Finite-field coupled cluster method for molecular properties

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Search for new physics with atoms and molecules:

- Promising alternative to high energy experiments
- Small scale
- (Relatively) inexpensive
- Various enhancement effects→ high sensitivity
- Versatile, sensitive to different phenomena:

variation of fundamental constants, parity violation, electron/proton EDM, search for dark matter, tests of Lorenz invariance…

- Tiny observable effects:
  - Very sensitive systems
  - Extremely precise measurements
  - Theoretical support is important

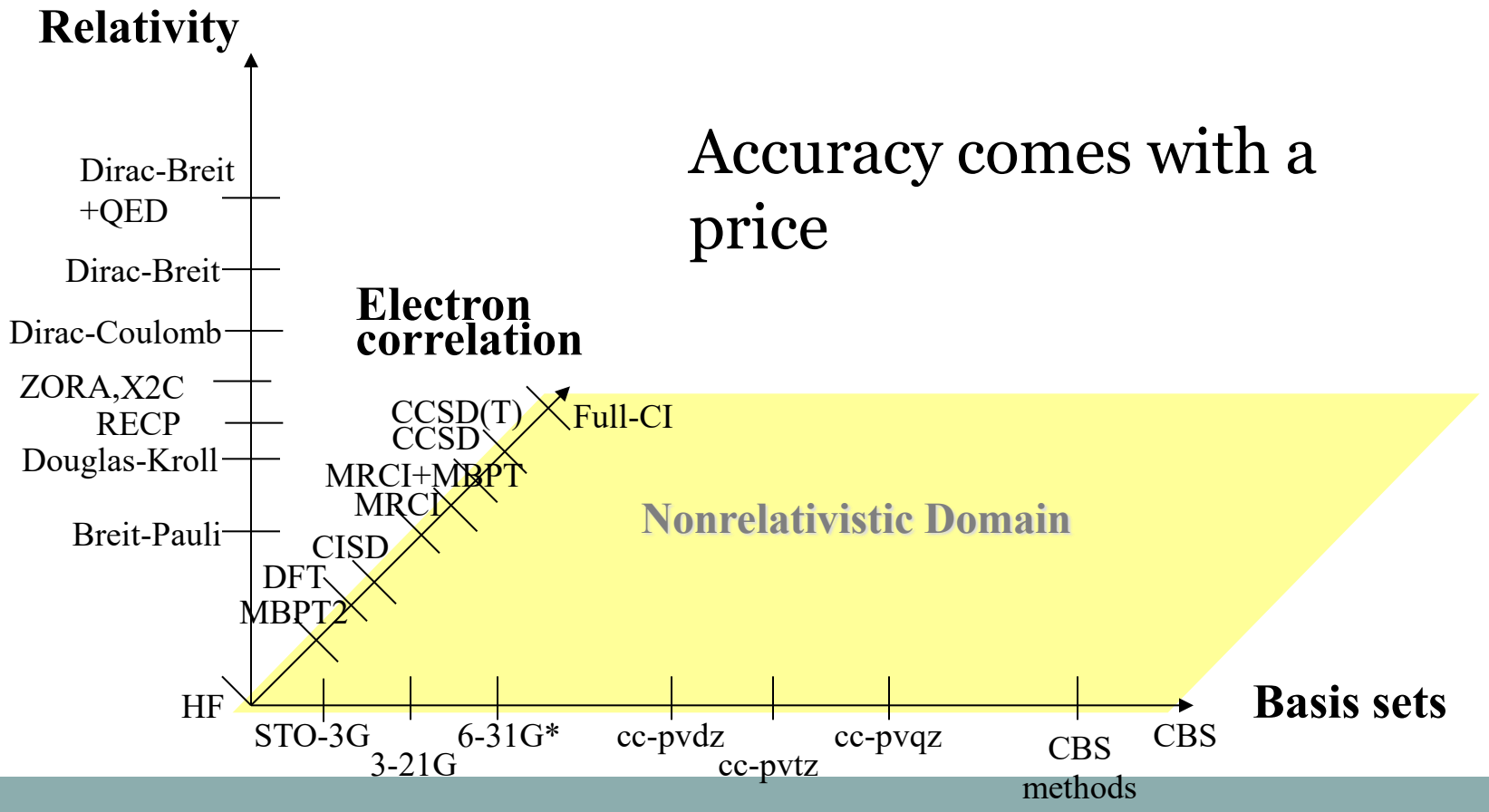
M.S. Safronova, D. Budker, D. DeMille, D.F.J. Kimball, A. Derevianko, C.W. Clark, Rev. Mod. Phys. **90** (2018)

What can theory contribute?

- Understanding the mechanisms whereby electronic structure is affected by the phenomena
- Identification of atomic/molecular candidates with enhanced sensitivity
- Supplying the necessary parameters for the interpretation of the results
- Calculations of the practical parameters needed for the experiment (spectra, lifetimes of levels, etc.)

