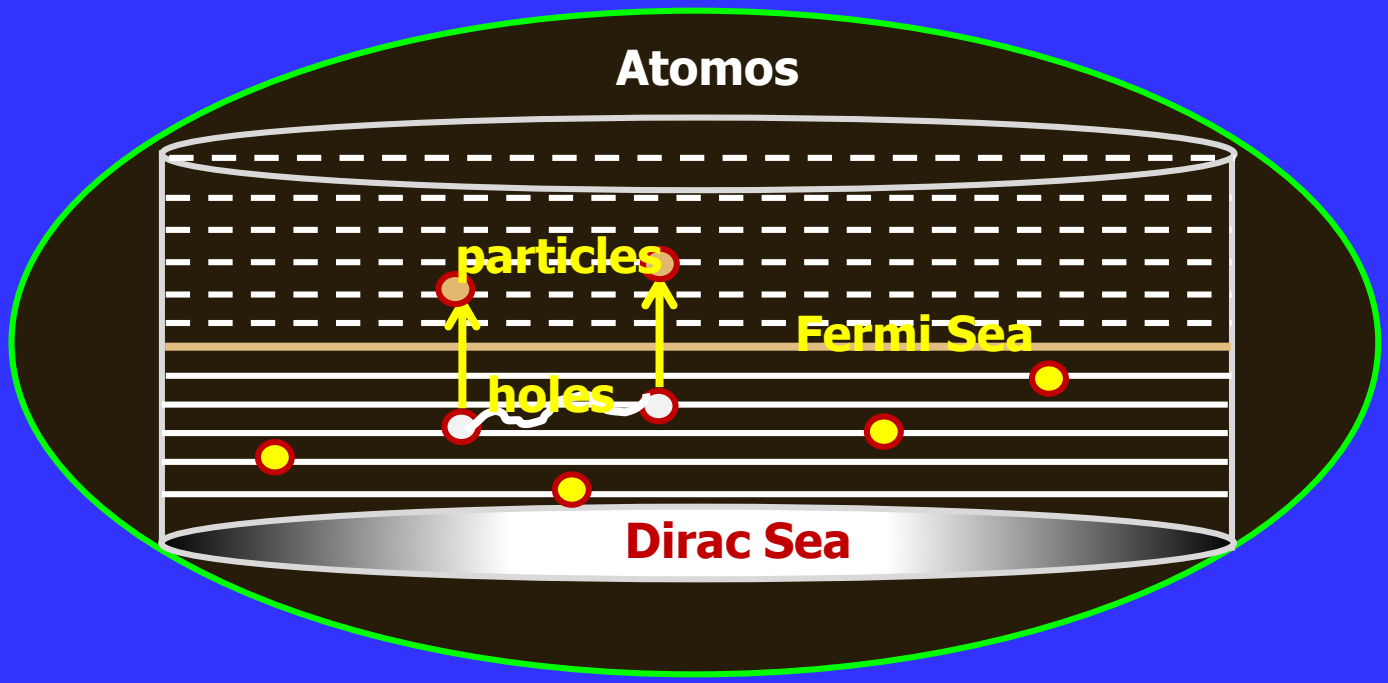
Recent Progresses and Challenges in Atomic Coupled-cluster Theory



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Demands for Accurate Many-body Methods

- To explain experimental results and understanding roles played by electron correlation effects
- Determining scattering cross-sections and to fathom plasma diagnostic processes
- Providing atomic data for astrophysics, testing QED effects, inferring nuclear momenta etc.
- Estimating systemstics for atomic clock experiments
- Investigating nuclear anapole moment through parity non-conservation (PNC) studies
- Probing Lorentz symmetry and Einstein's equivalence principle violations
- Inferring limits on CP violating parameters, finding out new bosons from istope shift calculations etc.

Outline

- General procedures to determine atomic wave functions
- Non-relativistic versus relativistic calculations
- RPA, CI and CC theories
- CI+MBPT hybrid method
- Expectation value determination using CC methods
  - (a) Finite-field approach
  - (b) Regular expectation value evaluation approach
  - (c) Normal coupled-cluster theory approach
  - (d) Analytic response CC theory approach
- Applications to Isotope Shift and EDM studies
- Summary

Hydrogen-like systems

Considering infinity nuclear mass:

Schroedinger/Dirac equation: $h|\psi\rangle = \varepsilon\,|\psi\rangle$

Non-relativistic Hamiltonian: $h = \frac{p^2}{2m_e} + V_N(r)$

Relativistic Hamiltonian: $h = c\,\vec{\alpha}\cdot\vec{p} + \beta m_e c^2 + V_N(r)$

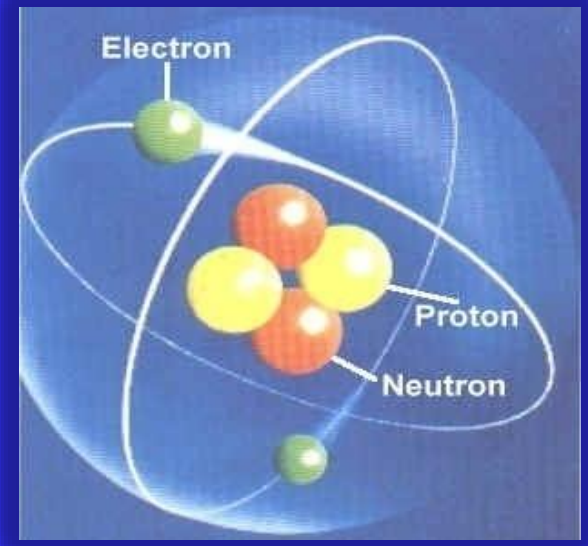
Consequences:

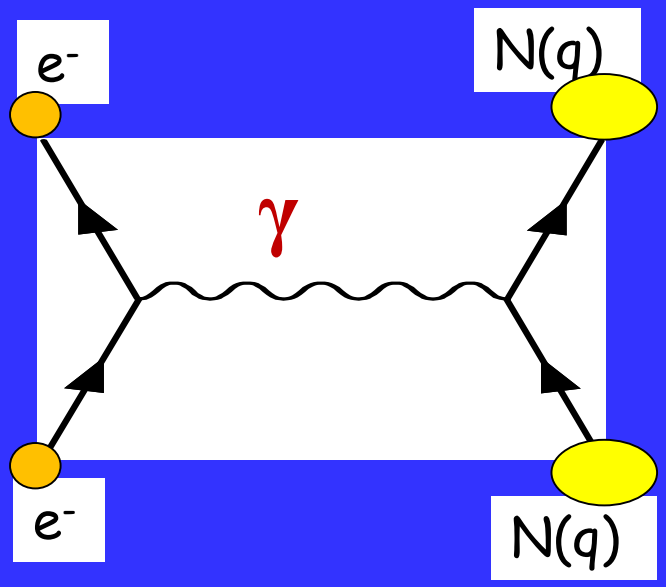
- Exact analytical solutions are obtained.
- Atomic states are described by *n, J, π* etc. quantum numbers.
- Purely spherical symmetric.

Electromagnetic interactions in an atomic system

Coulomb interaction

- Mediated by photons (*massless*; *long-range*)
- Strength scales ~ *Z*
- Gives atomic spectra (states *n, J* and *π*)
- Nucleus has electric charge, (*Ze*)





Non-relativistic Hamiltonian:

$$H = \sum_i \left[\frac{p_i^2}{2m_e} + V_N(r_i)\right] + \frac{1}{2}\sum_{i,j}\frac{1}{|\vec{r}_i - \vec{r}_j|}$$

Relativistic Hamiltonian:

$$H = \sum_i \left[c\,\vec{\alpha}_i \cdot \vec{p}_i + \beta_i m_e c^2 + V_N(r_i)\right] + \frac{1}{2}\sum_{i,j}\frac{1}{|\vec{r}_i - \vec{r}_j|}$$

Multi-electron atomic systems

Total Hamiltonian: $H = \sum_i h_i + \frac{1}{2}\sum_{i,j} g_{ij}$

Net wave function: $|\Psi\rangle = \frac{1}{\sqrt{N!}}\begin{bmatrix} |\psi_1(r_1\rangle & \cdots & |\psi_N(r_1)\rangle \\ \vdots & \ddots & \vdots \\ |\psi_1(r_N)\rangle & \cdots & |\psi_N(r_N)\rangle \end{bmatrix}$

Schroedinger/Dirac equation for single particle wave function:

$$H|\Psi\rangle = E|\Psi\rangle \qquad \text{such that } E = \sum_i \varepsilon_i$$

$$\Rightarrow \quad h_i\,|\psi_i\rangle + \frac{1}{2}\sum_j^N \left[\langle\psi_j|g_{ij}|\psi_j\rangle|\psi_i\rangle - \langle\psi_j|g_{ij}|\psi_i\rangle|\psi_j\rangle\right] = \varepsilon_i\,|\psi_i\rangle$$

Thus, it cannot be solved exactly.

