The role of relativistic many-body theory in electron EDM searches in cold molecules

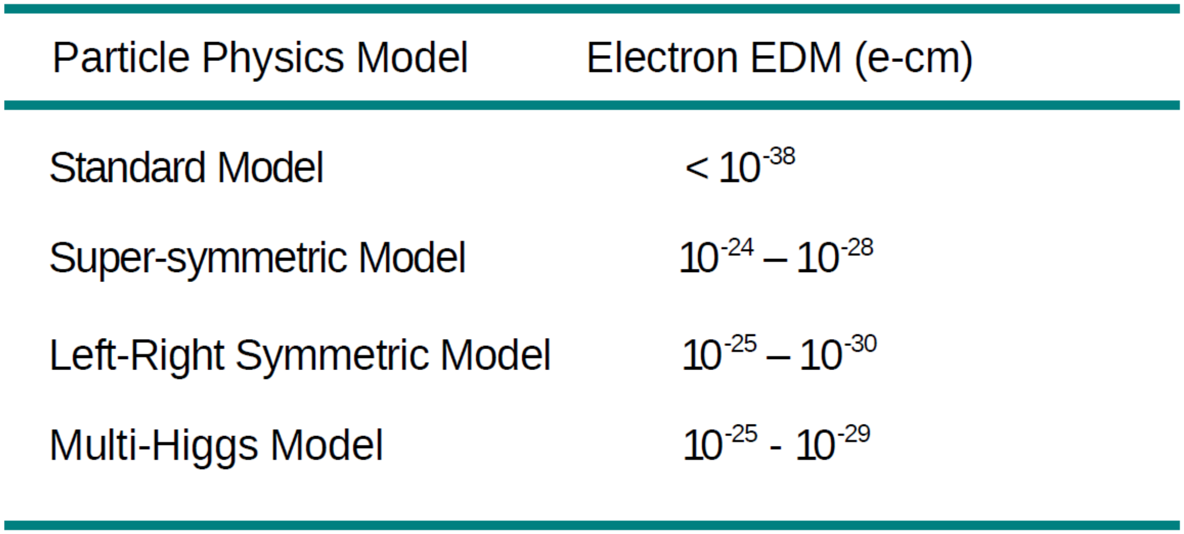
Bhanu Pratap Das
Department of Physics
Tokyo Institute of Technology
Tokyo, Japan

Collaborators:
V S Prasannaa, PRL, India
A Sunaga and M Abe, TMU, Japan
N Shitara and A Sakurai, Tokyo Tech, Japan

Outline of the talk

- Brief comments on EDM searches in molecules.
- The relativistic coupled cluster method and its applications to electron EDM searches in cold molecules (YbF, HgX, BaF, HgA, and YbOH).
- Previous and recent results for the electron EDM.

eEDM in the Standard Model (SM) & some of the theories beyond SM



Particle Physics Model	Electron EDM (e-cm)
Standard Model	$< 10^{-38}$
Super-symmetric Model	$10^{-24} – 10^{-28}$
Left-Right Symmetric Model	$10^{-25} – 10^{-30}$
Multi-Higgs Model	10^{-25} - 10^{-29}

The effective electric field on an electron

- An electric field (internal or external) in an atom or a molecule causes a shift, ΔE= - **$d_e E_{eff}$.**

$$\begin{aligned}\Delta E &= \langle\psi|\boldsymbol{H_{eEDM}}|\psi\rangle\\ &= -d_e\sum_{i=1}^{N_e}\langle\psi|\beta\boldsymbol{\sigma_i}\cdot\boldsymbol{E_i^{intl}}|\psi\rangle\\ &= -d_e E_{eff}\end{aligned}$$

Effective electric field

$$\sum_{i=1}^{N_e}-e\beta\sigma\cdot E_i^{intl}=[\beta\sigma\cdot\nabla,H_o]+2\frac{ic}{\hbar}\sum_{i=1}^{N_e}\beta\gamma_5p_i^2$$

$$\therefore E_{eff} = \sum_{i=1}^{N_e}\langle\psi|\beta\boldsymbol{\sigma_i}.\boldsymbol{E_i^{intl}}|\psi\rangle=-\frac{2ic}{e}\sum_{i=1}^{N_e}\langle\psi|\beta\gamma_5p_i^2|\psi\rangle$$

M Abe et al, Phys. Rev. A 90, 022501 (2014)

eEDM: Combination of experiment and theory

- ΔE_{expt} is measured in experiment.