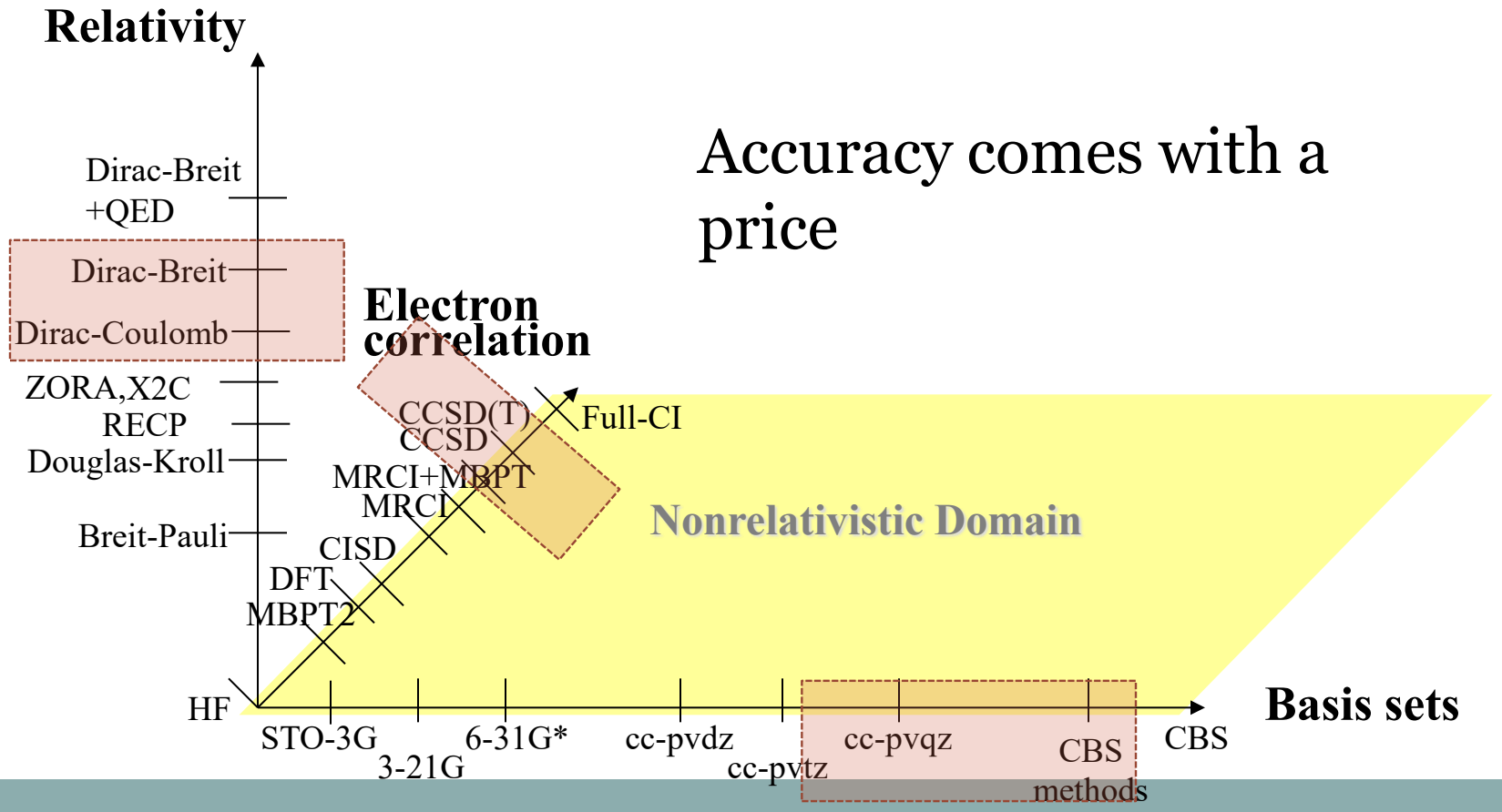
Theoretical input should be accurate and reliable.

Which brings us to the computational methods…



Accuracy comes with a price

Which brings us to the computational methods…



Accuracy comes with a price

Relativistic coupled cluster

- Extremely powerful and accurate method for electron correlation
- Exponential wave operator:

$$\Psi = \exp(S)\Psi_0 = \left(1 + S + \frac{S^2}{2!} + \cdots\right)\Psi_0$$

- S is the excitation operator:

$$S = S_1 + S_2 + \cdots + S_N;\ S_1 = \sum_{ia} s_i^a a_a^\dagger a_i;\ S_2 = \sum_{ijab} s_{ij}^{ab} a_a^\dagger a_b^\dagger a_j a_i$$

- CC energy equations:

$$\langle\Phi_0|(H - E_{\mathrm{CCSD}})\exp(S_1 + S_2)|\Phi_0\rangle = 0$$

Relativistic coupled cluster

- **CCSD(T)** - single reference coupled cluster

Closed shell systems/systems with one dominant configuration (good example: BaF, $X\,^2\Sigma$)

- **FSCCSD** – multireference Fock space coupled cluster

Open shell systems, excited states, bond dissociation (good example: ThO, $^3\Delta_1$)

Use the most suitable method, or both in complementary manner.

