborations of different fields are very important!

Particle Physics
(Theory)

\[-d_e \sum_i \langle \Psi | \beta \sigma_i \cdot E_{int} | \Psi \rangle\]

Atomic, Molecular, and Optical Physics
(Experiment)

Relativistic Quantum Chemistry
to calculate $E_{\text{eff}}$
Various kinds of CP violation

Paramagnetic systems:
- Electron EDM (PRA, 90, 022501 (2014) Abe et al.)
- Scalar and pseudoscalar (S-PS) interaction (PRA, 93, 042507, 2016. Sunaga et al.)

Diamagnetic systems:
- Schiff moment parameter (On going by Tsutsui, Fujita, and Abe)
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Analysis of the mechanism of enhancement of effective electric field ($E_{\text{eff}}$) for eEDM searches

prepared by Ayaki Sunaga (砂賀彩光)
eEDM searches

- Molecules for the eEDM experiments
  ...paramagnetic diatomic molecules

- Why is eEDM interesting NOW?

  \[ d_e \approx 10^{-38} \text{ e cm} \]

  \[ |d_e| \leq 1.1 \times 10^{-29} \text{ ecm} \]

Purpose of my work

- Hamiltonian of the eEDM interaction

\[ \hat{H}_{\text{EDM}} = - \sum_{j}^{N_e} d_e \beta \Sigma_j \cdot \hat{E}_{\text{int}} \]

\[ \equiv -d_e \langle \hat{E}_{\text{eff}} \rangle \]

- \( \beta \Sigma \) : four-component spin matrix
- \( \hat{E}_{\text{int}} \): internal electric field in a system
- \( E_{\text{eff}} \): effective electric field

Purpose: analysis of the enhancement of \( E_{\text{eff}} \)

Experimental observable

Calculation value

\[ \langle \hat{H}_{\text{EDM}} \rangle \equiv -d_e \langle \hat{E}_{\text{eff}} \rangle \]

\[ \langle \hat{H}_{\text{EDM}} \rangle \] is proportional to \( E_{\text{eff}} \)

Systems with larger \( E_{\text{eff}} \) are better for experiments.
Ultracold molecules

**Advantage of ultracold molecules**

- Large Coherence time ($\tau \sim 1s$, NaK molecule [1])
- Number of molecules ($N \sim 10^4$, YbLi molecule [2,3])

⇒ Reducing systematic error

**Our target: HgA (A = Li, Na, K)**

- Optical lattice clock of Hg has been reported [4,5].

⇒ Application to ultracold Hg molecules to eEDM experiment is expected!

We analyze $E_{eff}$ of HgA, comparing them with HgH and HgF.

Result of $E_{\text{eff}}$

Comparison between leading candidates and Hg systems

Why are $E_{\text{eff}}$ of HgA smaller than HgH and HgF?

Method:
Relativistic coupled cluster

Apparently, molecules with Hg have large $E_{\text{eff}}$…

References:
Comparison between HgH and HgK

- Energy diagram of molecular orbitals

\[ E_{\text{eff}}(\text{HgH}) \gg E_{\text{eff}}(\text{HgK}) \]

SOMO...Singly Occupied Molecular Orbital
Does $E_{\text{eff}}$ of alkali molecules always decrease?

Comparison between Hg and Sr molecules

The trends of Hg and Sr molecules are different:

SrA has relatively large $E_{\text{eff}}$.  
(e.g. $E_{\text{eff}}$ of SrLi is similar to that of SrF)

Method: Relativistic CCSD, Basis set: Dyall cv3z
Comparison between HgLi and SrLi

- Energy diagram of HgLi and SrLi

### Energy diagram

**HgLi**
- SOMO: Li’s 2s
- SOMO-1: Hg’s 6s
- Orbital energy diagram:
  - SOMO: Li’s 2s
  - SOMO-1: Hg’s 6s

**SrLi**
- SOMO: Sr’s 5s & Li’s 2s
- Orbital energy diagram:
  - SOMO: Sr’s 5s
  - SOMO-1: Li’s 2s

$E_{\text{eff}}$ of SrA is not so small, because energy of Sr’s 5s is high.
Trend of $W_s/E_{\text{eff}}$