- The effective electric field, E_{eff} , is calculated from theory.
- $\Delta E_{expt} = - d_e E_{eff} \eta (\mathbf{E}_{external})$

  $\Rightarrow d_e = - \Delta E_{expt} / (E_{eff} \eta (\mathbf{E}_{external}))$;

  Here, η is the polarization factor.

  It is a known quantity, since it is a function of $\mathbf{E}_{external}$.
- Calculate effective field, measure ΔE, η is known, hence obtain d_e.

$$\delta d_e \sim \frac{1}{2\pi E_{eff}\sqrt{NT\tau}\eta}$$

Calculation of the effective electric field

$$E_{eff} \;=\; \sum_{i=1}^{N_e} \langle \psi | \beta \boldsymbol{\sigma_i} . \boldsymbol{E_i^{intl}} | \psi \rangle$$

The wavefunctions are calculated using a suitable many-body method. Relativistic treatment is necessary. This is because for the non-relativistic case, the effective electric field is zero (Sandars, 1964, 1966, and 1968). Note that in the non-relativistic case, the electron still has its EDM, but it is due to all the interactions in the atom/ molecule treated non-relativistically that one gets the effective field to be zero.

Dirac-Fock method (DF)

- The relativistic version of the Hartee-Fock or Mean Field method.
- The wave function of the atom/ molecule is given by a many-electron wavefunction known as the Slater Determinant. $|\Phi_0\rangle = Det\ \varphi_1\varphi_2\varphi_3\ldots$
- $H_O\,|\Phi_O\rangle = E_O\,|\Phi_O\rangle; H_O = T + V_N + V_{DF}$; V_{DF} is an average
- Potential experienced by every electron due to all other electrons.
- A single particle orbital:

$$\varphi_i = \begin{pmatrix} \varphi_1^L \\ \varphi_2^L \\ \varphi_3^S \\ \varphi_4^S \end{pmatrix} = \begin{pmatrix} v \\ w \end{pmatrix}$$

Dirac-Fock method (DF)

$$t|\varphi_i\rangle + V_{DF}|\varphi_i\rangle = E_i|\varphi_i\rangle;$$

$$\begin{aligned} V_{DF}|\varphi_i\rangle &= \sum_{b=1}^{N_c}\langle\varphi_b|v|\varphi_b\rangle|\varphi_i\rangle \\ &- \sum_{b=1}^{N_c}\langle\varphi_b|v|\varphi_i\rangle|\varphi_b\rangle \end{aligned}$$

If $F \equiv t + V_{DF}$

$$\begin{aligned} F|\varphi_i\rangle &= E_i|\varphi_i\rangle \\ Let|\varphi_i\rangle &= \sum_n C_{in}|\chi_n\rangle \end{aligned}$$

$$FC = ESC$$

- The DF equations are solved iteratively, to get the coefficients, C.
- χ : basis sets. The choice of basis is one of the factors that determines the precision of the calculations. The other important factor that determines the precision is electron correlations.

Electron correlation

- The physical effects beyond those embodied in the mean field approximation.
- • $E_{corr} = E – E_{DF}$; E is the exact energy, E_{DF} is the Dirac-Fock energy, and E_{corr} is the correlation energy.
- Examples of many-electron theories that take electron correlation into account are: Configuration interaction (CI), Multi-Configuration Hartree-Fock/Dirac-Fock (MCHF/ DHF), Many-Body Perturbation Theory (MBPT), and Coupled Cluster Methods (CCM).