Finite Field Approach

- Obtaining expectation values/matrix elements within CC problematic (some implementations available/ongoing)
- Alternative: use finite field approach
- Established method: dipole moments, polarizabilities, effective field gradients…

Basic idea:

- $H=H^{(0)}+\lambda H'$
- Expectation value is obtained from the derivative of the energy with respect to λ

Finite Field Approach

- Example: effective electric field, E_{eff}

$$\hat{H}^{(0)} = \sum_{i}^{n} \left[c\boldsymbol{\alpha}_i \cdot \mathbf{p}_i + \beta_i c^2 + V_{nuc}(\mathbf{r}_i) \right] + \sum_{i<j} \frac{1}{r_{ij}}$$

$$H^{\text{EDM}} = 2cd_e \sum_{i=1}^{n} \imath\gamma^0(i)\gamma^5(i)\mathbf{p}^2(i)$$

$$E_{\text{eff}} = \langle \Psi | \, 2c \sum_{i=1}^{n} \imath\gamma^0(i)\gamma^5(i)\mathbf{p}^2(i) \, | \Psi \rangle = \langle \Psi | \, H^{\text{EDM}\prime} \, | \Psi \rangle$$

$$H^{\text{EDM}\prime} = H^{\text{EDM}}/d_e$$

Finite Field Approach

- Example: effective electric field, E_{eff}

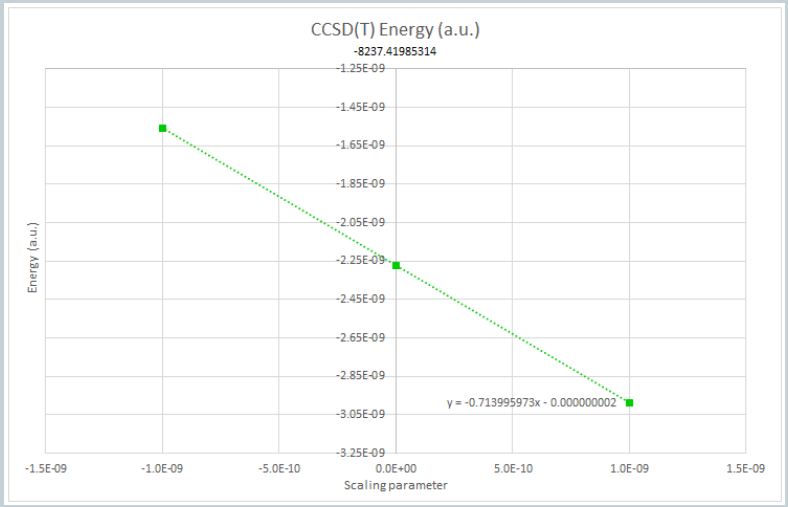
$$H^{\text{EDM}\prime} = 2c \sum_{i=1}^{n} \imath\gamma^0(i)\gamma^5(i)\mathbf{p}^2(i)$$

$$\frac{dE(\lambda)}{d\lambda} \approx \frac{E(\lambda) - E(-\lambda)}{2\lambda}$$

$$H = H^{(0)} + \lambda H^{\text{EDM}\prime} \qquad \lambda \equiv d_e$$

$$E(\lambda) = E(0) + \lambda \frac{dE(\lambda)}{d\lambda}\bigg|_{\lambda=0} + \ldots$$

$$E_{\text{eff}} = \frac{dE(\lambda)}{d\lambda}\bigg|_{\lambda=0}$$



Abe et al., PRA **97**, 032515 (2018)

Finite Field Approach

- Properties:
  - E_{eff}
  - Scalar-pseudoscalar interaction coefficient W_{S}
  - NAM interaction coefficient W_A
  - Magnetic hyperfine coupling constants
  - …
- Developers version of the DIRAC program
- CCSD(T), FSCC, DHF, MP2
- Systematic investigation of effect of computational parameters and uncertainty evaluation

Applications

- W_A in BaF
- E_{eff} and W_s in BaF
- E_{eff} in YbF

W_A coefficient in BaF

- Nuclear anapole moment is the dominant NSD-PV effect in heavy systems

$$H_{\mathrm{NSD}} = \frac{G_F}{\sqrt{2}I} \sum_i (\kappa_A + \kappa_{\mathrm{ax}} + \kappa_{\mathrm{hfs}}) (\boldsymbol{\alpha}_i \cdot \boldsymbol{I}) \rho(\boldsymbol{r}_i)$$

