Theory of Electric Dipole Moments of Atoms and Molecules

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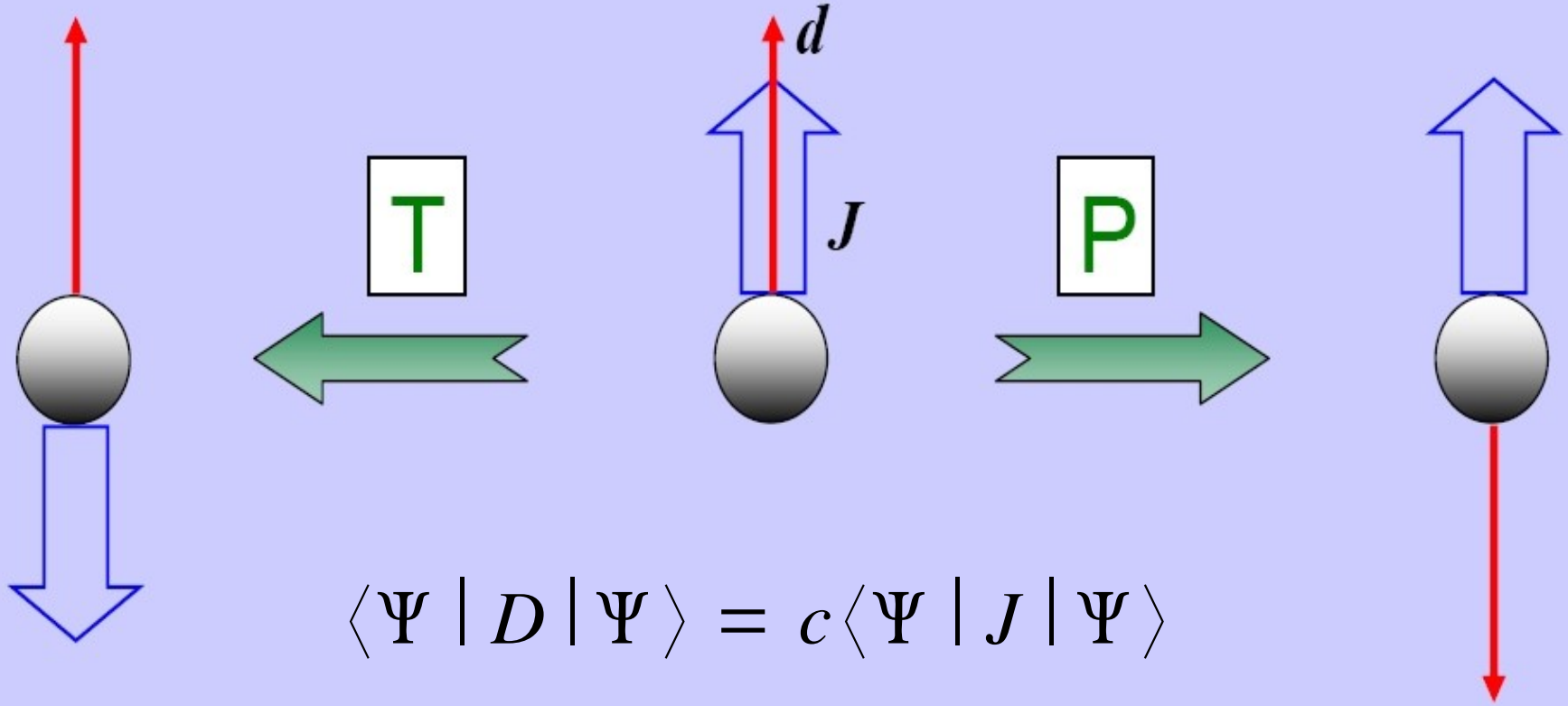
Outline of the talk

- General features of EDMs and relationship to the Standard Model
- Relationship between the electron EDM and atomic and molecular EDMs.
- Need for a relativistic many-body theory of atomic and molecular EDMs
- Future improvements in atomic and molecular theory of EDMs



$$\langle \Psi \mid D \mid \Psi \rangle = c \langle \Psi \mid J \mid \Psi \rangle$$

$$\Rightarrow D = 0$$

Permanent EDM of a particle VIOLATES both P - & T – invariance.
T-violation implies CP-violation via CPT theorem.