Mean-field theory (DHF method)

$$H = \sum_i h_i + \frac{1}{2}\sum_{i,j} g_{ij} = \sum_i [h_i + u_i] + \left[\frac{1}{2}\sum_{i,j} g_{ij} - \sum_i u_i\right]$$

$$= \sum_i f_i + \left[\frac{1}{2}\sum_{i,j} g_{ij} - \sum_i u_i\right] = H_0 + V_{res}$$

Mean-field theory:

$$H_0|\Phi_0\rangle = E_0|\Phi_0\rangle \quad \Rightarrow \; f_i\,|\phi_i\rangle = \varepsilon_i^0\,|\phi_i\rangle \quad \text{such that} \quad E_0 = \textstyle\sum_i \varepsilon_i^0$$

In the (Dirac) Hartree – Fock approach (variational):

$$|\psi_i\rangle = |\phi_i^0\rangle + \alpha|\partial\phi_i^0\rangle \quad \text{and} \quad \varepsilon_i = \varepsilon_i^0 + \alpha\,\partial\varepsilon_i^0$$

$|\Psi(\alpha)\rangle \to |\Phi_0(\alpha = 0)\rangle$ **is obtained by**

$$\frac{\partial E(\alpha)}{\partial \alpha} = \frac{\partial\langle\Psi(\alpha)|H|\Psi(\alpha)\rangle}{\partial\alpha} = 0$$

This follows: $E_0 \geq E$

$$\Rightarrow \; h_i\,|\phi_i^0\rangle + \sum_j^N [\langle\phi_j^0|g_{ij}|\phi_j^0\rangle|\phi_i^0\rangle - \langle\phi_j^0|g_{ij}|\phi_i^0\rangle|\phi_j^0\rangle] = \varepsilon_i^0\,|\phi_i^0\rangle$$

Atomic system: Spherical symmetry

Schroedinger wave function: $|\phi_s(r)\rangle = \dfrac{R_{nl}(r)}{r} \mathrm{Y}_{l,m}(\theta,\phi)\sigma_s$

Hartree-Fock equation: $F\ C = S\ C\ \varepsilon$

$R_{nl}(r) = \sum_{i=1}^{N_l} c_{nl}^{i}\ |\zeta_i\rangle \quad \Rightarrow N_l \times N_l$ dimension matrix

Dirac wave function: $|\phi_D(r)\rangle = \dfrac{1}{r}\begin{pmatrix} P_{n\kappa}(r) & \mathrm{X}_{\kappa,m}(\theta,\phi) \\ iQ_{n\kappa}(r) & \mathrm{X}_{-\kappa,m}(\theta,\phi) \end{pmatrix}$

$P_{n\kappa}(r) = \sum_{i=1}^{N_\kappa} c_{n\kappa}^{i,L}\ |\zeta_i^L\rangle$ and $Q_{n\kappa}(r) = \sum_{i=1}^{N_\kappa} c_{n\kappa}^{i,S}\ |\zeta_i^S\rangle$

$$\Rightarrow \begin{pmatrix} F_{LL} & F_{LS} \\ F_{SL} & F_{SS} \end{pmatrix} \begin{pmatrix} C_{n\kappa}^{L} \\ C_{n\kappa}^{S} \end{pmatrix} = \begin{pmatrix} S_{LL} & 0 \\ 0 & S_{SS} \end{pmatrix} \begin{pmatrix} C_{n\kappa}^{L} \\ C_{n\kappa}^{S} \end{pmatrix} \varepsilon$$

$\Rightarrow 2N_\kappa \times 2N_\kappa$ dimension matrix

Bloch's prescription

According to the Bloch's prescription, the Fock space is divided into model (P) and orthogonal (Q) space.

$$H = H_0 + \lambda V_{res} \qquad |\Psi\rangle = \Omega \; | \Phi_0\rangle$$

$$P = |\Phi_0\rangle\langle\Phi_0| \qquad \text{and} \qquad Q = 1 - P$$

Fock space of H_0

In perturbation approach:

$$\Omega = \Omega^{(0)} + \lambda\Omega^{(1)} + \lambda^2\Omega^{(2)} + \cdots = \sum_n \lambda^n \Omega^{(n)} \quad \text{with} \quad \Omega^{(0)} = 1$$
$$E = E^{(0)} + \lambda E^{(1)} + \lambda^2 E^{(2)} + \cdots = \sum_n \lambda^n E^{(n)}$$

Amplitude solving equation:

$$\left[\Omega^{(k)}, H_0\right] P = QV\,\Omega^{(k-1)} P - \sum_{m=1}^{(k-m)} PV_{res}\,\Omega^{(k-1)}\,P$$

Energy equation: $E^{(n)} = PV_{res}\,\Omega^{(n-1)} P$

In the presence of external perturbation

In this case: $H = H_{at} + \lambda_2 V_{int} = H_0 + \lambda_1 V_{res} + \lambda_2 V_{int}$

It can be approximated as

$$|\Psi\rangle = |\Psi^{(0)}\rangle + \lambda_2 |\Psi^{(1)}\rangle + \lambda_2^2 |\Psi^{(2)}\rangle + \cdots$$
$$= \left|\Phi_0^{(0,0)}\right\rangle + \lambda_1 \left|\Phi_0^{(1,0)}\right\rangle + \lambda_2 \left|\Phi_0^{(0,1)}\right\rangle + \lambda_1\lambda_2 \left|\Phi_0^{(1,1)}\right\rangle + \cdots$$

$$E = E^{(0)} + \lambda_2 E^{(1)} + \lambda_2^2 E^{(2)} + \cdots$$
$$= E_0^{(0,0)} + \lambda_1 E_0^{(1,0)} + \lambda_2 E_0^{(0,1)} + \lambda_1\lambda_2 E_0^{(1,1)} + \cdots$$

In perturbation:

$$\Omega = \Omega^{(0,0)} + \lambda_1 \Omega^{(1,0)} + \lambda_2\, \Omega^{(0,1)} + \lambda_1\lambda_2 \Omega^{(1,1)} + \cdots = \sum_{n,m} \Omega^{(n,m)}$$

with $\Omega^{(0,0)} = 1$, $\Omega^{(1,0)} = V_{res}$ and $\Omega^{(0,1)} = V_{int}$

Amplitude equation:

$$\left[\Omega^{(\beta,\alpha)}, H_0\right] P = Q V_{res} \Omega^{(\beta-1,\delta)} P + Q\, V_{int} \Omega^{(\beta,\delta-1)} P$$
$$- \sum_{m=1}^{\beta-1} \sum_{l=1}^{\delta-1} \left(\Omega^{(\beta-m,\delta-1)} P V_{res} \Omega^{(m-1,l)} P - \Omega^{(\beta-m,\delta-l)} P V_{int} \Omega^{(m,l-1)} P \right)$$

All-order in V_{res}; one-order in V_{int}

For: $\boldsymbol{H = H_0 + \lambda_1 V_{res} + \lambda_2 V_{int}}$

Wave functions can be approximated as

$$\left|\Psi^{(0)}\right\rangle = \left|\Phi_0^{(0,0)}\right\rangle + \lambda_1 \left|\Phi_0^{(1,0)}\right\rangle + \lambda_1^2 \left|\Phi_0^{(2,0)}\right\rangle + \cdots + \lambda_1^\infty \left|\Phi_0^{(\infty,0)}\right\rangle$$

$$\left|\Psi^{(1)}\right\rangle = \left|\Phi_0^{(0,1)}\right\rangle + \lambda_1 \left|\Phi_0^{(1,1)}\right\rangle + \lambda_1^2 \left|\Phi_0^{(2,1)}\right\rangle + \cdots + \lambda_1^\infty \left|\Phi_0^{(\infty,1)}\right\rangle$$

Energies are obtained by

$$\left|E^{(0)}\right\rangle = \left|E_0^{(0,0)}\right\rangle + \lambda_1 \left|E_0^{(1,0)}\right\rangle + \lambda_1^2 \left|E_0^{(2,0)}\right\rangle + \cdots + \lambda_1^\infty \left|E_0^{(\infty,0)}\right\rangle$$

$$\left|E^{(1)}\right\rangle = \left|E_0^{(0,1)}\right\rangle + \lambda_1 \left|E_0^{(1,1)}\right\rangle + \lambda_1^2 \left|E_0^{(2,1)}\right\rangle + \cdots + \lambda_1^\infty \left|E_0^{(\infty,1)}\right\rangle$$