- Planned measurement in BaF*
- W_A coefficient can be used to extract anapole from measurements

$$W_A = \frac{G_F}{\sqrt{2}} \left\langle +\tfrac{1}{2} \right| \sum_i \rho(\boldsymbol{r}_i) \alpha_+ \left| -\tfrac{1}{2} \right\rangle .$$

$$\alpha_+ = \alpha_x + i\alpha_y = \begin{pmatrix} 0 & \sigma_x \\ \sigma_x & 0 \end{pmatrix} + i \begin{pmatrix} 0 & \sigma_y \\ \sigma_y & 0 \end{pmatrix}$$

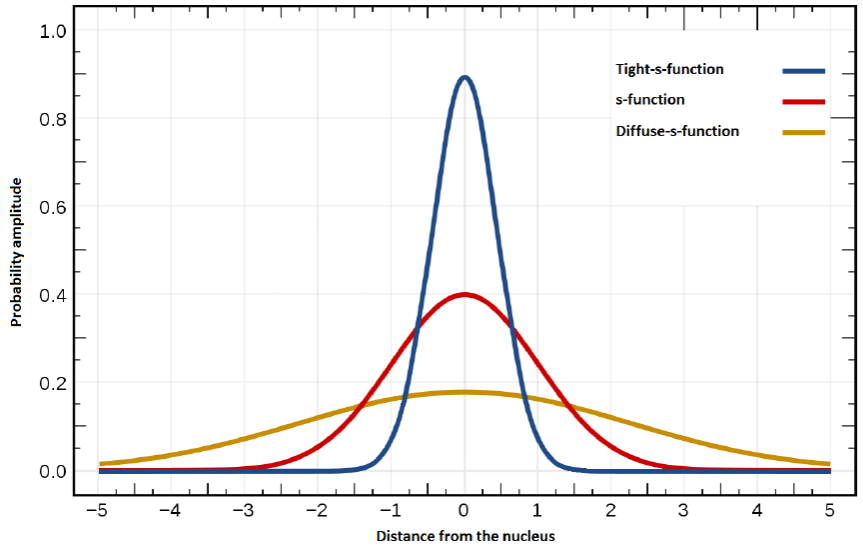
E. Altuntas et al., PRL **120**, 142501 (2018)

W_A coefficient in BaF

- Computational parameters:
  - Basis set
  - Correlation: method (DHF/DFT/MP2/CCSD(T)/FSCC)
  - Correlation (CC): higher excitations
  - Correlation (CC): number of correlated electrons and virtual orbitals
  - Treatment of relativity (Gaunt term)

Basis set effects

- We use relativistic basis sets of Dyall*
- Manually augment with diffuse and tight functions



$$g_{ijk} = N x^i y^j z^k e^{-\alpha r^2}$$

$$L = i + j + k$$

K. G. Dyall, JPCA **113**, 12638 (2009), Theor. Chem. Acc. **135**, 128 (2016)
D. Doeglas, Master Thesis

Basis set effects

- Basis set quality:

	v2z	v3z	v4z
N. functions	Ba: 25s19p13d F: 10s6p1d	Ba: 31s24p16d3f F: 14s8p2d1f	Ba: 35s30p19d4f3g F: 18s10p3d2f1g
W_A (Hz)	129.22	**141.42**	141.84

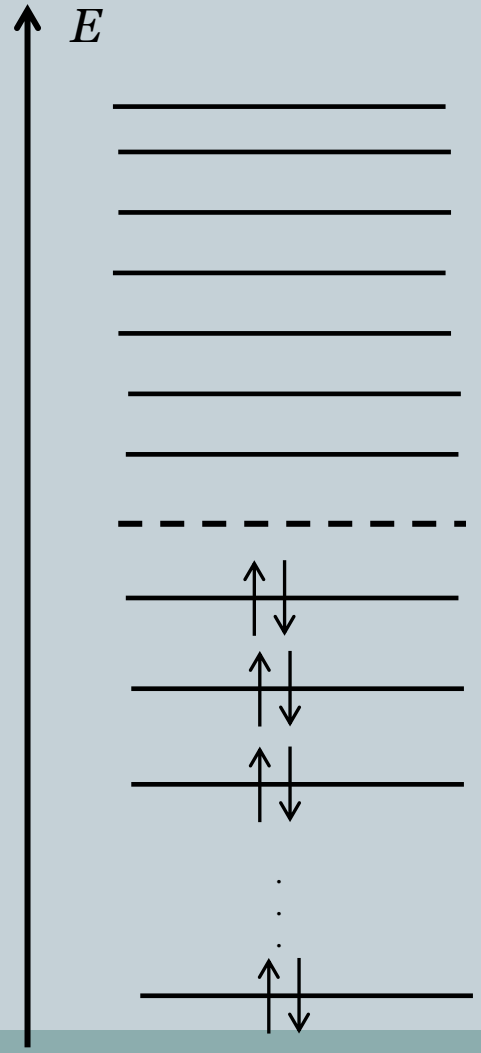
- Diffuse functions:

	v4z	s-aug-v4z (Ba)	s-aug-v4z (F)
W_A (Hz)	141.84	141.76	**141.05**

- Tight functions:

	v4z	v4z+ts	v4z+tp	v4z+td	v4z+tf	v4z+tg
W_A (Hz)	141.84	141.89	141.97	141.82	**143.02**	**142.31**