- $E_{\text{eff}}$, $W_s$, and $W_s/E_{\text{eff}}$ of Hg and Sr molecules

<table>
<thead>
<tr>
<th></th>
<th>HgH</th>
<th>HgF</th>
<th>HgLi</th>
<th>HgNa</th>
<th>HgK</th>
<th>SrH</th>
<th>SrF</th>
<th>SrLi</th>
<th>SrNa</th>
<th>SrK</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_{\text{eff}}$</td>
<td>120.1</td>
<td>115.7</td>
<td>37.8</td>
<td>20.3</td>
<td>16.2</td>
<td>2.6</td>
<td>2.1</td>
<td>2.0</td>
<td>1.5</td>
<td>1.0</td>
</tr>
<tr>
<td>$W_s$</td>
<td>277.9</td>
<td>266.7</td>
<td>86.4</td>
<td>46.5</td>
<td>37.1</td>
<td>2.3</td>
<td>1.9</td>
<td>1.8</td>
<td>1.3</td>
<td>0.9</td>
</tr>
<tr>
<td>$W_s/E_{\text{eff}}$</td>
<td>2.31</td>
<td>2.30</td>
<td>2.29</td>
<td>2.29</td>
<td>2.28</td>
<td>0.89</td>
<td>0.89</td>
<td>0.90</td>
<td>0.90</td>
<td>0.89</td>
</tr>
</tbody>
</table>

$E_{\text{eff}}$ (GV/cm), $W_s$ (kHz), $W_s/E_{\text{eff}}$ (kHz/(GV/cm)) Method: Relativistic CCSD, Basis set: Dyall cv3z

Ratio ($W_s/E_{\text{eff}}$) is independent from combined atom.

Measuring two systems with the different ratio is important to separate eEDM and S-PS interaction.

Ultracold SrLi may be a good system because the ratio is different from the ones in heavy element molecules.
Analytical expression of $W_s/E_{\text{eff}}$

$$W_s = 2 X \Gamma'_{\text{rel,S-PS}}$$

$$E_{\text{eff}} = X \Gamma_{\text{rel}}$$

$$X = \frac{4\sigma}{\sqrt{3}} \frac{c_s c_p}{(v_s v_p)^{3/2}}$$

$$\psi_{\text{SOMO}} = c_s |s\rangle + c_p |p\rangle + \sum_{\text{other}} c_{\text{other}} |\text{other}\rangle, \quad \gamma = \sqrt{1 - (Z\alpha)^2}$$

$$W_s/E_{\text{eff}} = 2\Gamma'_{\text{rel,s-ps}} / \Gamma_{\text{rel}} \propto \frac{\gamma^2}{\Gamma^2 (2\gamma + 1)} \left( \frac{1}{2ZR_{\text{nuc}}} \right)^{2-2\gamma} \left/ \frac{1}{\gamma (4\gamma^2 - 1)} \right.$$  

☑ Only Z dependent part survives.

☑ $W_s/E_{\text{eff}}$ increase as $Z$ becomes large.

$\Gamma'_{\text{rel,s-ps}} = \frac{G_F Z^3 \alpha}{2\pi \sqrt{2}} \frac{4\gamma^2}{\Gamma^2 (2\gamma + 1)} \left( \frac{1}{2ZR_{\text{nuc}}} \right)^{2-2\gamma}$

$\Gamma_{\text{rel}} = -\frac{4Z^3 \alpha^2}{\gamma (4\gamma^2 - 1)(v_s v_p)^{3/2}}$

$R_{\text{nuc}}$: Nuclear radius (~10^{-5} a.u.)

$\alpha$: Fine structure constant (~1/137)

The combination between molecules with small and large $Z$ is needed for separating eEDM and S-PS interactions.
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**Upper limit on various EDM**

Upper limits estimated by experimental errors

<table>
<thead>
<tr>
<th>Paramagnetic (electron EDM)</th>
<th>Diamagnetic systems (nuclear EDM)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Atoms</strong></td>
<td><strong>Atoms</strong></td>
</tr>
<tr>
<td>$</td>
<td>d_e</td>
</tr>
<tr>
<td>ThO (2018)</td>
<td>Hg (2016)</td>
</tr>
<tr>
<td>$</td>
<td>d_e</td>
</tr>
<tr>
<td>HfF$^+$ (2017)</td>
<td></td>
</tr>
<tr>
<td>$</td>
<td>d_e</td>
</tr>
</tbody>
</table>

- Lowest upper limit of EDM is found in Hg atom
- Lowest upper limits of eEDM is found in molecules

Diamagnetic molecular experiments are ongoing @ Yale University

Sources of nuclear EDM

(i) Volume effect
Due to proton and neutron EDM($d_p, d_n$)