EDM and Degeneracy :

Consider the degeneracy of opposite parity states in a physical system

$$|\Psi\rangle = a\,|\Psi_e\rangle + b\,|\Psi_o\rangle$$

$$D = \langle\Psi|e\ r|\Psi\rangle \neq 0$$

EDM can be nonzero for degenerate states.

P and T violations in non-degenerate systems implies nonzero EDM.

Sources of Atomic EDM

Elementary Particles	Nucleon	Nucleus	Coupling constant	Atomic
e (d_e)			d_e	D_a *(open shell)*
			C_S	D_a *(open shell)*
e-q	e-n	e-N		
			C_T	D_a *(closed shell)*
q (d_q)	d_n	d_N	Q	D_a *(closed shell)*
q-q	d_n, n-n	d_N	Q	D_a *(closed shell)*

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	$10^{-25} - 10^{-29}$

ATOMIC EDM DUE TO THE ELECTRON EDM

(NON-RELATIVISTIC CASE)

The interaction between the electron spin and internal electric field exerted by the nucleus and the other electrons gives,

$-d_e \sigma \cdot E^I$ where, $E^I = -\nabla \{ \sum_i V_N(r_i) + \sum_{i<j} V_C(r_{ij}) \}$

The total atomic Hamiltonian is then,

$$H = \sum_i \{ \frac{p_i^2}{2m} - \frac{Ze}{r_i} \} + \sum_{i<j} \frac{e^2}{r_{ij}} - d_e \sum_i \sigma_i \cdot E_i^I$$

Using perturbation theory : $H = H_O + H'$

$$H_O = \sum_i \{ \frac{p_i^2}{2m} - \frac{Ze}{r_i} \} + \sum_{i<j} \frac{e^2}{r_{ij}}; \qquad H' = -d_e \sum_i \vec{\sigma}_i \cdot \vec{E}_i^I; \qquad H_O |\Psi_\alpha^O\rangle = E_O |\Psi_\alpha^O\rangle$$

When there is an external electric field, induced electric dipole moment arises.

The induced electric dipole moment of an atom is given by

$$e\vec{r}$$

The atomic EDM is

$$\vec{D}_a = \sum_i \left\{ d_e \vec{\sigma}_i + e\vec{r}_i \right\}$$

Using perturbation theory

$$\langle D_a \rangle = \langle \Psi_\alpha | D_a | \Psi_\alpha \rangle$$

As d_e is small, d_e^2 term can be neglected.

$$|\Psi_\alpha\rangle = |\Psi_\alpha^O\rangle + d_e |\Psi_\alpha^1\rangle + d_e^2 |\Psi_\alpha^2\rangle + \cdots$$

Assume, the applied field is in the ***z*** *direction* $d_e \vec{\sigma}_z$

Is even under parity and $e\vec{z}$ is odd under parity

$|\Psi^O_\alpha\rangle$ and $|\Psi^1_\alpha\rangle$ are of opposite parity, then the non-vanishing terms of the EDM are:

$$\langle D_a \rangle = \underbrace{d_e \langle \Psi^O_\alpha | \sum_i \vec{\sigma}_{z_i} | \Psi^O_\alpha \rangle}_{D^O} + \underbrace{d_e\, e\{\langle \Psi^O_\alpha | \sum_i \vec{z}_i | \Psi^1_\alpha \rangle + \langle \Psi^1_\alpha | \sum_i \vec{z}_i | \Psi^0_\alpha \rangle\}}_{D^1}$$

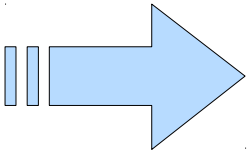
From the Time-independent Non-degenerate perturbation theory, we have,

$$|\Psi^1_\alpha\rangle = \sum_{I \neq \alpha} |\Psi^O_I\rangle \frac{\langle \Psi^O_I | H' | \Psi^O_\alpha \rangle}{E^O_\alpha - E^O_I}$$

$$H' = -d_e \vec{\sigma} \cdot \vec{E}_i$$

$$\langle D_a \rangle = \langle D^O \rangle + \langle D^1 \rangle$$

$$\langle D^O \rangle = d_e \langle \Psi^O_\alpha | \sum_i \vec{\sigma}_{z_i} | \Psi^O_\alpha \rangle \qquad \langle D^1 \rangle = -d_e \langle \Psi^O_\alpha | \sum_i \vec{\sigma}_{z_i} | \Psi^O_\alpha \rangle$$



$$\langle D_a \rangle = 0$$

(Sandars 1968)

Hence, in the non-relativistic scenario, even though the electron is assumed to have a EDM, when all the interactions in the atom are considered, the total atomic EDM becomes zero.