All-order many-body methods

Configuration interaction (CI) method:

$$\left|\Psi_n^{(0)}\right\rangle = C_0^{(\infty)}\left|\Phi_n^{(0)}\right\rangle + C_I^{(\infty)}\left|\Phi_I^{(0)}\right\rangle + C_{II}^{(\infty)}\left|\Phi_{II}^{(0)}\right\rangle + \cdots$$

$$\left|\Psi_n^{(1)}\right\rangle = C_0^{(\infty,1)}\left|\Phi_n^{(0)}\right\rangle + C_I^{(\infty,1)}\left|\Phi_I^{(0)}\right\rangle + C_{II}^{(\infty,1)}\left|\Phi_{II}^{(0)}\right\rangle + \cdots$$

Coupled-cluster (CC) method:

$$\left|\Psi_n^{(0)}\right\rangle = [1+T_I^{(0)} + T_{II}^{(0)} + \tfrac{1}{2}\,T_I^{(0)^2} + \cdots]\left|\Phi_n^{(0)}\right\rangle = e^{[T_I^{(0)}+T_{II}^{(0)}+\cdots]}\left|\Phi_n^{(0)}\right\rangle$$
$$= e^{T^{(0)}}\left|\Phi_n^{(0)}\right\rangle$$

$$T \to T^{(0)} + \lambda T^{(1)} \qquad \Rightarrow \left|\Psi_n^{(1)}\right\rangle = e^{T^{(0)}}\left(1+T^{(1)}\right)\left|\Phi_n^{(0)}\right\rangle$$

Random phase approximation (RPA):

$$\left|\Psi_{\mathrm{n}}^{(0)}\right\rangle \to |\Phi_0^{(0)}\rangle \quad \text{and} \quad \left|\Psi_{\mathrm{n}}^{(1)}\right\rangle \to \Omega_{I,CP}^{(\infty,1)}\left|\Phi_n^{(0)}\right\rangle = \Omega_{RPA}^{(1)}|\Phi_0\rangle$$

Approximated CI vs. CC methods

Configuration interaction (CI) method:

$$|\Psi_n\rangle = C_0|\Phi_n\rangle + C_I\,|\Phi_I\rangle + C_{II}\,|\Phi_{II}\rangle + \cdots + C_N\,|\Phi_N\rangle$$

Coupled-cluster (CC) method:

$$|\Psi_n\rangle = e^{T_I+T_{II}+\cdots+T_N}\,|\Phi_n\rangle = e^{T}|\Phi_n\rangle$$

Comparison between both:

$$C_0 \rightarrow 1 \qquad C_2 \rightarrow T_2 + \frac{1}{2}T_1^2$$

$$C_1 \rightarrow T_1 \qquad C_3 \rightarrow T_3 + T_1T_2 + \frac{1}{3!}T_1^3$$

so on …

Due to exponential ansatz, CCSD captures more correlation effects than CISD approximation.

Size-extensivity problem with truncated CI

$$|\Psi_0\rangle = C_0|\Phi_0\rangle + C_I\,|\Phi_I\rangle + C_{II}\,|\Phi_{II}\rangle + \cdots$$

$$H_0|\Phi_0\rangle = E_0^{(0)}|\Phi_0\rangle$$

$$H_0|\Phi_K\rangle = E_K^{(0)}|\Phi_K\rangle$$

$$\Rightarrow E_K^{(0)} = E_0^{(0)} + x - \epsilon_0^{(0)}$$

$$\langle\phi_0|h|\phi_0\rangle = \epsilon_0^{(0)}$$
$$\langle\phi_0|h|\phi_k\rangle = y$$
$$\langle\phi_k|h|\phi_k\rangle = x$$

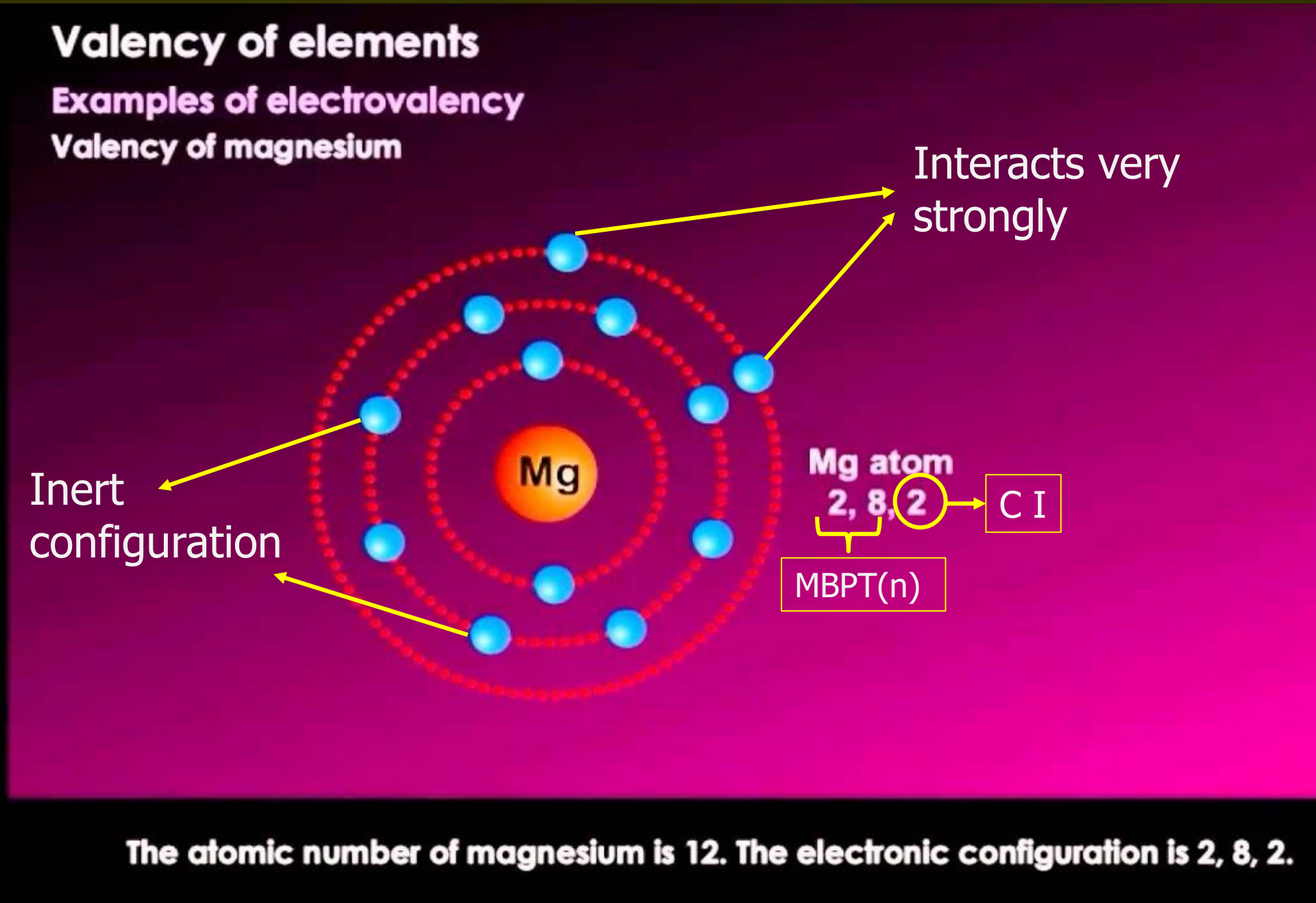
$$\sum_k \langle\Phi_K|[H|\Psi_0\rangle = E|\Psi_0\rangle]$$

$$\begin{bmatrix} E_0^{(0)} & y & \cdots & y \\ y^* & E_0^{(0)} + x - \epsilon_0^{(0)} & \cdots & 0 \\ \vdots & & \ddots & \vdots \end{bmatrix} \begin{pmatrix} C_0 \\ C_I \\ \vdots \end{pmatrix} = E_0 \begin{pmatrix} C_0 \\ C_I \\ \vdots \end{pmatrix}$$

$$\Rightarrow \Delta E = E_0 - E_0^{(0)} = \frac{x-\epsilon_0^{(0)}}{2} \pm \sqrt{\left(\frac{x-\epsilon_0^{(0)}}{2}\right)^2 + N|y|^2}$$

For $N \to \infty, \Delta E \propto |y|^2\sqrt{N}$

CI+MBPT method



Energy and wave function in (R)CC theory

Energy expression: $E_n = \langle H \rangle = \dfrac{\langle \Psi_n | H | \Psi_n \rangle}{\langle \Psi_n | \Psi_n \rangle}$

$$E_n = \frac{\langle \Phi_n | e^{T_n^+} H e^{T_n} | \Phi_n \rangle}{\langle \Phi_n | e^{T_n^+} e^{T_n} | \Phi_n \rangle} = \frac{\langle \Phi_n | e^{T_n^+} e^{T_n} e^{-T_n} H e^{T_n} | \Phi_n \rangle}{\langle \Phi_n | e^{T_n^+} e^{T_n} | \Phi_n \rangle}$$

$$= \frac{\Sigma_K \langle \Phi_n | e^{T_n^+} e^{T_n} | \Phi_K \rangle \langle \Phi_K | e^{-T_n} H e^{T_n} | \Phi_n \rangle}{\langle \Phi_n | e^{T_n^+} e^{T_n} | \Phi_n \rangle}$$

$$= \langle \Phi_n | e^{-T_n} H e^{T_n} | \Phi_n \rangle = \langle \Phi_n | (H e^{T_n})_c | \Phi_n \rangle$$

Excitation amplitudes: $\langle \Phi_K | (H e^{T_n})_c | \Phi_n \rangle = 0$

It gets naturally terminated. Its appears in the form **A*X=B**; Jacobi iterative method is used.