Correlation space



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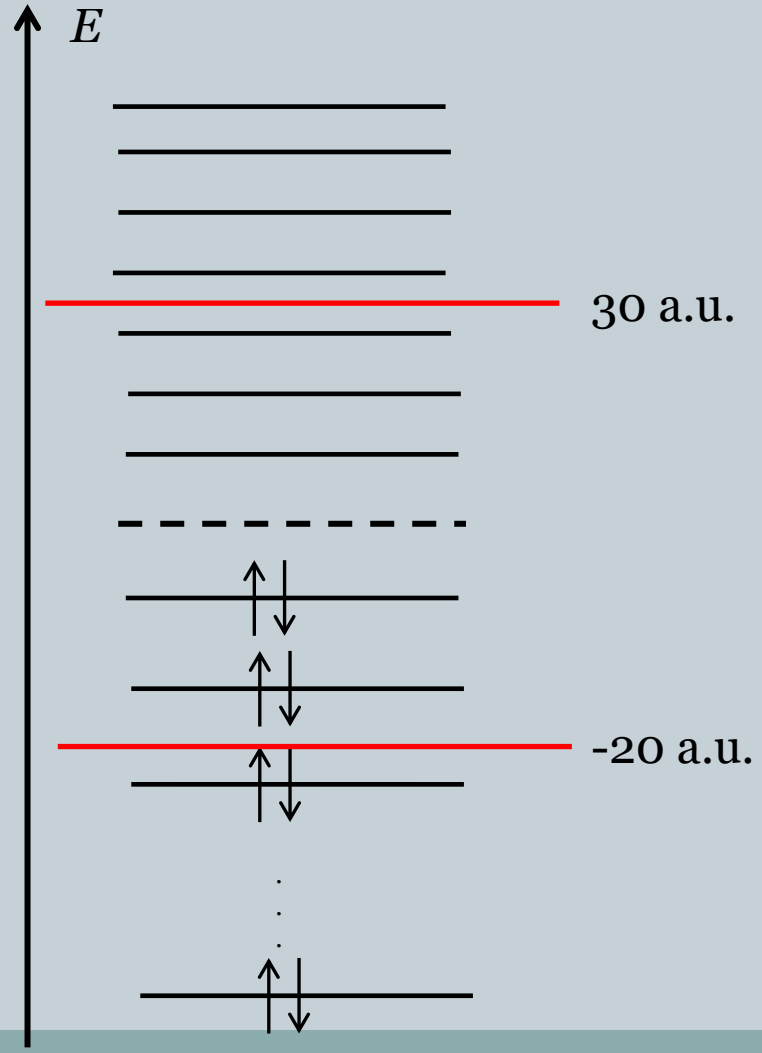

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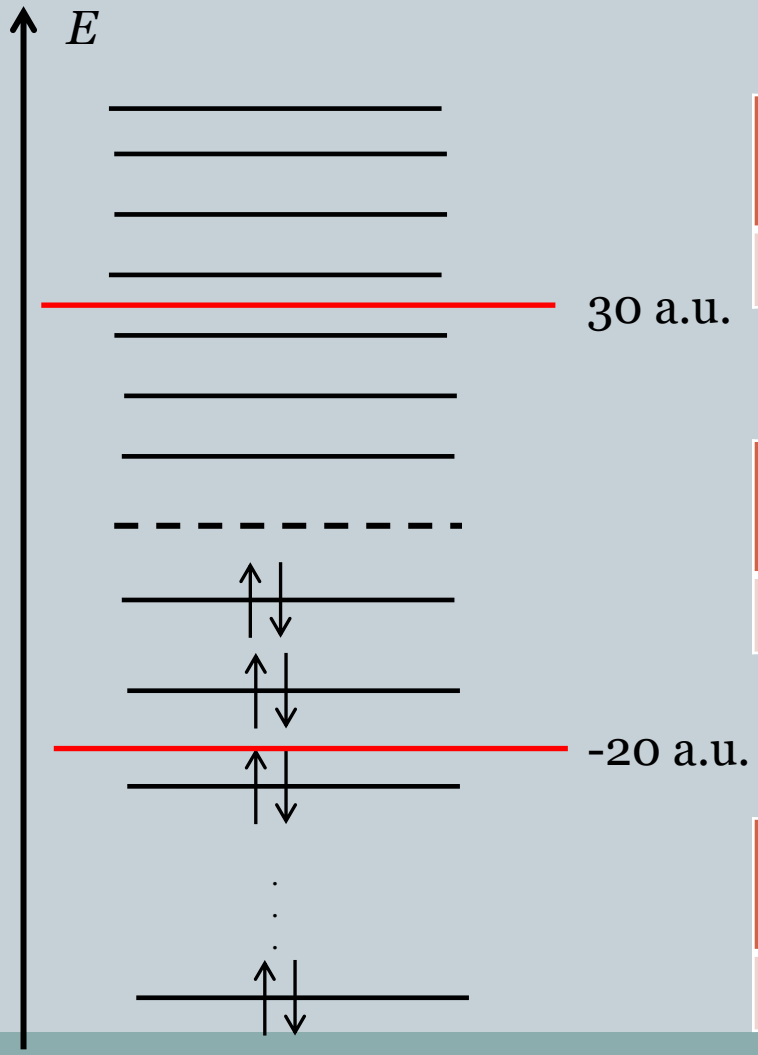