ATOMIC EDM DUE TO THE ELECTRON EDM

(RELATIVISTIC CASE)

The total atomic Hamiltonian, including intrinsic electron EDM is,

$$H = \underbrace{\sum_i \left\{ c\,\alpha_i \cdot p_i + \beta_i m c^2 - \frac{Z e}{r_i} \right\} + \sum_{i<j} \frac{e^2}{r_{ij}}}_{H_0} \; \underbrace{- d_e \sum_i \beta_i \sigma_i \cdot E_i^I}_{H'}$$

The expectation value of atomic EDM in the presence of applied electric field is given by,

$$\langle D_a \rangle = \underbrace{d_e \langle \Psi_\alpha^O | \sum_i \beta_i \sigma_{z_i} | \Psi_\alpha^O \rangle}_{D^O} + \underbrace{d_e\, e \left\{ \langle \Psi_\alpha^O | \sum_i z_i | \Psi_\alpha^1 \rangle + \langle \Psi_\alpha^1 | \sum_i z_i | \Psi_\alpha^0 \rangle \right\}}_{D^1}$$

Finally, the expression for Atomic EDM reduces to,

$$\langle D_a \rangle = \frac{2 c d_e}{\hbar} \sum_{I \neq \alpha} \left[\frac{\langle \Psi_\alpha^O | \vec{z} | \Psi_I^O \rangle \langle \Psi_I^O | i \beta \gamma_5 p^2 | \Psi_\alpha^O \rangle}{E_\alpha^O - E_I^O} + h.c. \right]$$

$\Rightarrow$ $\langle D_a \rangle \neq 0$: Relativistic

Sandars (1968) and Das (1988)

$$Effective\, H_{EDM} = \frac{2 i c d_e}{\hbar} \beta \gamma_5 p^2$$

R =< D_a> / d_e : is the enhancement factor

Energy Shift $\Rightarrow$ $\Delta E = -\langle D_a . E_{ext} \rangle = -R\, E_{ext} d_e$

Effective field seen by an electron in an atom = $R\, E_{ext}$

Effective field in certain molecules can be several orders of magnitude larger than in an atom

Theory of Atomic EDMs

The relativistic atomic Hamiltonian is,

$$H_a = \sum_i \{ c\,\alpha_i \cdot p_i + \beta_i m c^2 + V_N(r_i) \} + \sum_{i<j} \frac{e^2}{r_{ij}}$$

Treating H_{EDM} as a first-order perturbation, the atomic wave function is given by

$$|\Psi\rangle = |\Psi^{(0)}\rangle + d_e |\Psi^{(1)}\rangle$$

The atomic EDM is given by $$D_a = \frac{\langle \Psi | D | \Psi \rangle}{\langle \Psi | \Psi \rangle}$$

$$R = \frac{D_a}{d_e} = \frac{\langle \Psi^{(0)} | D | \Psi^{(1)} \rangle + \langle \Psi^{(1)} | D | \Psi^{(0)} \rangle}{\langle \Psi^{(0)} | \Psi^{(0)} \rangle}$$

This ratio, known as the **enhancement factor**, is calculated by **relativistic many-body theory.**

Unique many-body problem involving the interplay of the long range Coulomb interaction and short range P- and T-violating interactions.

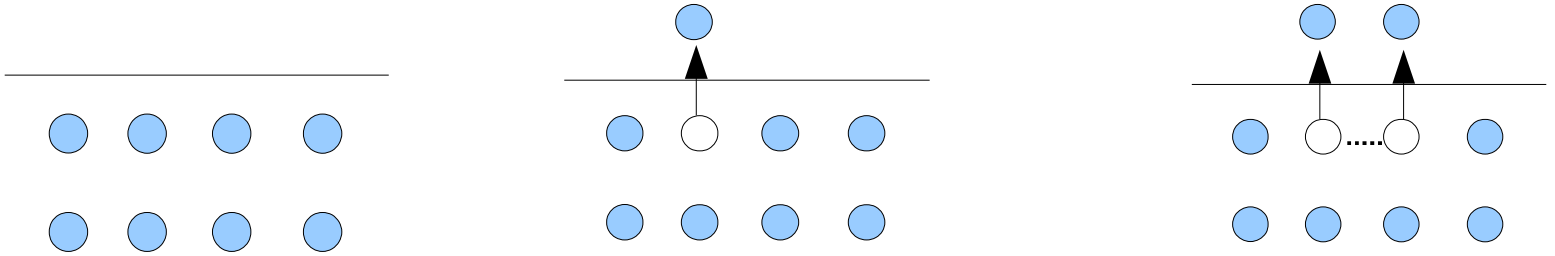
Accuracy depends on precision to which $|\Psi^{(0)}\rangle$ and $|\Psi^{(1)}\rangle$ are calculated.