Expectation value evaluation in (R)CC theory

Property: $$\langle O \rangle = \frac{\langle \Psi_n | O | \Psi_n \rangle}{\langle \Psi_n | \Psi_n \rangle} = \frac{\langle \Phi_n | e^{T_n^+} O e^{T_n} | \Phi_n \rangle}{\langle \Phi_n | e^{T_n^+} e^{T_n} | \Phi_n \rangle}$$

- Possesses two non-terminating series.
- Unmanageable with two-body operators like SMS operator.
- It does not satisfy the Hellmann-Feynman theorem.
- But any property can be evaluated.

Hellmann-Feynman Theorem:

$$\frac{\partial E_\lambda}{\partial \lambda} = E_\lambda \frac{\partial}{\partial \lambda} \langle \Psi_\lambda | \Psi_\lambda \rangle + \left\langle \Psi_\lambda \middle| \frac{\partial H_\lambda}{\partial \lambda} \middle| \Psi_\lambda \right\rangle = \left\langle \Psi_\lambda \middle| \frac{\partial H_\lambda}{\partial \lambda} \middle| \Psi_\lambda \right\rangle$$

$$\Rightarrow \frac{\partial}{\partial \lambda} \langle \Psi_\lambda | \Psi_\lambda \rangle = 0 \quad \textbf{and} \quad \langle O \rangle \equiv E^{(1)} \leftrightarrow H = H_{at} + \lambda O$$

⇒ Energy and property evaluating diagrams should be same.

Finite-field (FF) approach

New Hamiltonian: $H_\lambda = H_{at} + \lambda O$

$$E_\lambda = E_{at}^{(0)} + \lambda E_{at}^{(1)} + \lambda^2 E_{at}^{(2)} + \cdots$$

$$\langle O \rangle \equiv E_{at}^{(1)} \approx \left. \frac{\partial E_\lambda}{\partial \lambda} \right|_{\lambda \to 0}$$

$$\begin{pmatrix} Note: \lambda^2 \ terms \\ may \ not \ be \ small. \end{pmatrix}$$

- All the terms get naturally terminated.
- Not much additional computational costs required.
- Satisfies the Hellmann-Feynman theorem.
- Properties described by scalar operators can only be evaluated.
- Neglects $\mathfrak{O}(\lambda^2)$ contributions, which may not be small.
- Choice of λ depends on properties of interest ($\boldsymbol{F}$, $\boldsymbol{K}^{NMS}$, and $\boldsymbol{K}^{SMS}$ cannot be calculated accurately by considering same λ).

Normal or Extended (R)CC method

In NCC: $|\Psi_n\rangle = e^{T_n}|\Phi_n\rangle$ and $\langle\tilde{\Psi}_n| = \langle\Phi_n|(1+\tilde{T}_n)\,e^{-T_n}$

In ECC: $|\Psi_n\rangle = e^{T_n}|\Phi_n\rangle$ and $\langle\tilde{\Psi}_n| = \langle\Phi_n|e^{\tilde{T}_n}e^{-T_n}$

where $\tilde{T}_n$ is a de-excitation operator similar to T_n^+.

This follows: $\langle\tilde{\Psi}_n|\Psi_n\rangle = \langle\Phi_n|e^{\tilde{T}_n}e^{-T_n}e^{T_n}|\Phi_n\rangle = 1.$

It means $\langle\tilde{\Psi}_n| = \dfrac{\langle\Psi_n|}{\langle\Psi_n|\Psi_n\rangle} = \dfrac{\langle\Phi_n|e^{T_n^+}}{\langle\Phi_n|e^{T_n^+}e^{T_n}|\Phi_n\rangle}$

$$\Rightarrow \langle\Phi_n|e^{\tilde{T}_n} = \frac{\langle\Phi_n|e^{T_n^+}e^{T_n}}{\langle\Phi_n|e^{T_n^+}e^{T_n}|\Phi_n\rangle}$$

It implies T_n and $\tilde{T}_n$ are dependent, but they are treated as independent (variational) parameters in the (R)NCCM.

Energy and property calculations

Energy: $H|\Psi_n\rangle = E_n|\Psi_n\rangle$ and $\langle\tilde{\Psi}_n|H = \langle\Phi_n|E_n$

$$E_n = \langle\tilde{\Psi}_n|H|\Psi_n\rangle = \langle\Phi_n|(He^{T_n})_c|\Phi_n\rangle + \langle\Phi_n|e^{\tilde{T}_n}(He^{T_n})_c|\Phi_n\rangle$$

0

Amplitude:

$$\langle\Phi_n|e^{\tilde{T}_n}(He^{T_n})_c|\Phi_K\rangle = -\langle\Phi_n|e^{\tilde{T}_n}(He^{T_n})_c|\Phi_K\rangle$$

Property:

$$\langle O\rangle = \langle\tilde{\Psi}_n|O|\Psi_n\rangle = \langle\Phi_n|(Oe^{T_n})_c|\Phi_n\rangle + \langle\Phi_n|e^{\tilde{T}_n}(Oe^{T_n})_c|\Phi_n\rangle$$

- All the terms get naturally terminated.
- Satisfies the Hellmann-Feynman theorem.
- Any properties can be evaluated.
- Additional operators are introduced; computationally expensive.

Analytic Response (R)CC method

In the AR RCC method, we express

$$H_\lambda = H_{at} + \lambda O \quad \text{and} \quad |\Psi_n\rangle \simeq |\Psi_n^{(0)}\rangle + \lambda\,|\Psi_n^{(1)}\rangle$$

First-order eqn.: $(H_{at} - E_n^{(0)})|\Psi_n^{(1)}\rangle = (E_n^{(1)} - O)\,|\Psi_n^{(0)}\rangle$

$$|\Psi_n\rangle = e^T|\Phi_n\rangle = e^{T_n^{(0)}+\lambda T_n^{(1)}}|\Phi_n\rangle$$

$$\Rightarrow \left|\Psi_n^{(0)}\right\rangle = \; e^{T_n^{(0)}}\,|\Phi_n\rangle$$

$$\text{and} \quad \left|\Psi_n^{(1)}\right\rangle = \; e^{T_n^{(0)}}\left(1 + T_n^{(1)}\right)|\Phi_n\rangle$$

It yields that:

$$\langle O\rangle \equiv E_n^{(1)} = \langle\Phi_n\left|(H_{at}e^{T_n^{(0)}}T_n^{(1)})_c + \left(Oe^{T_n^{(0)}}\right)_c\right|\Phi_n\rangle$$

Advantages of AR RCC method

- All the terms are terminated.
- It satisfies the Hellmann-Feynman theorem (as it is derived from energy expression).
- Any properties can be evaluated.
- Free from choice of any perturbative parameter.
- Computational efforts are less than NCC method.

First development in atomic physics!