Many-body perturbation theory: non-relativistic and relativistic

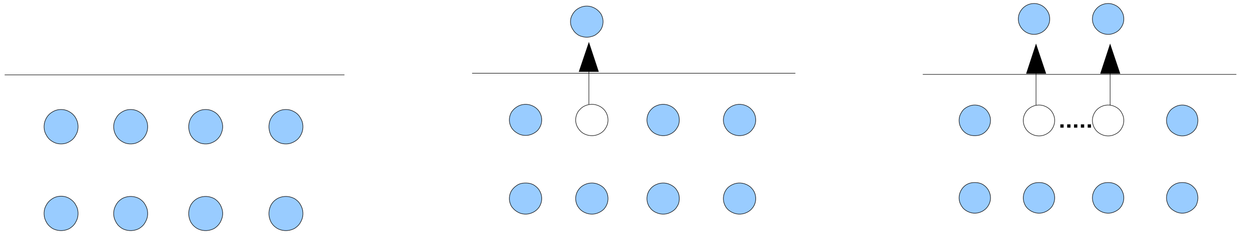
The difference between the actual 1/r_{ij} potential and the MF potential is the perturbation to the Hamiltonian.

$$H_0|\Phi_k\rangle = E_k|\Phi_k\rangle$$

$|\Phi_k\rangle$ is a k particle-k hole excitation.
For the k=0 case, $H_0|\Phi_0\rangle = E_0|\Phi_0\rangle$.
And $E_k = E_0 - \Delta E_k$; where the second term contains the energies of orbitals associated with a k particle-k hole excitation. For example:
$\Delta E_1 = E_0 - \epsilon_i + \epsilon_a$
$\Delta E_2 = E_0 - \epsilon_i - \epsilon_j + \epsilon_a + \epsilon_b$

$$\begin{aligned}
H_0 &= \sum_i t_i + \sum_i V_i^{DF} \\
H|\psi\rangle &= E|\psi\rangle; \\
H &= \sum_i t_i + \sum_{ij} \frac{1}{r_{ij}} \\
\therefore H' &= H - H_0 \\
&= \sum_{ij} \frac{1}{r_{ij}} - \sum_i V_i^{DF} \\
And, |\psi\rangle &= |\Phi_0\rangle + |\Phi_0^{(1)}\rangle + |\Phi_0^{(2)}\rangle + \ldots
\end{aligned}$$

Coupled Cluster Method: non-relativistic and relativistic



$|\Phi_0\rangle$ $T_1|\Phi_0\rangle$ $T_2|\Phi_0\rangle$

$$H|\psi\rangle = E|\psi\rangle$$

Coupled-cluster (CC) wavefunction: $|\psi\rangle = e^{T}|\Phi_0\rangle$ Here, $T = T_1 + T_2 + \ldots + T_N$

In MBPT, $|\psi\rangle = |\Phi_0\rangle + |\Phi_0^{(1)}\rangle + |\Phi_0^{(2)}\rangle + \ldots$

By expanding this in a complete set of particle-hole states, we find that $|\psi\rangle = e^{T}|\Phi_0\rangle$

Therefore, the CC wavefunction has electron correlation to all-orders of perturbation, in the residual Coulomb interaction.

CC is also both size extensive and size consistent.

At any level of particle-hole excitation, it captures more physical effects than other methods such as truncated configuration interaction or finite-order MBPT.

The CC method has been referred to as the gold-standard of many-body theory of atoms and molecules.

Coupled Cluster Method: non-relativistic and relativistic

$$
\begin{aligned}
H|\psi\rangle &= E|\psi\rangle \\
He^{T}|\Phi_0\rangle &= Ee^{T}|\Phi_0\rangle \\
e^{-T}He^{T}|\Phi_0\rangle &= E|\Phi_0\rangle \\
\langle\Phi_0|e^{-T}He^{T}|\Phi_0\rangle &= E
\end{aligned}
$$

This expression for energy terminates.
The CCSD approximation: $T = T_1+T_2$

The CCSD amplitude equations are:

$$
\begin{aligned}
\langle\Phi_i^a|e^{-T}He^{T}|\Phi_0\rangle &= 0 \\
\langle\Phi_{ij}^{ab}|e^{-T}He^{T}|\Phi_0\rangle &= 0
\end{aligned}
$$

H is the Dirac-Coulomb Hamiltonian, for the relativistic case. The reference DF state is made up of orbitals that are four-component spinors.

The Hellman-Feynman Theorem

$$\begin{aligned}
H(\lambda)|\psi(\lambda)\rangle &= E(\lambda)|\psi(\lambda)\rangle \\
where\ H(\lambda) &= H_0 + \lambda H' \\
and\ E(\lambda) &= E_0 + \lambda E_1 + \cdots \\
Also\ E(\lambda) &= E_0 + \lambda \left.\frac{dE}{d\lambda}\right|_0 + \cdots \\
\therefore E_1 &= \frac{dE}{d\lambda} \\
Hellman - Feynman\ theorem\ :\ \frac{dE(\lambda)}{d\lambda} &= \langle\psi(\lambda)|\frac{dH(\lambda)}{d\lambda}|\psi(\lambda)\rangle \\
In\ our\ case\ :\ \frac{dH(\lambda)}{d\lambda} &= H' \\
\therefore E_1 &= \langle\psi^{(0)}|H'|\psi^{(0)}\rangle
\end{aligned}$$

Note that due to the Hellman-Feynman theorem, any first order property can be evaluated as wither an expectation value or an energy derivative.

Expectation value approach

1. Solve the Dirac Fock (DF) equations, get the DF orbitals.
2. Solve the CCSD equations, get t amplitudes.
3. Solve expectation value problem.

$$\langle O\rangle = \frac{\langle\psi|O|\psi\rangle}{\langle\psi|\psi\rangle}$$

$$O_N = O - \langle\Phi_0|O|\Phi_0\rangle$$

$$\langle O\rangle = \langle\Phi_0|e^{T\dagger}O_N e^{T}|\Phi_0\rangle_C + \langle\Phi_0|O|\Phi_0\rangle$$

This expression is due to Cizek (1969

Truncation required!

We consider only the linear terms in e^T in the expectation value for E_{eff}.

$$\mathcal{E}_{\rm eff} = \frac{1}{d_e}\langle\Phi_0|(1+T_1+T_2)^\dagger(H^{\rm eff}_{\rm EDM})_N(1+T_1+T_2)|\Phi_0\rangle_c + \frac{1}{d_e}\langle\Phi_0|H^{\rm eff}_{\rm EDM}|\Phi_0\rangle$$

The Finite Field Coupled Cluster Method (FFCC)

- The basic idea is that we can evaluate a property by either an expectation value expression or an energy derivative. We do not need to truncate if we use this approach!

$$H_0|\psi^0\rangle = E_0|\psi^0\rangle$$

$$H(\lambda) \quad = \quad H_0 + \lambda H'$$

$$H(\lambda)|\psi(\lambda)\rangle = E(\lambda)|\psi(\lambda)\rangle$$

$$E(\lambda) = E_0 + \lambda E_1 + \ldots;\ E_1 = \langle\psi^0|H'|\psi^0\rangle$$

$$Also,\ E(\lambda) = E_0 + \lambda\frac{\partial E}{\partial\lambda}|_{\lambda=0} + \ldots$$

$$\frac{\partial E}{\partial\lambda}|_{\lambda=0} = \frac{E(\lambda) - E_0}{\lambda}$$

Comparing the two expressions:

$$E_1 = \frac{\partial E}{\partial\lambda}|_{\lambda=0}$$

λ is d_e for eEDM, and:

$$\begin{aligned} E_1 &= \frac{\partial E}{\partial\lambda}|_{\lambda=0} \\ &= E_{eff} \end{aligned}$$

The method can also be applied to other first order properties, like the molecular electric dipole moment.

The analytical derivative approach

The analytical counterpart of FFCC.

$$
\begin{aligned}
H_0|\psi^0\rangle &= E_0|\psi^0\rangle \\
where\ |\psi^0\rangle &= e^T|\Phi_0\rangle \\
H(\lambda)|\psi(\lambda)\rangle &= E(\lambda)|\psi(\lambda)\rangle \\
where\ H(\lambda) &= H + \lambda H' \\
E(\lambda) &= E_0 + \lambda E_1 + \cdots \\
|\psi(\lambda)\rangle &= e^{T(\lambda)}|\Phi_0\rangle \qquad \text{where } T(\lambda)=T+\lambda T^{(1)} \\
&= e^T e^{\lambda T^{(1)}}|\Phi_0\rangle
\end{aligned}
$$

Equating terms of order lambda:

$$
\boxed{
\begin{aligned}
\langle\Phi_0|([H,T^{(1)}] + H'e^T)_C|\Phi_0\rangle &= E_1 \\
\langle\Phi_0^*|(e^{-T}H_N e^T T^{(1)})_C|\Phi_0\rangle &= 0
\end{aligned}
}
$$

These are the energy and amplitude equations, to be solved, to obtain E_1. Note that before solving these equations, one must solve the usual CC equations.
The effective electric field can be obtained, once we know E_1, since it is A first order property. In this case, H' is the eEDM operator.