Relativistic Wavefunctions of Atoms

Atoms of interest for EDM studies are relativistic many-body systems;

Wavefunctions of these atoms can be written in the mean field approximation

$$|\Phi_0\rangle = Det\ \{\phi_1 \phi_2 \cdots \phi_N\}$$ (Relativistic Dirac-Fock wavefunction)



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

$$T_1 = \sum_{a,p} t_{ap}\, a\dagger_p a_a \qquad T_2 = \sum_{a,b,p,q} t_{abpq}\, a\dagger_p a\dagger_q a_b a_a \qquad T = T_1 + T_2 + \cdots$$

Relativistic Coupled-cluster (CC) wavefunction;

$$|\Psi^{(0)}\rangle = \exp(T)\,|\Phi_0\rangle$$

CC wfn. has electron correlation to all-orders of perturbation theory for any level of excitation.

In presence of EDM, $|\Psi\rangle = |\Psi^{(0)}\rangle + d_e|\Psi^{(1)}\rangle = \exp\{T + d_e T^1\}\,|\Phi_0\rangle$

First-order EDM Perturbed RCC wfn. satisfies :

$$(H_0 - E_0)|\,\Psi^{(1)}\rangle = -\,H_{PTV}\,|\Psi^{(0)}\rangle$$

EDM enhancement factor in the RCC method

Unperturbed RCC wave function:

$$|\Psi^{(0)}\rangle = e^{T^{(0)}}\{1+S_v^{(0)}\}|\Phi\rangle$$

Perturbed RCC wave function:

$$|\Psi\rangle = e^{T^{(0)}+d_e T^{(1)}}\left\{(1+S_v^{(0)})+d_e S_v^{(1)}\right\}|\Phi\rangle$$

$$|\Psi\rangle = |\Psi^{(0)}+d_e|\Psi^{(1)}\rangle$$

EDM enhancement factor:

$$D_a = \frac{\langle\Psi|D|\Psi\rangle}{\langle\Psi|\Psi\rangle} \qquad R = \frac{D_a}{d_e} = \frac{\langle\Psi^{(0)}|D|\Psi^{(1)}\rangle + \langle\Psi^{(1)}|D|\Psi^{(0)}\rangle}{\langle\Psi^{(0)}|\Psi^{(0)}\rangle}$$

$$= \frac{\langle\Phi|\bar{D}S_v^{(1)}+\bar{D}T^{(1)}+\bar{D}T^{(1)}S_v^{(0)}+S_v^{(0)\dagger}\bar{D}S_v^{(1)}+S_v^{(0)\dagger}\bar{D}T^{(1)}+S_v^{(0)\dagger}\bar{D}T^{(1)}S_v^{(0)}|\Phi\rangle + h.c.}{\langle\Psi^{(0)}|\Psi^{(0)}\rangle}$$

where $\overline{D} = e^{T^{(0)\dagger}} D e^{T^{(0)}}$

RCCSD(T) term	Cs EDM enhancement factor		Tl EDM enhancement factor			
DF	94.19		-422.02			
$\overline{D}\,T^{(1)}$	5.18		-333.33			
$\overline{D}\,S_v^{(1)}$	122.21		-101.07			
$S_v^{(0)\dagger}\overline{D}\,T^{(1)}$	0.53		-24.82			
$\overline{D}\,T^{(1)}S_v^{(0)}$	-0.01		-7.12			
$S_v^{(0)\dagger}\overline{D}\,S_v^{(1)}$	-7.34		-4.26			
$S_v^{(0)\dagger}\overline{D}\,T^{(1)}S_v^{(0)}$	-0.05		-0.56			
Total	**120.53**	**124***	**-466.31**	**-582***	**-585****	**-573*****

T and **S** are core and valence excitation operators.