Equation-of-motion CC method

Ground state: $|\Psi_0\rangle = e^T|\Phi_0\rangle$

Excited state with definite J and π:

$$|\Psi_K(J,\pi)\rangle = R_K(J,\pi)|\Psi_0\rangle = R_K(J,\pi)e^T|\Phi_0\rangle$$

Here $R_K(J,\pi) = r_0 + R_1(J,\pi) + R_2(J,\pi) + \cdots$

Equation of motion: $H|\Psi_K(J,\pi)\rangle = E_K|\Psi_K(J,\pi)\rangle$

$$\Rightarrow \left(He^T\right)_c R_K(J,\pi)|\Phi_0\rangle = (E_K - E_0)R_K(J,\pi)|\Phi_0\rangle$$

And, $\langle\widetilde{\Psi}_K(J,\pi)| = \langle\widetilde{\Psi}_0|L_K(J,\pi)$ with $L_K(J,\pi) = l_0 + L_1(J,\pi) + \cdots$

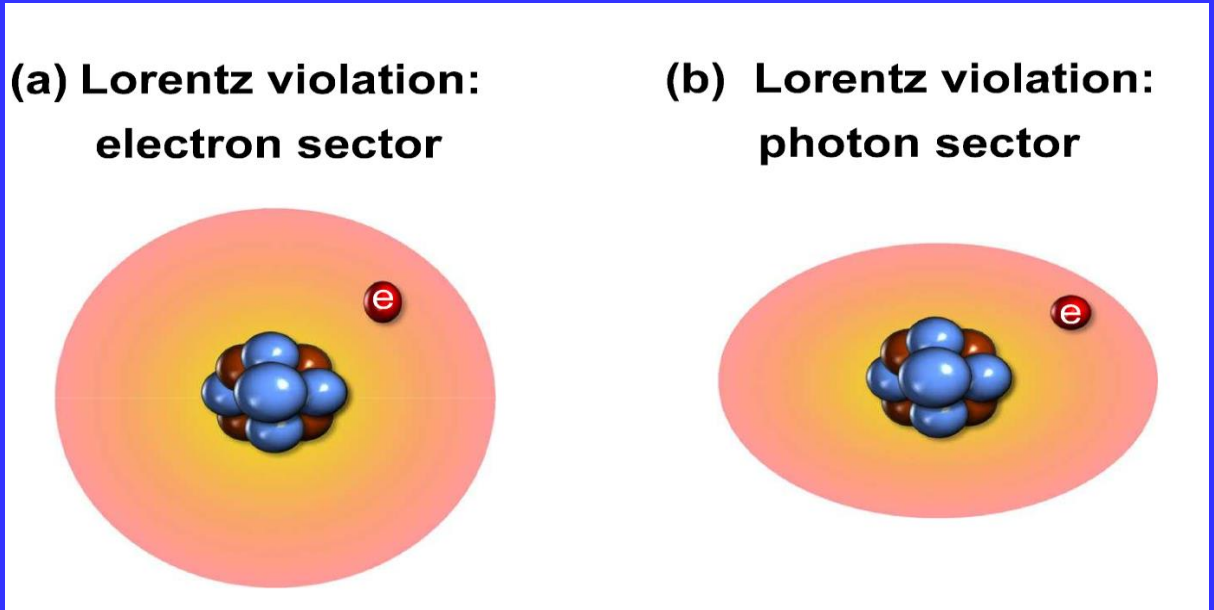
Amplitude solving equations for R_K (similar for L_K):

$$\left[\begin{pmatrix} P(He^T)_cP & P(He^T)_cQ \\ Q(He^T)_cP & Q(He^T)_cQ \end{pmatrix}\begin{pmatrix} r_0P \\ QR_KP \end{pmatrix}\right]_c = \Delta E_K \begin{pmatrix} r_0P \\ QR_KP \end{pmatrix}.$$

Probing Lorentz symmetry violation

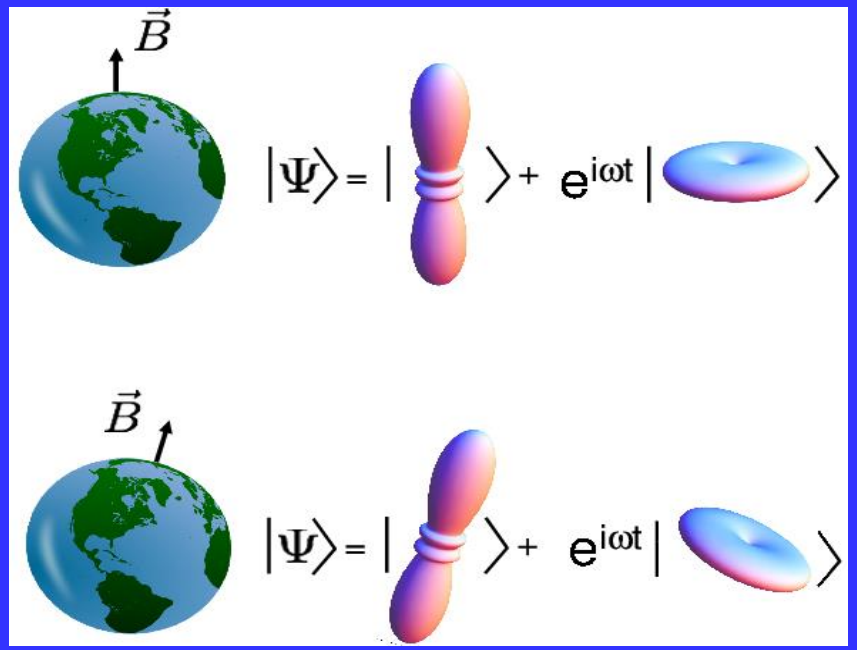
Lorentz symmetry: Measurements are independent of frame of references moving with constant velocity (inertial frame). Lorentz invariance and Einstein equivalence principle are the foundations of the general relativity theory.

Modern theories that are attempting to unify gravity with the standard model (SM) assert that Lorentz symmetry is valid only at large length scales and may violate at short length scales due to physics beyond SM.



Experiment in Ca^+

Michelson–Morley type experiment in an atomic system with electron-nucleus bonds as interferometer arms and lights (photon clouds) as reference. [Nature 517, 592 (2015)]



By changing the direction of magnetic field with respect to the Sun, interference between the $m_j = \pm 1/2$ and $m_j = \pm 5/2$ levels of $3d_{5/2}$ state in Ca^+ were created.

$$H_{int}^{Lnz} = -\frac{p^2}{2}\left(C_0^{(0)} - \frac{2U}{3c^2}c_{00}\right) - \frac{1}{6}C_0^{(2)}T_0^{(2)}$$ **Here *U* is the Newtonian gravitational potential, $C_0^{(0/2)}$ and c_{00} are Lorentz symmetry violating parameters respectively and $T_0^{(2)} = p^2 - 3p_z^2$.**

Roles of atomic calculations

LETTER

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Michelson–Morley analogue for electrons using trapped ions to test Lorentz symmetry

T. Pruttivarasin[1,2], M. Ramm[1], S. G. Porsev[3,4], I. I. Tupitsyn[5], M. S. Safronova[3,6], M. A. Hohensee[1,7] & H. Häffner[1]

Extended Data Table 1 | Lowest-order DF, DF+RPA, CI+SD and all-order results for the $\langle 3d\,^2D_J|p^2|3d\,^2D_J\rangle$ and $\langle 3d\,^2D_J||T^{(2)}||3d\,^2D_J\rangle$ matrix elements in Ca^+ in atomic units

Matrix element	DF(FC)	DF	RPA	CI+SD	All-order	VT	Final
$\langle 3d\,^2D_{3/2}\|p^2\|3d\,^2D_{3/2}\rangle$	3.05	0.67	0.66	0.73	0.83	0.748	0.75(9)
$\langle 3d\,^2D_{5/2}\|p^2\|3d\,^2D_{5/2}\rangle$	3.04	0.66	0.66	0.73	0.83	0.748	0.75(9)
$\langle 3d\,^2D_{3/2}\|\|T^{(2)}\|\|3d\,^2D_{3/2}\rangle$	5.45	6.22	5.72	6.89	7.09		7.09(12)
$\langle 3d\,^2D_{5/2}\|\|T^{(2)}\|\|3d\,^2D_{5/2}\rangle$	7.12	8.11	7.47	8.98	9.25		9.25(15)

The virial theorem values are listed in column VT. The values in columns DF(FC) and DF are lowest-order Dirac–Fock values calculated with and without the frozen-core approximation.

With linear terms from RCC method.

Expectation values using RCC methods

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Rapid Communications

High-precision determination of Lorentz-symmetry-violating parameters in Ca^+

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	$\langle \lvert p^2 \rvert \rangle$		$\langle \lvert\lvert T^{(2)} \rvert\rvert \rangle$		Reference
Method	$3D_{3/2}$	$3D_{5/2}$	$3D_{3/2}$	$3D_{5/2}$	
DHF	3.050	3.039	5.454	7.116	This work
	3.05	3.04	5.45	7.12	[12]
RMBPT(2)	1.279	0.794	7.052	9.092	This work
RPA	0.66	0.66	5.72	7.47	[12]
CI+SD	0.73	0.73	6.89	8.98	[12]
RLCCSD	−0.037	−0.887	7.551	9.682	This work
All-order	0.83	0.83	7.09	9.25	[12]
$RCCSD^2$	0.421	−0.298	7.295	9.375	This work
RCCSD	0.392	−0.311	6.956	8.878	This work
RCCSD(T)	0.389	−0.318	6.975	8.901	This work
RCCSDpT	0.244	−0.412	6.965	8.875	This work
RCCSDTv	0.065	−0.630	6.953	8.867	This work
RCCSDT	0.011	−0.787	6.961	8.879	This work
		Relativistic corrections			
+Breit	0.012	−0.786	6.966	8.889	This work
+QED	0.012	−0.786	6.967	8.890	This work
Final	Unsure	Unsure	6.97(5)	8.89(7)	This work
	0.75(9)	0.75(9)	7.09(12)	9.25(15)	[12]
VT	0.748	0.748			[22]