Nuclear EDM

(ii) Schiff moment effect
Due to asymmetry of proton charge

Nuclear EDM

$d_p$: proton EDM
$d_n$: neutron EDM

Nucleus

neutron

proton

proton

Nucleus
Interaction energy of nuclear EDM

Electric field by electrons

Interaction energy

\[ \Delta E = - D \cdot E_e \]

(Observable)

\[ D = \text{Volume effect} + \text{Schiff moment effect} \]
Interaction energy of nuclear EDM

(i) Volume effect

\[ \Delta E^V = RX \]

(ii) Schiff moment effect

\[ \Delta E^Q = -6QX \]

\[ R = \frac{1}{6} \left( \sum_{n=1}^{A} 3 \left( \langle d_n^2 \rangle - \langle r_n^2 \rangle_{ch} \right) \right) \Psi_N \]

\[ + \frac{1}{5} \left( \sum_{n=1}^{A} \left[ r_n^2 \left( r_n \cdot d_n \right) - d_n r_n^2 / 3 \right] \right) \Psi_N \]

\[ Q = \frac{1}{6} \left[ \frac{3}{5} \left( \sum_{n=1}^{A} q_n r_n \right) \Psi_N \right] \]

\[ - \frac{1}{Z} \left( \sum_{n=1}^{A} q_n r_n^2 \right) \Psi_N \times \left( \sum_{n=1}^{A} \frac{q_n r_n}{r_n^2} \right) \Psi_N \]

\[ R, Q : \text{Parameters from nuclear wave function } \Psi_N \]

\[ X : \text{Parameter from electronic wave function} \]

Large \( X \rightarrow \) Large \( \Delta E \) : good experimental system
Factor $X$ from electronic state

$$X = \frac{2\pi}{3} \left[ \frac{\partial}{\partial z} \rho(r) \right]_{x,y,z=0}$$

$\rho(r)$: Electron density

(z axis $\equiv$ molecular axis)

Derivative of $\rho(0)$ (electron density at the center of nucleus) with respect to molecular axis

Large relativistic effect!

<table>
<thead>
<tr>
<th>Previous works</th>
<th>mole.</th>
<th>Method</th>
<th>Relativity</th>
<th>Correlation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quiney et al. (1998)</td>
<td>TIF</td>
<td>Dirac-Fock</td>
<td>$\bullet$</td>
<td>$\times$</td>
</tr>
<tr>
<td>Parpia (1997)</td>
<td>TIF</td>
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<td>Petrov et al. (2002)</td>
<td>TIF</td>
<td>GRECP+2cmpCCSD</td>
<td>$\triangle$</td>
<td>$\circ$</td>
</tr>
<tr>
<td>Kudashov et al. (2013)</td>
<td>RaO</td>
<td>GRECP+2cmpCCSD</td>
<td>$\triangle$</td>
<td>$\circ$</td>
</tr>
</tbody>
</table>

No works are enough to accurate both in relativity and electron correlation.
Relativistic case: Dirac equation

Time independent Dirac eq. \[
\left(c \alpha \cdot \hat{p} + \beta mc^2 \right)\psi(\mathbf{r}) = E\psi(\mathbf{r})
\]

Four dimensional operator and wave function

\[
\alpha_i = \begin{pmatrix} 0 & \sigma_i \\ \sigma_i & 0 \end{pmatrix}, \quad \beta = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}
\]

\[
\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}, \quad I = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}
\]

Free particle’s Dirac eq.

\[
\begin{pmatrix}
E - mc^2 & 0 & -i\hbar \frac{\partial}{\partial z} & -i\hbar \left( \frac{\partial}{\partial x} - i \frac{\partial}{\partial y} \right) \\
0 & E - mc^2 & -i\hbar \left( \frac{\partial}{\partial x} + i \frac{\partial}{\partial y} \right) & i\hbar \frac{\partial}{\partial z} \\
-i\hbar \frac{\partial}{\partial z} & -i\hbar \left( \frac{\partial}{\partial x} - i \frac{\partial}{\partial y} \right) & E + mc^2 & 0 \\
-i\hbar \left( \frac{\partial}{\partial x} + i \frac{\partial}{\partial y} \right) & i\hbar \frac{\partial}{\partial z} & 0 & E + mc^2 \\
\end{pmatrix}
\begin{pmatrix}
\varphi_1 \\
\varphi_2 \\
\varphi_3 \\
\varphi_4 \\
\end{pmatrix}
= \begin{pmatrix}
0 \\
0 \\
0 \\
0 \\
\end{pmatrix}
\]
Coupled cluster singles and doubles (CCSD)

\[ |\Phi_{\text{CCSD}}\rangle = \exp(\hat{T}_1 + \hat{T}_2) |\Phi_{\text{HF}}\rangle \]