Cs: Nataraj et al., Phys. Rev. Lett. (2008)
Tl: Nataraj et al,. Phys. Rev. Lett. (2011)

*Dzuba and Flambaum PRA (2009)
**Liu and Kelly PRA(1992)
***Porsev et al PRL(2012)

New Electron EDM limit

The measured value of D_a in combination with the calculated value of D_a/d_e will give d_e .

From Tl EDM experiment (Regan et al, PRL 2002) and theory (Nataraj et al, PRL 2011) :

$$d_e < 2.0 \times 10^{-27}\ \text{e-cm (90\% confidence limit)}$$

This is a new upper limit for the electron EDM

Most recent new limit from YbF:

$$d_e < 1.0 \times 10^{-27}\ \text{e-cm (90\% confidence limit)}$$

Hudson et al, Nature, 2011

Ongoing EDM Experiments and Theory Using Paramagnetic Atoms

Experiments :

Rb: Weiss, Penn State

Cs: Gould, LBNL ; Heinzen, UT, Austin; Weiss, Penn State

Fr: Sakemi, Tohoku

Ra*: Jungmann, KVI, Netherlands

Theory : Flambaum, UNSW, Sydney ; Porsev and Kozlov, St. Petersburg, State Univ.; Safronova, U of Delaware; Sahoo, PRL, Ahmedabad; Nataraj, IIT Roorkee, Das, IIA, Bangalore

Improved accuracies in experiments and relativistic many-body theory for d_e might be possible in the future.

Molecular EDMs

$$H = H_m - d_e \sum_i \beta_i \boldsymbol{\sigma_i} \cdot \boldsymbol{E_i^I}$$

The shift in energy is given by:

$$\Delta E = -\langle \Psi_m | d_e \sum_i \beta_i \boldsymbol{\sigma_i} \cdot \boldsymbol{E_i^I} | \Psi_m \rangle$$

The effective electric field in certain molecules interacting with the electron EDM can be several orders of magnitude larger than those in atoms. It can be expressed as

$$\frac{\Delta E}{d_e} = -\langle \Psi_m | \sum_i \beta_i \boldsymbol{\sigma_i} \cdot \boldsymbol{E_i^I} | \Psi_m \rangle = -2ic \langle \Psi_m | \beta \gamma_5 p^2 | \Psi_m \rangle$$

Some of the current molecular EDM experiments that are underway are :

YbF : Hinds, Imperial College, London

PbO * and ThO : DeMille, Yale, Doyle and Gabrielse, Harvard

HfF $^+$: Cornell, JILA, Colorado

The sensitivities of these experiments could be 2-3 orders of magnitude better than that of the best electron EDM limit from atomic Tl.

Calculations of the effective fields in molecules are currently in their infancy.

Calculations of effective fields in molecules using Coupled Cluster Theory

The effective field can be expressed as an expectation value as mentioned in the previous slide.

Expectation Values in CC Theory

Normal Coupled Cluster Method

$$H|\Psi\rangle = E|\Psi\rangle$$

$$\langle\tilde{\Psi}|H = \langle\tilde{\Psi}|E$$

$|\Psi\rangle = e^{S}|\Phi_0\rangle$ where $S = S_1 + S_2 + \ldots$ and $S_1 = \sum_{a,p} S_a^p a_p^\dagger a_a ; S_2 = \sum_{ab,pq} S_{ab}^{pq} a_p^\dagger a_q^\dagger a_b a_a$

$\langle\Psi| = \langle\Phi_0| e^{S^\dagger}$

$\langle\tilde{\Psi}| = \langle\Phi_0|\tilde{S}\, e^{-S}$ where $\tilde{S} = 1 + \tilde{S}_1 + \tilde{S}_2 + \ldots$ and $\tilde{S}_1 = \sum_{a,p} \tilde{S}_a^p a_a^\dagger a_p ; \tilde{S}_2 = \sum_{ab,pq} \tilde{S}_{ab}^{pq} a_a^\dagger a_b^\dagger a_q a_p$