FF vs. AR approaches

	FF approach		AG approach	
Method	$3D_{3/2}$	$3D_{5/2}$	$3D_{3/2}$	$3D_{5/2}$
DHF	0.646	0.645	3.050	3.039
RMBPT(2)	0.728	0.726	2.142	1.889
RLCCSD	0.741	0.739	0.591	0.589
RCCSD	0.725	0.723	0.785	0.779
RCCSD(T)	0.718	0.716	0.750	0.745
RCCSDTv	0.240	−0.009	0.677	0.673
RCCSDT	0.203	−0.035	0.658	0.656
	Relativistic corrections			
+Breit	0.205	−0.033	0.660	0.658
+QED	0.205	−0.033	0.661	0.658
Final	Unsure	Unsure	0.660(5)	0.660(5)

$$\delta E_{3D_{3/2}} = \left[-2.17(2)\Gamma_L + \left(2.13(2) - 1.71(1)M_J^2\right)C_0^{(2)}\right], \quad \text{with } \Gamma_L = C_0^{(0)} - \tfrac{2U}{3c^2}c_{00}$$

$$\delta E_{3D_{5/2}} = \left[-2.17(2)\Gamma_L + \left(2.08(2) - 0.713(6)M_J^2\right)C_0^{(2)}\right],$$

$$\delta E_{3D_{5/2}}(M_J = 5/2) - \delta E_{3D_{5/2}}(M_J = 1/2)$$

$$= -4.28(4)C_0^{(2)} \times 10^{15}\ \text{Hz}.$$

Combining with experimental result:

$$C_0^{(2)} \simeq 2.6 \times 10^{-18},$$

Different components of Isotope Shift

Isotope shift (IS) of a state in an atom:

$$\delta E_i^{AA'} = F_i \delta\langle r_N^2 \rangle_{AA'} + (K_i^{NMS} + K_i^{SMS}) \frac{(M_A - M_{A'})}{M_A M_{A'}}$$

F_i is the field-shift constant; $\delta\langle r_N^2 \rangle$ is the change in nuclear radii. K_i^{NMS} and K_i^{SMS} are the normal and specific mass-shift constants.

$$\boldsymbol{F_i = \left\langle \frac{\delta V_{nuc}(r)}{\delta\langle r_N^2 \rangle} \right\rangle}$$

$$\boldsymbol{K_i^{NMS} = \frac{1}{2}\left\langle p^2 - \frac{\alpha_e Z}{r}\left(\alpha \cdot p + (\alpha \cdot C^1)^2\right)\right\rangle}$$

Comp. Challenging

$$\boldsymbol{K_i^{SMS} = \frac{1}{2}\left\langle \sum_{kl} p_k \cdot p_l - \frac{\alpha_e Z}{r_k}\left(\alpha_k \cdot p_l + (\alpha_k \cdot C_k^1)(\alpha_l \cdot C_l^1)\right)\right\rangle}$$

Another approach for Field shift constant

Energy of an atomic state: $E_n^A(R_N) = \langle \Psi_n | H(R_N) | \Psi_n \rangle$

Hamiltonian: $$\boldsymbol{H(R_N) = \sum_i [K.E. + V_N(r_i, R_N)] + \frac{1}{2}\sum_{i,j} \frac{1}{|\vec{r}_i - \vec{r}_j|}}$$

$$R_N \equiv f\left(\langle \delta r_N^2 \rangle\right) \Rightarrow \quad E_n^{A'}(R_N + \delta R_N) - E_n^A(R_N) = g\left(\langle \delta r_N^2 \rangle^{AA'}\right)$$

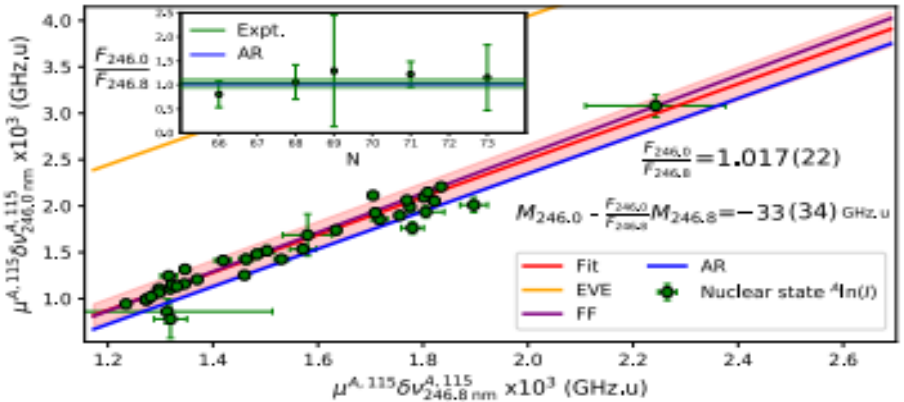
Thus,

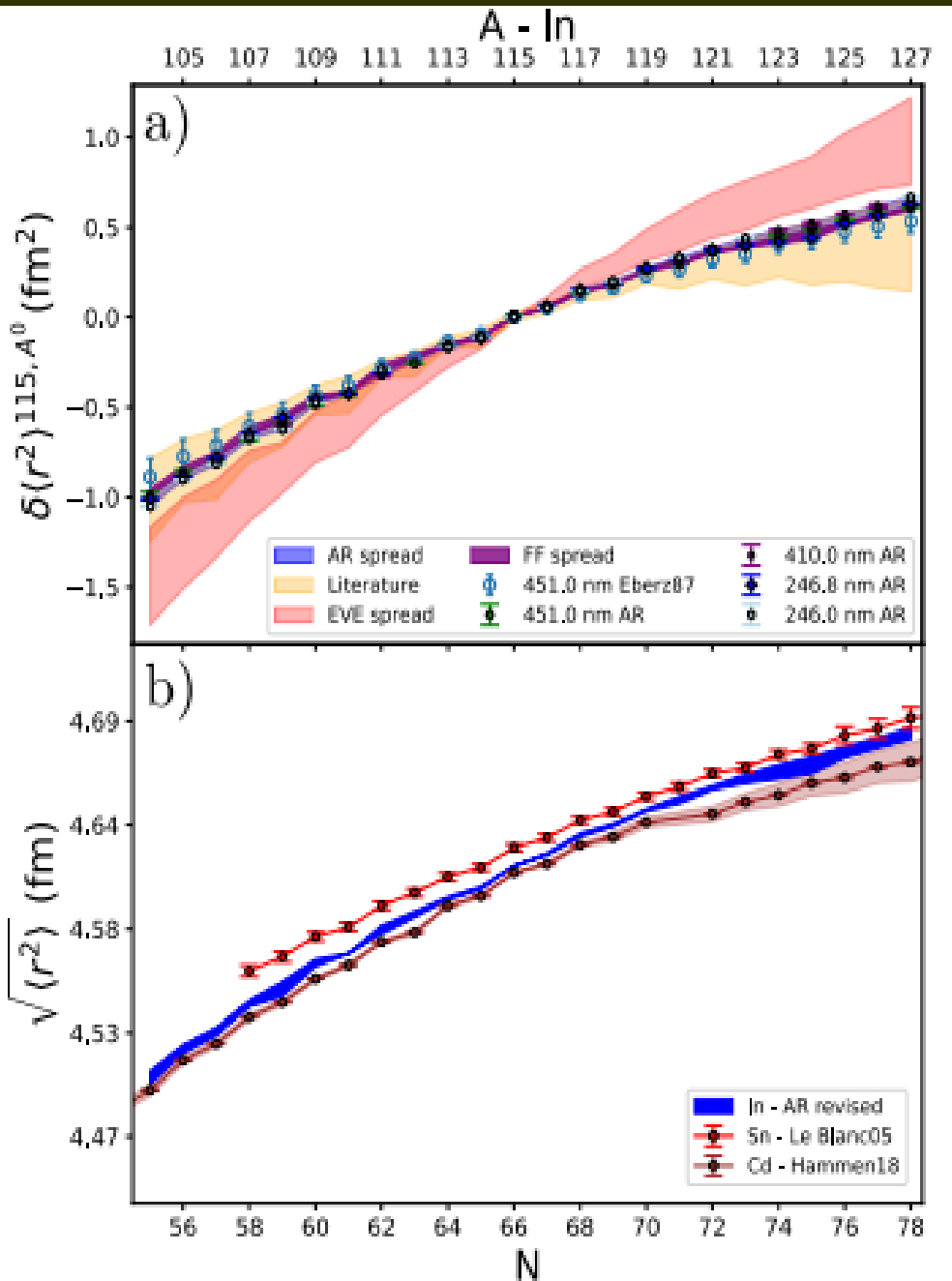
$$E_n^{AA'}(R_N + \delta R_N) = E_n^{AA'}(R_N) + F_n \langle \delta r_N^2 \rangle^{AA'} + \mathfrak{O}\left(\langle \delta r_N^2 \rangle^{AA'}\right)^2$$

CCSD results of indium atom

Sahoo et al, under review.