An effective method when the HF determinant is the only dominant determinant.
Objectives

• Extend the eEDM program to calculate $X$ at the 4-component Dirac-CCSD level

• Determine the most accurate values of $X$ for TIF and some other molecules

Sorry but these data will be opened in our future papers.
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Is the representation of X really enough??

\[ X = \frac{2\pi}{3} \left[ \frac{\partial}{\partial z} \rho(\vec{r}) \right] \]

Derivative of \( \rho(0) \) with respect to molecular axis

\( \rho(\vec{r}) \) : Electron density (z axis \( \equiv \) molecular axis)

Why 0? Why only center of the nucleus?
Flambaum and Ginges, PRA, 65, 032113, 2002
“Nuclear Schiff moment and time-invariance violation in atoms”

\[ \varphi(R) = \int \frac{e\rho(r)}{|R-r|} d^3r + \frac{1}{Z} (d \cdot \nabla) \int \frac{\rho(r)}{|R-r|} d^3r \]

Electrostatic potential created by nucleus at \( R \)
*This \( \rho \) is nuclear density

Legendre polynomial & collect only the first-order P&T odd term

Atomic \( s \) function

Atomic \( p \) function

\[ \langle s | -e \varphi^{(1)}(R) | p \rangle = -e^2 \langle s | n | p \rangle \cdot \left\{ \int_0^r \left[ \left( \frac{1}{Z} \langle r \rangle - r \right) \int_0^r U_{sp} dR + \frac{r}{r^3} \int_0^r U_{sp} R^3 dR \right] \rho ~ d^3r \right\} \]

Maclaurin expansion

\[ U_{sp}(R) = f_s(R)f_p(R) + g_s(R)g_p(R) = \sum_{k=1}^{\infty} b_k R^k \]

Radial distribution functions of large and small component
Flambaum and Ginges, PRA, 65, 032113, 2002
“Nuclear Schiff moment and time-invariance violation in atoms”

\[ U_{sp}(R) = f_s(R)f_p(R) + g_s(R)g_p(R) = \sum_{k=1}^{\infty} b_k R^k \] 

Maclaurin expansion

Stop only at \( k = 1 \)

\[ \int_0^r U_{sp} dR \approx \left( \frac{f_s f_p + g_s g_p}{R} \right) \bigg|_{R \to 0} = \left( \nabla \psi_s^\dagger \psi_p \right)_{R \to 0} = X \]

Schiff moment operator (old one)

\[ \langle s | - e \varphi^{(1)} | p \rangle = - \frac{e^2 b_1}{2} \langle s | n | p \rangle \cdot \left[ \frac{1}{Z} \langle r \rangle \langle r^2 \rangle - \frac{3}{5} \langle r r^2 \rangle \right] \]

\[ = 4\pi e S \cdot (\nabla \psi_s^\dagger \psi_p)_{R \to 0} \cdot \]

Schiff moment

\[ S = \frac{e}{10} \left[ \langle r^2 r \rangle - \frac{5}{3Z} \langle r^2 \rangle \langle r \rangle \right] = SI/I \]
Flambaum and Ginges, PRA, 65, 032113, 2002
“Nuclear Schiff moment and time-invariance violation in atoms”

Maclaurin expansion

\[ U_{sp}(R) = f_s(R)f_p(R) + g_s(R)g_p(R) = \sum_{k=1}^{\infty} b_k R^k \]

Flambaum & Ginges operator

\[ \langle s| - e\varphi^{(1)}|p \rangle = 4\pi e L \cdot (\nabla \psi_s \psi_p)_{R \to 0} \]

\[ L = e \sum_{k=1}^{\infty} b_k \frac{1}{(k+1)(k+4)} \left[ \langle rr^{k+1} \rangle - \frac{k+4}{3Z} \langle r \rangle \langle r^{k+1} \rangle \right] = L1/1 \]

\[ \frac{b_3}{b_1} = -\frac{3Z^2\alpha^2}{5} \]

$L$ (Local DM) contains higher-order terms but $b_k$ are determined from analytical expression of wave function (WF) using a finite nucleus model.

Is it also hold in multi-electronic molecular WF?
Sorry but this discussion is now closed and we will open it in a paper.