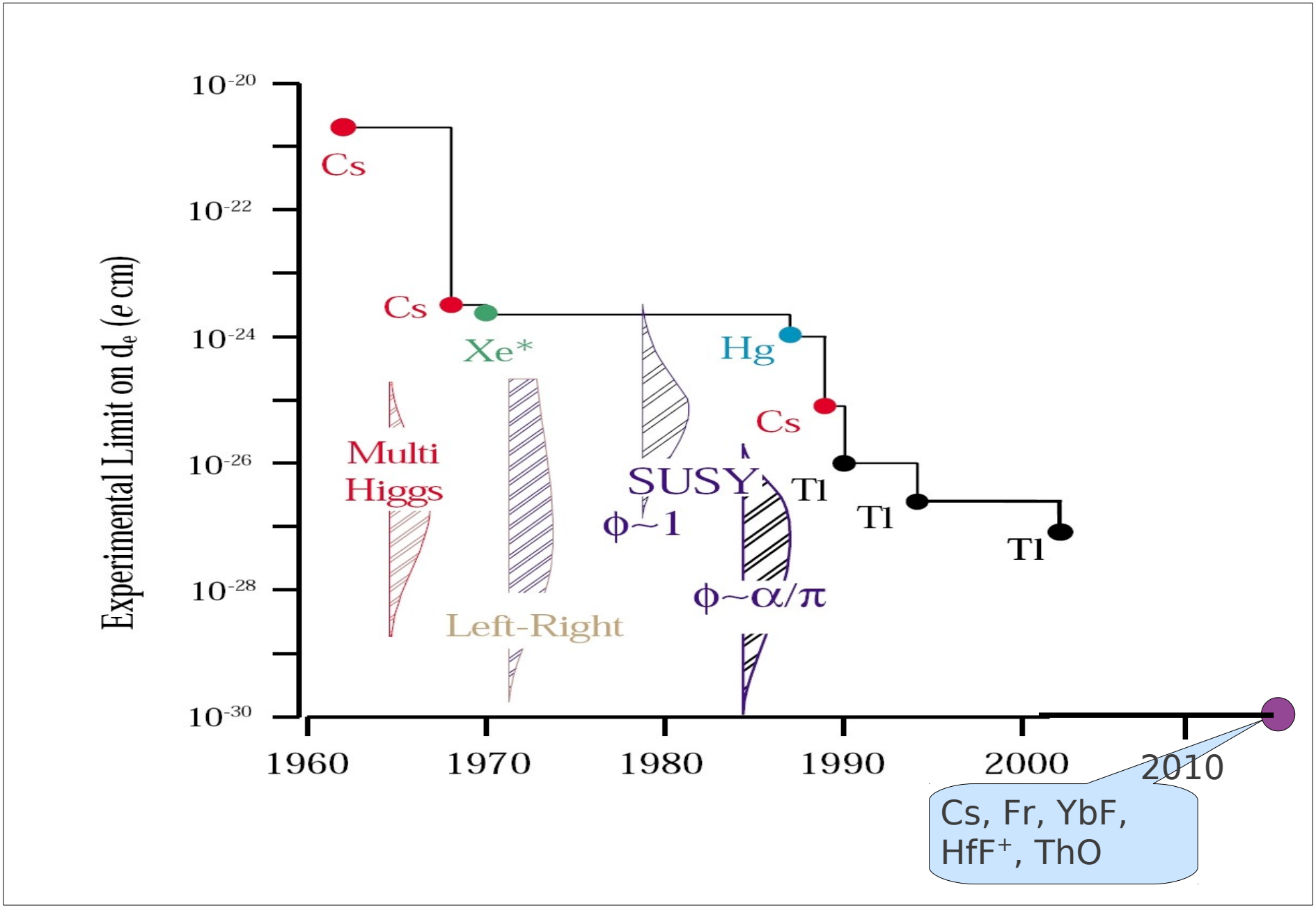
$S, \tilde{S}$ amplitudes are solved using suitable equations :

$$\langle A\rangle = \frac{\langle\tilde{\Psi}|A|\Psi\rangle}{\langle\tilde{\Psi}|\Psi\rangle} = \langle\tilde{\Psi}|A|\Psi\rangle = \langle\Phi_0|\tilde{S}e^{-S}A\,e^{S}|\Phi_0\rangle$$

For molecular EDMs, $A = 2ic d_e \beta\gamma_5 p^2$

Future : Extended Coupled Cluster Method

Limits on d_e : Past, Present and Future



Conclusions

Atomic and molecular EDMs arising the electron EDM could serve as excellent probes of physics beyond the standard model and shed light on CP violation.