Virtual space cutoff	30 a.u.	500 a.u.
W_A (Hz)	144.4	148.4

	Standard corr. space	all e, 500 a.u.
W_A (Hz)	143.0	148.4

Correlated electrons	-20 a.u. cutoff	all electrons
W_A (Hz)	143.5	148.4

Correlation treatment and final result

Method	W_A (Hz)
DHF	112.3
DFT(CAMB3LYP)	112.9
MP2	138.3
CCSD	150.7
CCSD(T)	148.4
FSCC	148.8

Source of error	$\lvert\Delta W_A\rvert$ (Hz)
Basis set	0.5
Virtual space cut-off	1.0
Higher excitations	1.5
Full Breit; QED	0.7
Numerical	0.5
Total	2

Gaunt contribution: -0.7 Hz (on DHF level)

$$W_A(\text{CCSD(T)+Gaunt}) = 147.7 \pm 2 \text{ Hz}$$

Recommended value

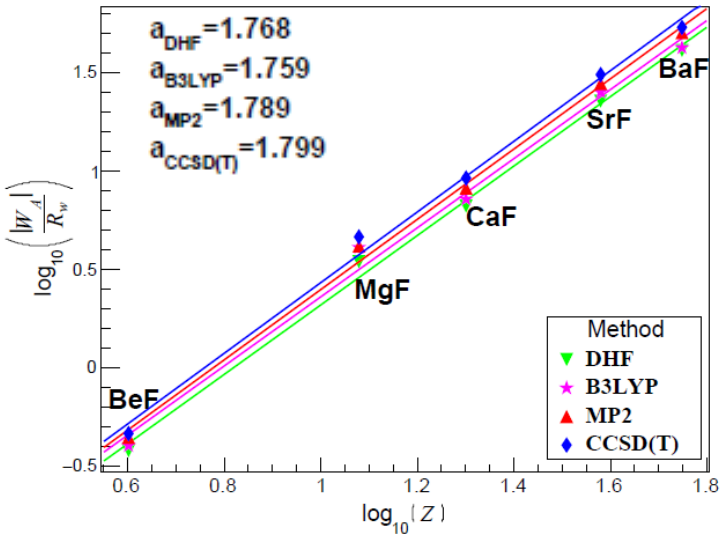
Method	W_A (Hz)	Ref.
CCSD(T)+Gaunt	**147.7±2**	**Present**
RECP+SCF+EO	181	Kozlov et al., PRA **56** R3326 (1997)
Semiempirical	164	DeMille et al., PRL **100**, 023003 (2008)
4c-RASCI	160	Nayak and Das, PRA **79**, 060502 (2009)
Scaled ZORA-HF	190	Isaev & Berger, PRA **86**, 062515 (2012)
DHF/DFT+CP	146	Borschevsky et al., PRA **88**, 022125 (2013)

Trends in the group

- W_A is expected to scale as $Z^2 R_W$

$$R_W = \frac{2\gamma+1}{3}\left(\frac{a_B}{2Zr_0A^{\frac{1}{3}}}\right)^{2-2\gamma}\frac{4}{[\Gamma(2\gamma+1)]^2},$$
$$\gamma = \sqrt{1-(Z\alpha)^2}.$$

Molecule	DHF	B3LYP	MP2	CCSD(T)
BeF	0.38	0.40	0.44	0.46
MgF	3.67	4.34	4.41	4.91
CaF	7.74	8.39	9.55	10.75
SrF	37.29	41.50	45.79	50.87
BaF	112.27	116.02	138.23	147.16



Flambaum et al., Phys. Lett. B 146, 367 (1984)

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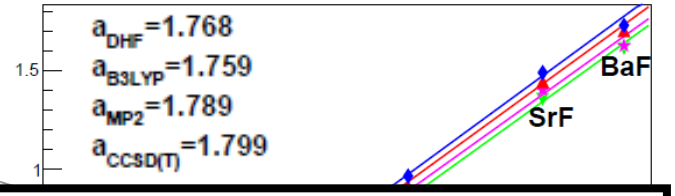

PHYSICAL REVIEW A **98**, 032510 (2018)