Method	$5P_{1/2}$	$5P_{3/2}$	$6S_{1/2}$	$7S_{1/2}$	$8S_{1/2}$	$9S_{1/2}$
			F (GHz/fm^2)			
FF	1.544	1.491	-0.437	-0.155	-0.069	-0.033
EVE	1.275	1.299	-0.408	-0.135	-0.061	-0.033
AR	1.435	1.442	-0.412	-0.149	-0.064	-0.035
			K^{NMS} (GHz.u)			
FF	749	711	364	170	98	63
EVE	1340	375	458	201	113	71
AR	872	805	362	176	100	64
Energy†	768	731	367	171	99	65
			K^{SMS} (GHz.u)			
FF	-470	-403	119	38	17	9
EVE	-1048	-899	136	42	18	10
AR	-614	-488	117	39	16	9
Exp.*	-536(122)	-507(111)	169(51)	55(42)	24(80)	-13(66)
			$\delta E^{113,115}$ (MHz)			
Exp.	277(10)	272(6)	17(6)	12(6)	9(12)	2(10)





α_0^d value of Cd atom

Sahoo & Yu, PRA **98**, 012513 (2018)

Method	Our work		Others	
	Finite-Field	Perturb.	Finite-Field	Perturb.
DHF	63.657	49.612	62.78; 63.37	49.647
MBPT(2)	37.288	50.746	39.14; 38.52	
MBPT(3)		37.345	45.97; 45.86	35.728
MBPT(4)			45.06; 47.10	
RPA		63.685		
PRCC				49.24
CCSD	48.073	45.494	48.43; 48.09	44.63
NCCSD		44.804		45.898
CCSD(T)		46.289	46.80; 46.25	
NCCSD(T)		45.603		
CCSDT	45.852			
CCSDTQ	46.015			

Recommended 46.02(50)

Experiment 49.65(1.65)

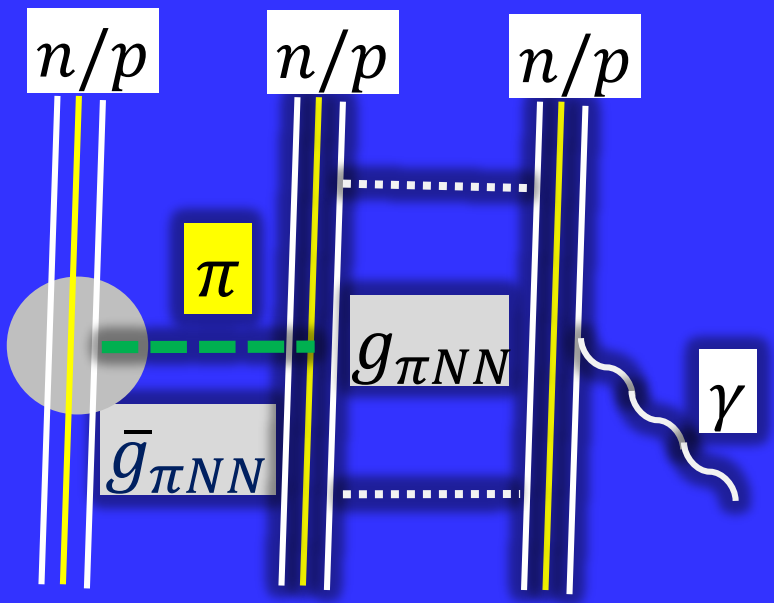
Nuclear EDM due to pion exchange

$$H_{int}(r) = e\vec{r} \cdot \left[\int_0^\infty d^3r' \left(\frac{\langle \vec{r}' \rangle}{Zr^3} - \frac{\vec{r}'}{r^3} + \frac{\vec{r}'}{\vec{r}'^3} \right) \rho_n(r') \right] = \frac{\vec{S} \cdot \vec{r}}{B} \rho_n(r)$$

$$S = g_{\pi NN} \left[a_0 \bar{g}^{(0)}_{\pi NN} + a_1 \bar{g}^{(1)}_{\pi NN} + a_2 \bar{g}^{(2)}_{\pi NN} \right]$$

$$\approx \left[b_1 \, d_n + b_2 d_p \right]$$

where parity conserving parameter $g_{\pi NN} \approx 13.5$ and a_0, a_1, a_2, b_1 and b_2 are determined using Skyrme interactions.



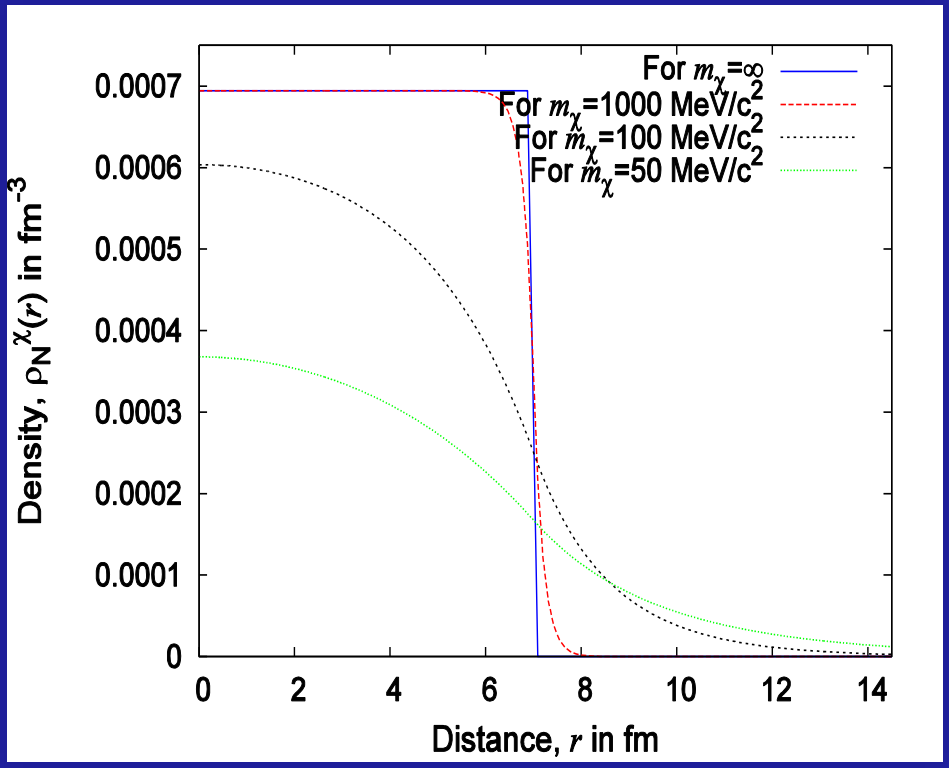
$$\bar{g}^{(1)}_{\pi NN} = 2 \times 10^{-12} (\tilde{d}_u - \tilde{d}_d)$$

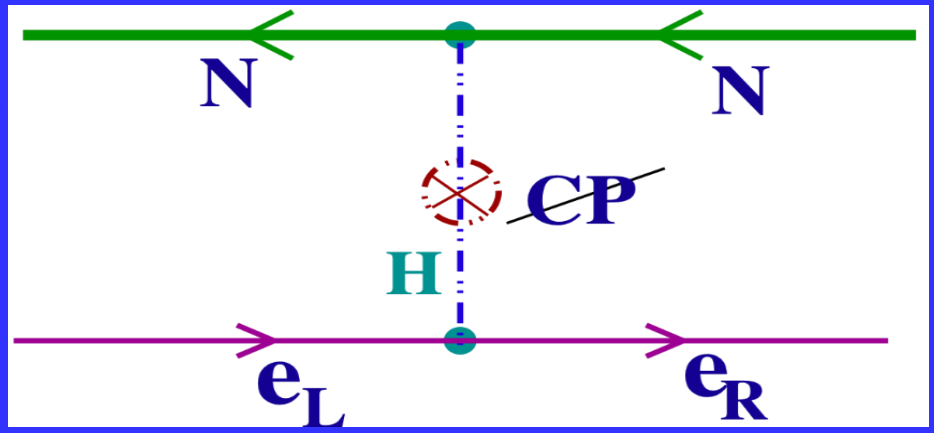
$$\bar{g}^{(0)}_{\pi NN} \approx -0.018(7)\bar{\theta} \approx -1.02(\tilde{d}_u + \tilde{d}_d)$$