Relativistic many-body theory plays a crucial role in determining an upper limit for the electron EDM

The current best electron EDM limits come from Tl and YbF

Several Atomic (Rb, Cs, Fr, etc.) and Molecular (YbF, HfF^+, ThO, etc) EDM experiments are underway. Results of some of these experiments could in combination with relativistic many-body calculations improve the limit for the electron EDM.

"The electric dipole moments of neutrons and atoms seem to me to offer one of the most exciting possibilities for progress in particle physics. Experiments here move very slowly but there has been a lot of progress recently in calculating EDMs with results that are encouraging for future experiments."

Steven Weinberg,

Conference Summary, XXVI International Conference on High Energy Physics, Dallas, 1992

"I am personally interested in the EDM tests, since I first proposed them and began looking for them 56 years ago, as tests of P, then T, and then CP. Originally I wanted to be the first person to discover an EDM, but now I at least want to know the answer. I have therefore personally established the time limited " Ramsey Prize of $5000 for the first person, or group, during my lifetime to announce the convincing discovery of a non zero electric dipole moment for any elementary particle or atomic nucleus." Since I am now 91 years old, please hurry. "

Norman Ramsey

International Conference on Atomic Physics, 2006, Innsbruck

Aside

METHOD OF CALCULATION

. . . Dirac - Fock Theory

For a relativistic N-particle system, we have a Dirac-Fock equation given by,

$$H_0 = \sum_I \left\{ c\,\vec{\alpha}_I \cdot \vec{p}_I + (\beta_I - 1)\, m\, c^2 + V_N(r_I) \right\} + \sum_{I<J} \frac{e^2}{r_{IJ}}$$

We represent the ground state wave function Φ as an N×N Slater determinant,

$$\Phi_0 = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_1(x_1) & \phi_1(x_2) & \phi_1(x_3) & \cdots & \phi_1(x_N) \\ \phi_2(x_1) & \phi_2(x_2) & \phi_2(x_3) & \cdots & \phi_2(x_N) \\ \cdots & \cdots & \cdots & \cdots & \cdots \\ \phi_N(x_1) & \phi_N(x_2) & \phi_N(x_3) & \cdots & \phi_N(x_N) \end{vmatrix}$$

The single particle wave functions ϕ_i's expressed in Dirac form as,

$$\Phi_a = \frac{1}{r} \begin{pmatrix} P_a(r)\chi_{\kappa_a, m_a} \\ iQ_a(r)\chi_{-\kappa_a, m_a} \end{pmatrix}$$

. . . Coupled Cluster Theory

The coupled cluster wave function for a closed shell atom is given by,

$$|\Psi_0\rangle = e^{T^{(0)}} \,|\, \Phi_0\rangle$$

Since the system considered here has only one valence electron, it reduces to

$$|\Psi_v\rangle = e^{T^{(0)}}\{1+S^{(0)}\}|\Phi_v\rangle$$

Where, $T^{(0)} = T_1^{(0)} + T_2^{(0)} + \cdots$ and $S^{(0)} = S_1^{(0)} + S_2^{(0)} + \cdots$

The RCC operator amplitudes can be solved in two steps; first we solve for closed shell amplitudes using the following equations:

$$\langle \Phi_0 \,|\, \overline{H}_0 \,|\, \Phi_0 \rangle = E_g \quad \text{and} \quad \langle \Phi_0^* \,|\, \overline{H}_0 \,|\, \Phi_0 \rangle = 0$$

Where, $\overline{H}_0 = e^{-T^{(0)}} H_0 e^{T^{(0)}}$

The open shell operators can be obtained by solving the following two equations :

$$H_{EDM}^{eff} = 2\, i\, c\, d_e\, \beta\, \gamma_5\, p^2$$

$$\langle \Phi_v^* \,|\, \overline{H}_{op} \{1 + S_v^{(0)}\} \,|\, \Phi_v \rangle = -\Delta E_v \langle \Phi_v^* \,|\, \{S_v^{(0)}\} \,|\, \Phi_v \rangle$$

Where, ΔE_v is the negative of the ionization potential of the valence electron v.