Normal CCM

$$\begin{aligned} H|\psi\rangle &= E|\psi\rangle \\ \langle\tilde{\psi}|H &= \langle\tilde{\psi}|E \end{aligned}$$

where

$$|\psi\rangle = e^{\boldsymbol{T}}|\Phi_0\rangle; \boldsymbol{T} = \sum_{I\neq0} T_I C_I^{+} \qquad \langle\tilde{\psi}| = \tilde{\boldsymbol{T}} e^{-\boldsymbol{T}}\langle\Phi_0|; \tilde{\boldsymbol{T}} = \sum_{I\neq0} 1 + \tilde{T}_I C_I^{-}$$

$$\langle\Phi_0|C_I^{+} e^{-\boldsymbol{T}}\boldsymbol{H}e^{\boldsymbol{T}}|\Phi_0\rangle = 0$$

Ket equation; identical to CC

$$\langle\Phi_0|\tilde{T}e^{-\boldsymbol{T}}[\boldsymbol{H}, C_I^{+}]e^{\boldsymbol{T}}|\Phi_0\rangle = 0$$

Bra equation

Arponen (1983), Arponen and Bishop (1985).

Expectation value of an operator, A:

$$\langle\boldsymbol{A}\rangle = \frac{\langle\tilde{\psi}|\boldsymbol{A}|\psi\rangle}{\langle\psi|\psi\rangle}$$

Therefore,

$$\langle\boldsymbol{A}\rangle = \langle\Phi_0|\tilde{\boldsymbol{T}}e^{-\boldsymbol{T}}\boldsymbol{A}e^{\boldsymbol{T}}|\Phi_0\rangle$$

This series terminates and satisfies the Hellman-Feynman theorem.

Results for E_{eff} in YbF

- The best limit comes from ThO, but a new result from YbF is expected soon.
- The limit on eEDM from YbF is: $d_e < 10.5 \times 10^{-28}$ e-cm (90% confidence limit), Hudson et al, Nature, 2011.
- We obtain a value of -23.1 GV/cm for E_{eff} in YbF, using a relativistic CCSD method, in the linear expectation value approximation, with an estimated error of less than 10% (M Abe et al, Phys. Rev. A 90, 022501 (2014)).

Results for E_{eff} in YbF

- Our first calculation was based on the relativistic CCSD method. A fairly large basis was used (Yb: 35s,30p,19d,13f,5g,3h,2i, F: 13s,10p,4d,3f). The results were obtained by only taking into account the linear terms in the expectation value expression.
- We overcome this limitation in finite field approach, since the effective field can be considered as the derivative of energy, with respect to eEDM. There is no truncation here.
- Previous calculations on YbF were based on the Dirac-Fock approximation (F A Parpia, J Phys B, 1998), effective core potential methods (Titov et al, Phys Rev Lett, 1996), and the CI-SD method (Nayak and Chaudhuri, Chem Phys Lett, 2006). Latest result: GHF-ZORA and GKS-ZORA (Gaul and Berger, J Chem Phys, 2017).
- We used basis sets that were optimized differently than for the previous calculations, for both Yb and F.
- Using FFCC, we obtain -23 GV/cm, which is in good agreement with the linear expectation value result of -23.1 GV/cm.

Results for HgX

Molecule	Basis	DF	LE-CCSD	FF-CCSD
HgF	DZ	-104.25	-115.42	-116.37
HgCl	DZ	-103.57	-113.56	-114.31
HgBr	DZ	-97.89	-109.29	-109.56
HgI	DZ	-96.85	-109.30	-109.56
BaF	QZ	-4.80	-6.50	-6.46

The units are in GV/cm. For the FFCC approach, we used a two point and six point central difference formula to evaluate the derivative. We used the following values of lambda: 10^{-3}, 10^{-4}, 10^{-5}, and 10^{-6}.