Tensor-pseudotensor (T-PT) interaction in atoms

$$H_{EDM}^{e-N}(r) = \frac{i\,G_F}{\sqrt{2}} \sum_{e,N} C_T^{e-N} \left[\bar{\Psi}_N(r')\sigma_{\mu\nu}\Psi_N(r')\right] V_\chi(r,r') \left[\bar{\Psi}_e(r)\gamma^5\Psi_e(r)\right]$$

$$= \sqrt{2}\, i\, G_F C_T \sum_e \rho_N^\chi(r_e) \quad \vec{I}_N \cdot \vec{\gamma}_e$$





$$V_\chi(r,r') = \frac{e^{-m_\chi c|r-r'|}}{4\pi\,|r-r'|}$$

Results for ^{199}Hg EDM

Method	$R^{T\text{-}PT}$	R^{NSM}	α_0^d
DHF	-2.39	-1.20	40.95
MBPT(2)	-4.48	-2.30	34.18
MBPT(3)	-3.33	-1.72	22.98
RPA	-5.89	-2.94	44.98
CI+MBPT	-5.1	-2.6	32.99
MCDF	-4.84	-2.22	
PRCC	-4.3	-2.46	33.29
LCCSD	-4.52	-2.34	33.91
CCSD$^{(2)}$	-3.82	-2.00	33.76
CCSD$^{(4)}$	-4.14	-2.05	35.13
CCSD$^{(5)}$	-4.02	-2.00	34.98
CCSD$^{(\infty)}$	-3.17	-1.76	34.51
NCCSD	-3.30	-1.77	34.22
Experiment			33.91(34)

Sahoo and Das, Phys. Rev. Letts. 120, 203001 (2018).

Limits on T-violating quantities

$D^{Expt}(^{199}Hg) = (2.20 \pm 2.75_{stat} \pm 1.48_{syst}) \times 10^{-30}\ e$-cm

$\Rightarrow |D(^{199}Hg)| < 7.4 \times 10^{-30}$ e cm (95% C.L.)

B. Graner, Y. Chen, E. G. Lindahl and B. R. Heckel, Phys. Rev. Lett. 116, 161601 (2016).

Nuclear calculations:

$$S = 13.5[0.01\bar{g}^{(0)}_{\pi NN} \pm 0.02\bar{g}^{(1)}_{\pi NN} + 0.02\bar{g}^{(2)}_{\pi NN}]\,|e|fm^3$$

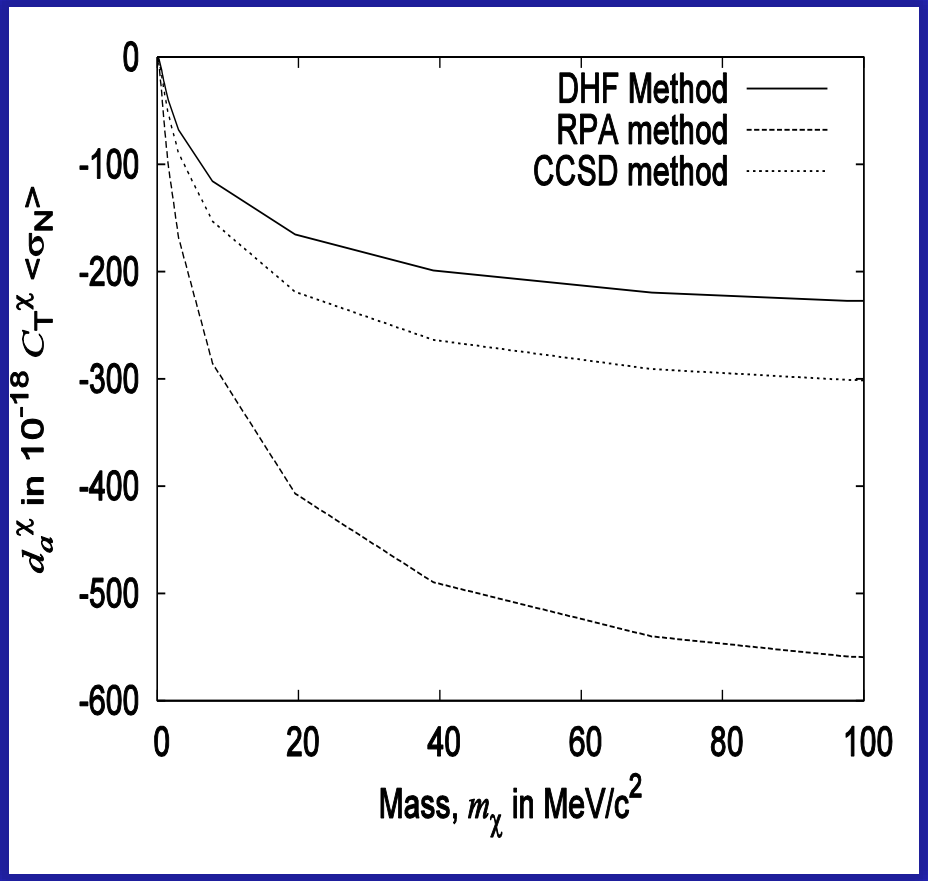
$$S = [1.9\,d_n + 0.2\,d_p]$$

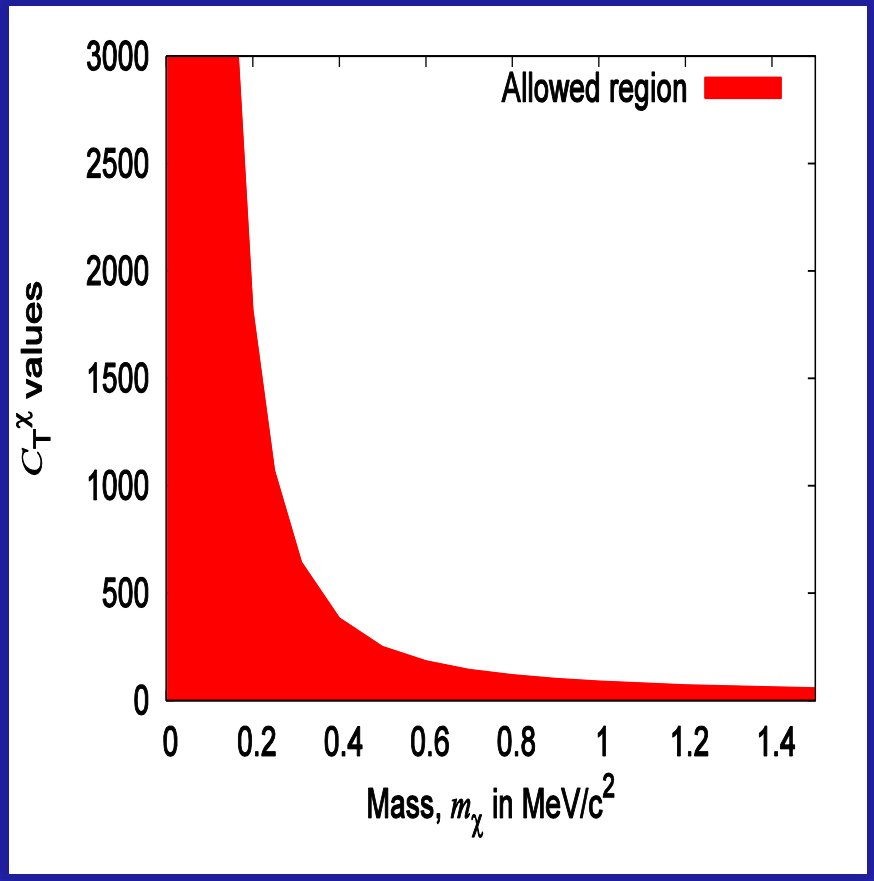
Prog. Part. Nuc. Phys, 71, 21 (2013).

Atomic Expt+Theory	Standard Model (SM)
$d_n < 3.0 \times 10^{-27}\ e-cm$	$d_n \sim 10^{-32}\ e-cm$
$d_p < 2.1 \times 10^{-26}\ e-cm$	$d_p \sim 10^{-32}\ e-cm$
$\lvert\tilde{d}_u - \tilde{d}_d\rvert < 2.7 \times 10^{-27}\ e-cm$	$d_u, d_d \sim 10^{-34}\ e-cm$
$\lvert\bar{\theta}\rvert < 1.1 \times 10^{-10}$	$0 \le \bar{\theta} \le 2\pi$

Strong CP problem.

Limit on mass of a dark matter candidate





B. K. Sahoo, Phys. Rev. D 95, 013002 (2017).

Conclusion and Outlook

- Accurate relativistic many-body methods are necessary for studying fundamental physics.
- We have developed FF, EVE, AR and Normal coupled-cluster methods to carry out isotope shift and EDM calculations.
- RCC method in the AR approach is developed for Lorentz symmetry violation studies.
- Nuclear charge radii of Indium isotopes are estimated, and compared with Sn and Cd isotopes.
- Accurate limits on nuclear CP violating parameters are inferred.

- NCC method for open-shell systems.
- Equation-of-motion RCC method for two-valence systems.
- Extended RCC method.

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