The total atomic Hamiltonian in the presence of EDM as a perturbation is given by,

$$|\Psi_v\rangle = e^{\left(T^{(0)} + d_e T^{(1)}\right)} \{1 + S^{(0)} + d_e S^{(1)}\} |\Phi_v\rangle$$

The effective (one-body) perturbed EDM operator is given by,

$$\langle \Phi_v \,|\, \overline{H}_{op} \{1 + S_v^{(0)}\} \,|\, \Phi_v \rangle = -\Delta E_v$$

Thus, the modified atomic wave function is given by,

$$H = H_0 + H_{EDM}$$

The perturbed cluster amplitudes can be obtained by solving the following equations self consistently :

$$\langle \Phi_0^* \,|\, \overline{H}_N^{(0)}\, T^{(1)} + \overline{H}_{EDM}^{eff} \,|\, \Phi_0 \rangle \;=\; 0$$

$$\langle \Phi_v^* \,|\, (\,\overline{H}_N^{(0)} - \Delta E_v\,)\, S_v^{(1)} + (\,\overline{H}_N^{(0)}\, T^{(1)} + \overline{H}_{EDM}^{eff}\,)\{\,1 + S_v^{(0)}\} \,|\, \Phi_v \rangle \;=\; 0$$

Where, $\quad H_N \;=\; H_0 - \langle \Phi_0 \,|\, H_0 \,|\, \Phi_0 \rangle$

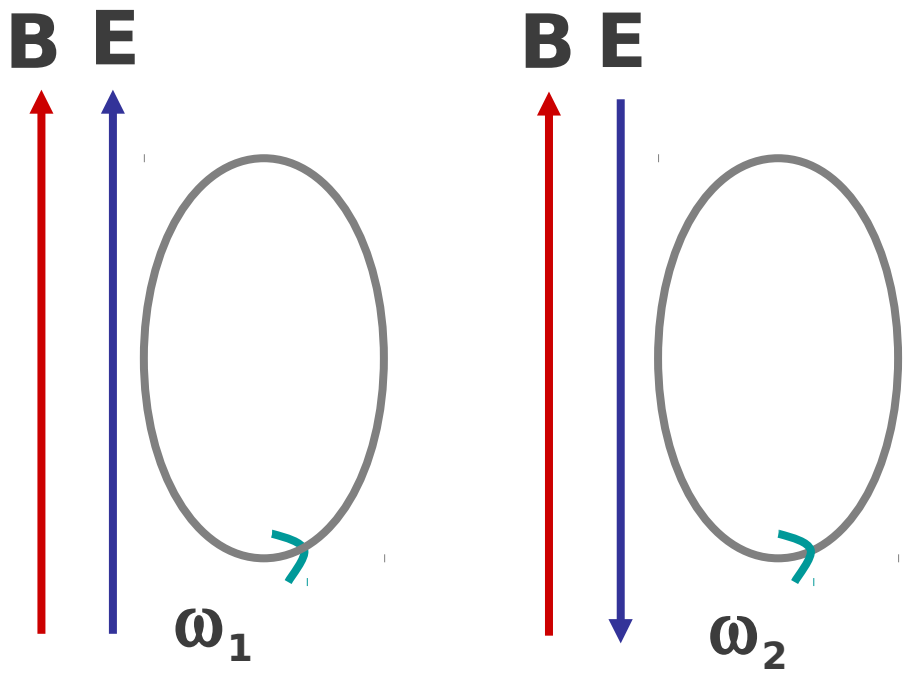
The atomic EDM is given by,

$$\langle D_a \rangle \;=\; \frac{\langle \Psi_v \,|\, D_a \,|\, \Psi_v \rangle}{\langle \Psi_v \,|\, \Psi_v \rangle}$$

EXPERIMENTS ON ATOMIC EDM

. . . Principle of Measurement

$$H_I = -\vec{D}_a \cdot \vec{E} - \vec{\mu} \cdot \vec{B}$$



$$\omega_1 = \frac{2\mu \cdot B + 2D_a \cdot E}{\hbar}$$

$$\omega_2 = \frac{2\mu \cdot B - 2D_a \cdot E}{\hbar}$$

$$\Delta\omega = \omega_1 - \omega_2 = \frac{4D_a \cdot E}{\hbar}$$

If the atomic EDM $D_a \sim 10^{-26}$ *e-cm* and $E = 10^5$ V/cm;

$\Delta\omega \sim 10^{-5}$ Hz

$$B_m = \frac{v \times E}{c^2}$$

Major source of error: