Relativistic calculations of parity and time reversal violation effects in molecules

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Mr. Sunaga
Mr. Tsutsui
1. Electron EDM in molecules (paramagnetic)
   Improved value of effective electric field \( (E_{\text{eff}}) \) in YbF molecule

2. Nuclear EDM in molecules (diamagnetic)
   Molecular enhancement parameter \((X)\) for the nuclear Schiff moment in diamagnetic molecules (TIF)
1. Electron EDM in molecules (paramagnetic)
   Improved value of effective electric field ($E_{\text{eff}}$) in YbF molecule

2. Nuclear EDM in molecules (diamagnetic)
   Molecular enhancement parameter ($X$) for the nuclear Schiff moment in diamagnetic molecules (TIF)
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

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

A Sakharov’s condition
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!
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 $\tau_{\text{max}} \approx \sigma_{\text{max}} \sqrt{m/(kBT)}$. Here, $m$ is the molecular mass, $T$ is the translational temperature, and $\sigma_{\text{max}}$ 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 $T \approx 4$ K by supersonic expansion or buffer gas cooling have been limited to $\tau_{\text{max}} \approx 1$ 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)

Atomic, Molecular, and Optical Physics (Experiment)

Relativistic Quantum Chemistry

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

to calculate \( E_{\text{eff}} \)
Computational methods

<table>
<thead>
<tr>
<th></th>
<th>Relativity</th>
<th>Basis set</th>
<th>Electron correlation</th>
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<tbody>
<tr>
<td>Titov et al.</td>
<td>2 comp. (spin-free)</td>
<td>GRECP</td>
<td>CCSDT</td>
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<td>Berger et al.</td>
<td>2 comp. (ZORA)</td>
<td>All-electron</td>
<td>DFT (B3LYP)</td>
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<td>Nayak &amp; Fleig</td>
<td>4 component</td>
<td>All-electron</td>
<td>GASCI</td>
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<tr>
<td>Our methods</td>
<td>4 component</td>
<td>All-electron</td>
<td>CCSD, CASPT2</td>
</tr>
</tbody>
</table>

Relativity (Dirac-Coulomb)

Basis sets (Dyall QZ)

Electron correlation (CCSD, CASPT2)

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

1e and 2e excitation operators
Expectation calculations at CCSD

1. Linear expectation approximation (LECC)

- Expand as a Taylor series and truncate at linear terms

\[
\langle \widehat{O} \rangle = \langle DF | \exp\left(\hat{T}_1 + \hat{T}_2\right) \hat{O}_N \exp\left(\hat{T}_1 + \hat{T}_2\right) | DF \rangle_C + \langle DF | \hat{O} | DF \rangle
\]

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

2. Finite field perturbation approach (FFCC)

- Apply finite field perturbations from the correlation calculations

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

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

\[
\frac{dE_{\text{corr}}(\lambda)}{d\lambda} \bigg|_{\lambda=0} \approx \frac{E_{\text{corr}}(\lambda) - E_{\text{corr}}(-\lambda)}{2\lambda}
\]
## Detailed comparisons between LECC and FFCC

<table>
<thead>
<tr>
<th>Mr. Prasannaa</th>
<th>PDM (Debye)</th>
<th>E\textsubscript{eff} (GV/cm)</th>
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<tbody>
<tr>
<td></td>
<td>DF</td>
<td>LECC</td>
</tr>
<tr>
<td>BeF (DZ)</td>
<td>1.32</td>
<td>0.93</td>
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<td>BeF (TZ)</td>
<td>1.31</td>
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<td>BeF (QZ)</td>
<td>1.30</td>
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<td>MgF (DZ)</td>
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<td>BaF (QZ)</td>
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LECC results agree with FFCC results in $E_{\text{eff}}$ of Alkali-Earth Fluorides.
Detailed comparisons between LECC and FFCC

Mr. Prasannaa

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<tr>
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<th></th>
<th></th>
<th></th>
<th>E eff (GV/cm)</th>
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<tr>
<td></td>
<td>DF</td>
<td>LECC</td>
<td>FFCC</td>
<td>Diff (%)</td>
<td>DF</td>
<td>LECC</td>
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<td>Diff (%)</td>
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<tr>
<td>HgF</td>
<td>3.96</td>
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<td>2.92</td>
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<td>HgI</td>
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<td>1.64</td>
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<td>3.72</td>
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<td>40.20</td>
<td>37.24</td>
<td>37.91</td>
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</table>

Dyall-DZ

- LECC results agree with FFCC results in $E_{\text{eff}}$ of Mercury halides and PbF.
- PDMs show large differences but they can be due to using the poor basis set (DZ).
1. Electron EDM in molecules (paramagnetic)
   Improved value of effective electric field \( (E_{\text{eff}}) \) in YbF molecule

2. Nuclear EDM in molecules (diamagnetic)
   Molecular enhancement parameter \( (X) \) for the nuclear Schiff moment in diamagnetic molecules (TlF)
P and T symmetry violations in a diamagnetic molecule

\[ H_{\text{eff}} = -d \sigma_N \cdot \lambda \]

- **Nuclear spin operator**
- **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

$\begin{align*}
\mathbf{d}^V &= d_p X R \\
\mathbf{d}^M &= -2d_p \left( \frac{1}{2M_N c} + \frac{g_N}{2Z m_p c} \right) \sum_j \langle \psi_j \left| \left( \frac{\alpha \times l}{r^3} \right)_j \right| \psi_j \rangle
\end{align*}$

A weak neutral current interaction

$\begin{align*}
\mathbf{d}^T &= \sqrt{2i} C_T \sum_j \langle \psi_j \left| e_p (r_j) (\gamma_0 \alpha)_{j,\lambda} \right| \psi_j \rangle
\end{align*}$

An nuclear EDM induced by $P,T$-odd nuclear forces

$\begin{align*}
\mathbf{d}^Q &= -6Q X
\end{align*}$

These parameters are calculated from the electronic wave function.
We have developed the program to calculate the quantity of $X$.

The derivative of the electron density at the nucleus along with the molecular axis is given by:

$\lambda = \frac{2\pi}{3} \left[ \nabla \left( \psi_j^+(0) \psi_j(0) \right) \right]$

The coupling constants $d$ are as follows:

- $d^V$: volume effect
- $d^M$: magnetic effect
- $d^T$: weak-neutral current effect
- $d^Q$: Schiff moment effect

Four sources:

- A proton EDM
- A weak neutral current interaction
- An nuclear EDM induced by $PT$-odd nuclear forces

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

$$X = \sum_{j=1}^{N_{occ}} X_j$$

$$X_j = \frac{2\pi}{3} \left[ \nabla \left( \psi_j^+(0) \psi_j(0) \right) \right]$$

The derivative of the electron density at the nucleus along with the molecular axis.
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 $\theta$-parameter [1]. Our recent measurements indicate that optical cycling is possible on the $X_1\Sigma^+ \rightarrow B_3\Pi_1$ 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, $\sim 104$ 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 199Hg, 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 $E_{\text{eff}}$ and $X$ parameter at the relativistic CCSD level.

1. $E_{\text{eff}}$ in YbF molecule
   - LECC is a good approximation of FFCC for $E_{\text{eff}}$ 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%.