In a recent arXiv preprint, the authors explore laser cooling possibilities for HgF, and Estimate the statistical sensitivities for an eEDM experiment to be ~9 x 10^{-31} (beam experiment) and ~10^{-32} (trap experiment) (Zhenghai Yang et al, arXiv 1811.03908).

V S Prasannaa, A C Vutha, M Abe, B P Das, Phys Rev Lett, 114, 183001 (2015).
M Abe, V S Prasannaa, B P Das, Phys Rev A, 97, 032515 (2018).

Results for HgF: error estimates

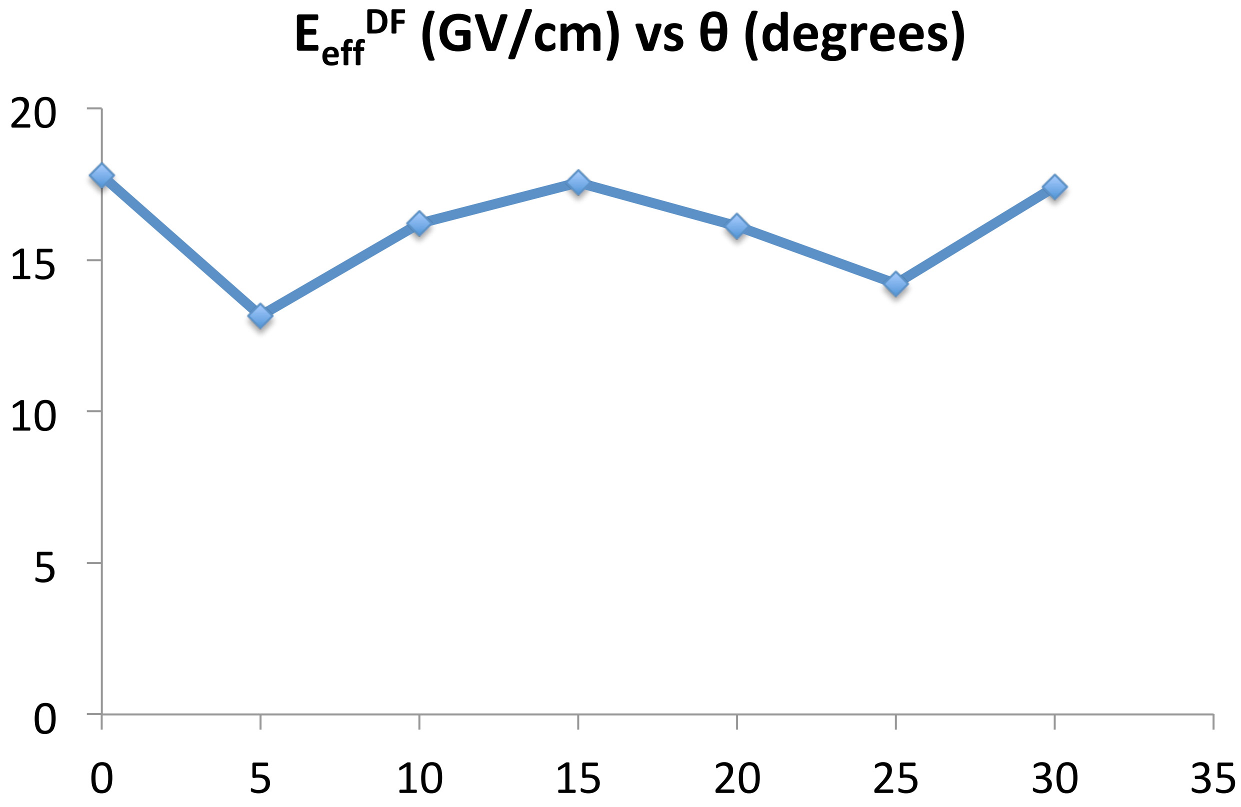
Molecule	Error (% fraction)		
HgF	1a. Basis	1b. Basis: diffuse	Correlation effects
	3.02	2.4	3.3

We take HgF as a representative case for estimating the error in our calculations.
Source (1-a): percentage fraction difference between the TZ and DZ FFCC results.
Source (1-b): percentage fraction difference between DZ cases with and without diffuse functions.
Source (2): percentage fraction difference between FFCCSD(T) and FFCCSD results, at DZ level of basis.

New potential candidates for eEDM experiments

- **Mercury alkalis (HgA; A=Li, Na, and K):** hold promise because they can be produced in large numbers with improved cooling and photoassociation techniques. Also, lattice-trapped experiments would mean much larger coherence times. Their effective electric fields are comparable to YbF (HgLi: -38 GV/cm, HgNa: -20 GV/cm, and HgK: -16 GV/cm) (A Sunaga et al, arXiV 1810.10177). Estimated sensitivity: ~ 10^{-30} e-cm.
- **YbOH:** attractive future candidates due to laser cooling possibilities. Its E_{eff} is around -23 GV/cm (submitted to PRL). Estimated sensitivity is four orders better than the current best limit set by ThO, which is 0.87 x 10^{-28} e-cm (Kozyrev and Hutzler, PRL, 119, 133002 (2017)).

New potential candidates for eEDM experiments: YbOH



Limits for d_e: Present Status

- **Limit from YbF:**

$d_e < 10.5 \times 10^{-28}$ e-cm (90% confidence limit)

Hudson et al, Nature, 2011. New result expected soon.

- **Limit from HfF+:**

$d_e < 1.3 \times 10^{-28}$ e-cm (90% confidence limit)

Cairncross et al, PRL, 2017 (to be published).

- **Limit from ThO:**

$d_e < 0.87 \times 10^{-28}$ e-cm (90% confidence limit) : Current best limit for d_e.

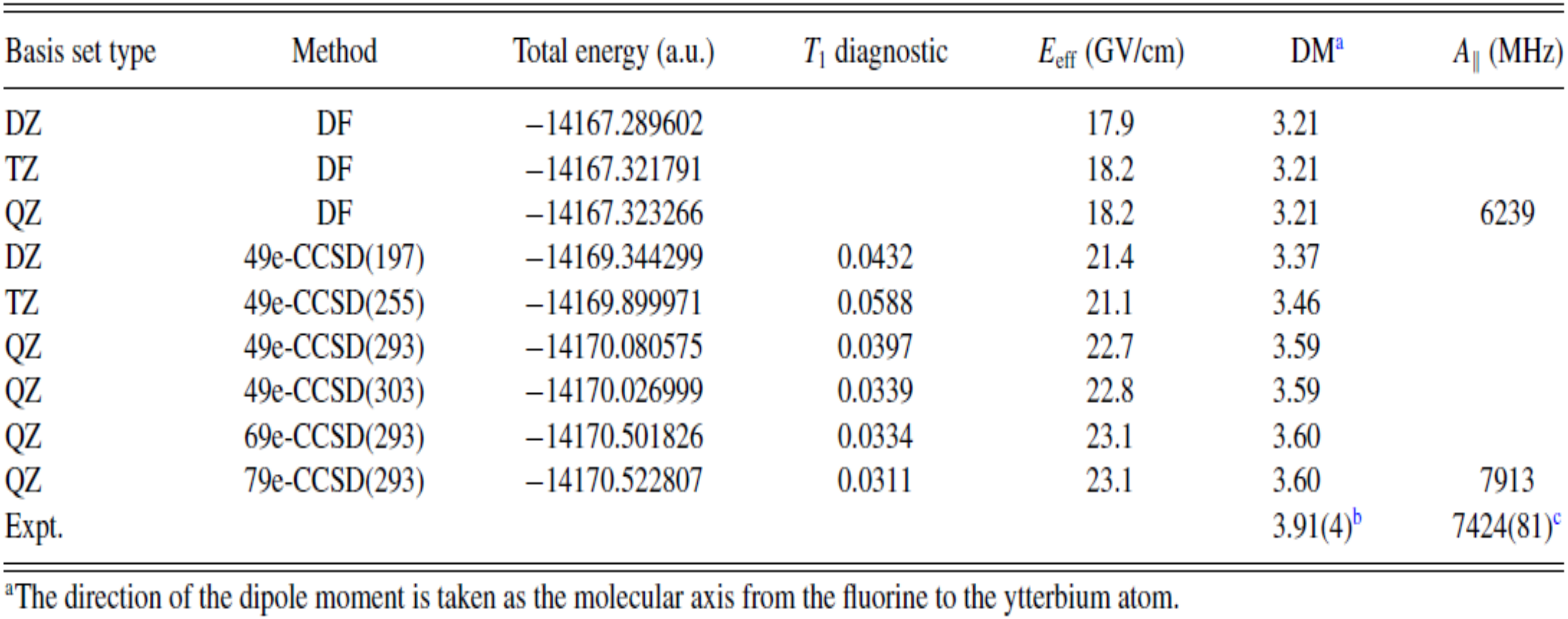
Baron et al, Science, 2014.
E_{eff}=80 GV/cm (Skripnikov), 75 GV/cm (Fleig).

Conclusions and outlook

- Relativistic many-body theory is indispensable in the searches of electron EDM. It is necessary to determine the upper limit for eEDM and also for identifying promising candidates for eEDM searches.
- With new results expected for the electron EDM experiments, improvements in relativistic many-body calculations in molecules are desirable.
- Relativistic coupled cluster theory is well suited for the EDM searches mentioned above. It would be necessary to develop different variants of the theory for this purpose: Extended CC method (Arponen, 1983, and Bishop, 1998), tensor network tailored CC theory for open-shell molecules (Kvall, Legeza, and collaborators, 2018), quantum computation approaches (Troyer and collaborators: ‘quantum algorithms for electronic structure calculations: particle-hole Hamiltonian and optimized wave function expansions’, PRA, 2018).

ASIDE

Results for YbF



Basis set type	Method	Total energy (a.u.)	T_1 diagnostic	E_{eff} (GV/cm)	DM[a]	$A_{\parallel}$ (MHz)
DZ	DF	−14167.289602		17.9	3.21	
TZ	DF	−14167.321791		18.2	3.21	
QZ	DF	−14167.323266		18.2	3.21	6239
DZ	49e-CCSD(197)	−14169.344299	0.0432	21.4	3.37	
TZ	49e-CCSD(255)	−14169.899971	0.0588	21.1	3.46	
QZ	49e-CCSD(293)	−14170.080575	0.0397	22.7	3.59	
QZ	49e-CCSD(303)	−14170.026999	0.0339	22.8	3.59	
QZ	69e-CCSD(293)	−14170.501826	0.0334	23.1	3.60	
QZ	79e-CCSD(293)	−14170.522807	0.0311	23.1	3.60	7913
Expt.					3.91(4)[b]	7424(81)[c]

[a] The direction of the dipole moment is taken as the molecular axis from the fluorine to the ytterbium atom.

M Abe et al, Phys. Rev. A 90, 022501 (2014).

DF Results for HgX

The DF contribution can be rewritten as: $\sum_{k=1}^{q}\sum_{l=q+1}^{2q} C_k^{*S} C_l^{L} \langle \chi_{v,k}^{S} | p^2 | \chi_{v,l}^{L} \rangle$

Atom	Mixing	HgF	HgCl	HgBr	HgI
Hg	$s - p_{1/2}$	-266.29	-262.07	-249.39	-242.34
Hg	$p_{1/2} - s$	373.37	367.74	349.42	339.56
Hg	$p_{3/2} - d_{3/2}$	31.22	25.22	21.84	20.99
Hg	$d_{3/2} - p_{3/2}$	-32.26	-26.35	-22.48	-21.84
Hg	$d_{5/2} - f_{5/2}$	-0.91	-0.51	-0.39	-0.33
Hg	$f_{5/2} - d_{5/2}$	0.92	0.52	0.4	0.33
X	$s - p_{1/2}$	-2.78	-4.85	-10.58	-17.19
X	$p_{1/2} - s$	2.79	4.92	11.17	19.87
Total:		106.06	104.62	99.99	99.05
DF		105.47	104.03	99.55	98.99
	$s - p_{1/2}$ and $p_{1/2} - s$	107.08	105.67	100.03	97.22

All results above are to be multiplied by -1.

V. S. Prasannaa, M. Abe, V. M. Bannur, and B. P. Das
Phys. Rev. A 95, 042513 (2017) - Published 21 April 2017.