Nuclear anapole moment interaction in BaF from relativistic coupled-cluster theory

Yongliang Hao,[1] Miroslav Iliaš,[2] Ephraim Eliav,[3] Peter Schwerdtfeger,[4,5] Victor V. Flambaum,[6,7] and Anastasia Borschevsky[1,*]

E_{Eff} and W_s in BaF

NL-*e*EDM
Measuring the electron-EDM with BaF molecules

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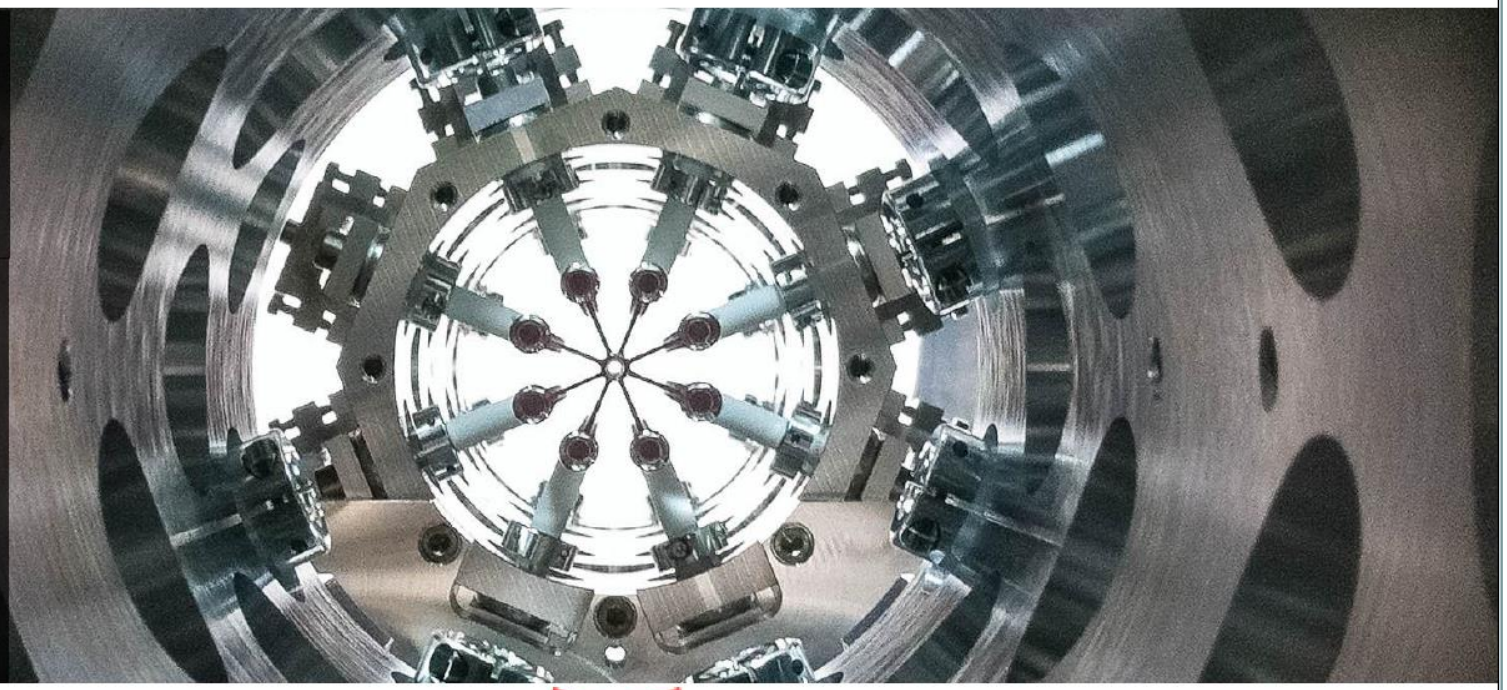

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THE EUROPEAN PHYSICAL JOURNAL D

Regular Article

Measuring the electric dipole moment of the electron in BaF

The NL-*e*EDM collaboration: Parul Aggarwal[1,2], Hendrick L. Bethlem[3], Anastasia Borschevsky[1,2], Malika Denis[1,2], Kevin Esajas[1,2], Pi A.B. Haase[1,2], Yongliang Hao[1,2], Steven Hoekstra[1,2,a], Klaus Jungmann[1,2], Thomas B. Meijknecht[1,2], Maarten C. Mooij[2,3], Rob G.E. Timmermans[1,2], Wim Ubachs[3], Lorenz Willmann[1,2], and Artem Zapara[1,2]

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E_{Eff} and W_s in BaF

- In paramagnetic systems two main contributions to the EDM are the eEDM (d_e) and the S-PS electron-nucleon interaction (C_S)

$$\hat{H}_S = i\frac{G_F}{\sqrt{2}} Z C_S \sum_e \gamma_e^0 \gamma_e^5 \rho(\boldsymbol{r}_e)$$

- Associated interaction coefficient:

$$W_S = \frac{1}{\Omega}\langle \psi_\Omega | \hat{H}_S | \psi_\Omega \rangle$$

Computational scheme

- Extensive tests were carried out
- Final computational scheme:
  - E_{eff}: Dyall's v4z basis set+ tight f function
    All electrons correlated, virtual cut-off: 2000 a.u.
    CCSD(T)+Gaunt
  - W_s: Dyall's s-aug-v4z basis set+ tight f function
    All electrons correlated, virtual cut-off: 2000 a.u.
    CCSD(T)+Gaunt

Results

Method	E_{eff} (GV/cm)	Ref.
CCSD(T)+Gaunt	**6.33±0.14**	**Present**
RECP+SCF+EO	7.5	Kozlov et al., PRA **56** R3326 (1997)
4c-RASCI	7.28	Nayak and Chaudhuri, J. Phys. B **39** 1231 (2006)
4c-CISD	4.32	Fukuda et al., PRA **93**, 012518 (2016)
GKS ZORA	6.0	Gaul and Berger, JCP **86**, 014109 (2017)
CCSD(T)	6.46	Abe et al., PRA **97** 032515 (2018)
CCSD	6.6	Sunaga et al., PRA **98**, 042511 (2018)

Results

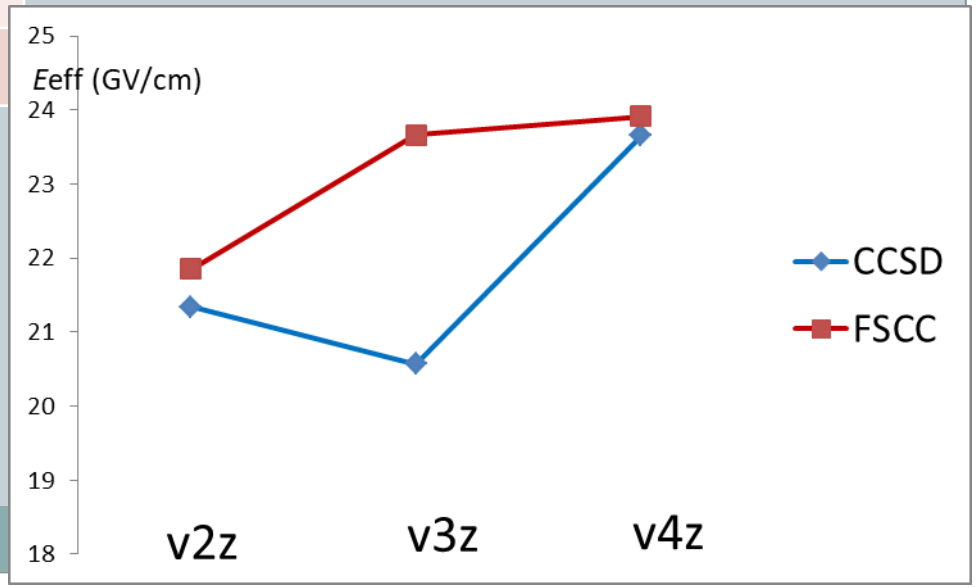
Method	W_s (KHz)	Ref.
CCSD(T)+Gaunt	**8.30±0.16**	**Present**
RECP+SCF+EO	5.9	Kozlov et al., PRA **56** R3326 (1997)
4c-RASCI	9.7	Nayak et al., PRA **75** 022510 (2007)
MBPT	8.4	Nayak and Chaudhuri, PRA **78**, 012506 (2008)
CCSD	8.4	Sunaga et al., PRA **98**, 042511 (2018)

E_{eff} in YbF: multireference character

- Ground state $^2\Sigma$ ($f^{14}\ s^1$), but has a low-lying excited state ($f^{13}\ s^2$)
- Miltireference character; (T) are unstable. Use CCSD?

E_{eff} (GV/cm)	CCSD	FSCC
v2z	21.34	21.85
v3z	20.57	23.66
v4z	23.65	23.91

Here, FSCC is better suited.



Magnetic hyperfine coupling constants

- Getting an accuracy estimate
- Useful in experiments
- New implementation, first test case: Cs
- Use FSCC to treat excited states
- Large basis sets (t-aug-ae4z)

Yongliang Hao: W_A, **Pi Haase** and **Malika Denis**: E_{eff}, **Diewertje Doeglas**: W_s, **Anne de Vries**: hyperfine structure

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Thank you for your attention!

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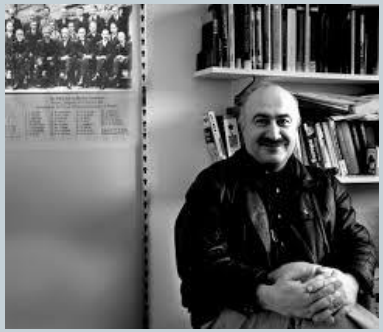

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