ELECTRONIC STRUCTURE OF EXOTIC ATOMS AND MOLECULES

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- University of Groningen

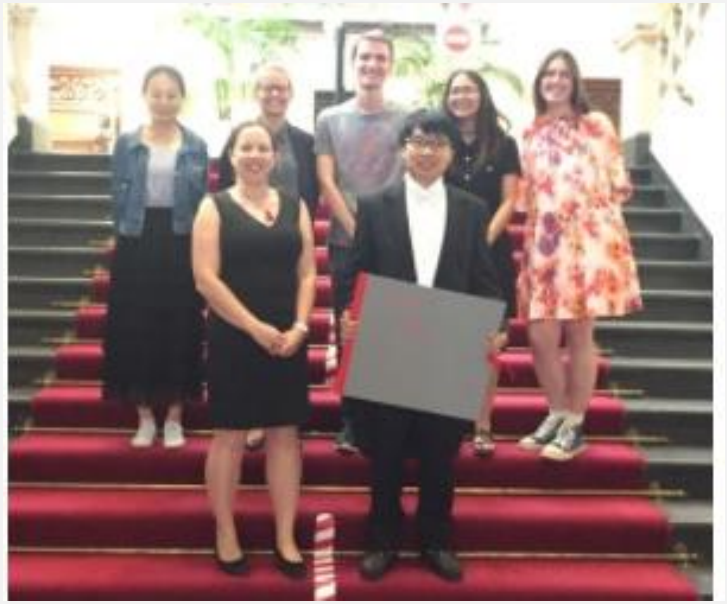
<u>Research:</u>

Using computational chemistry tools to address fundamental problems in physics:

- Search for new physics with low-energy precision measurements
  - Violation of fundamental symmetries in atoms and in molecules
  - Search for variation of fundamental constants

- Highly accurate calculations of spectra and properties of heavy and superheavy atoms and highly charged ions

Most work done in collaboration with experimental groups



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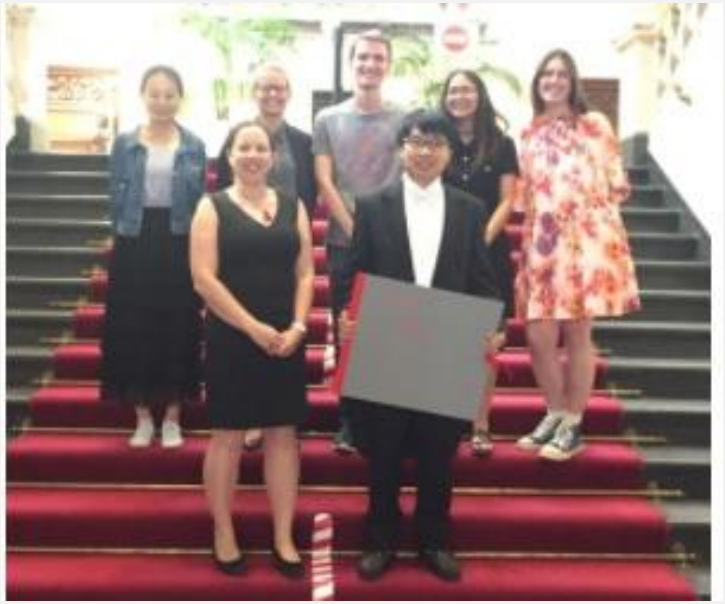
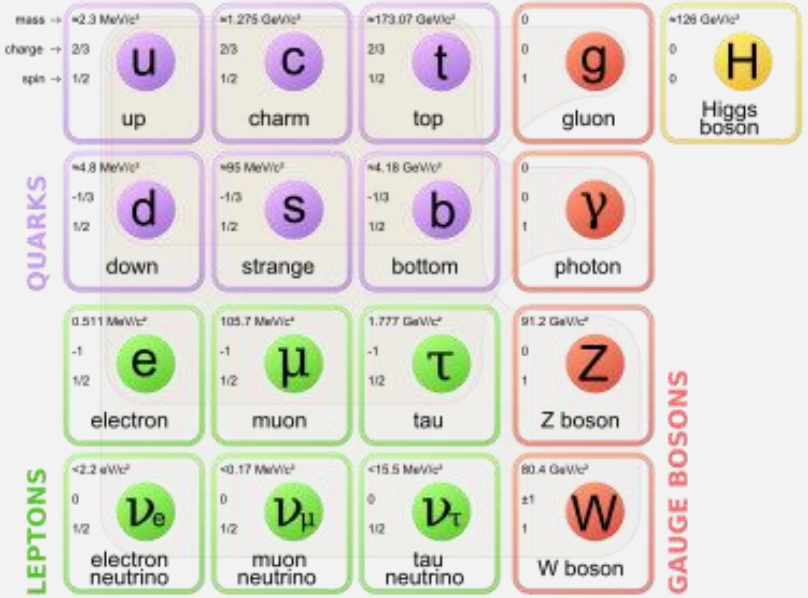


MOTIVATION

Why look for physics beyond the Standard Model (SM)?

- The SM is currently the best fitting physical description of the world around us.
- So far successfully explained the majority of observed natural phenomena and has strong predictive power (Higgs boson, top quark, tau neutrino)
- But… it is incomplete

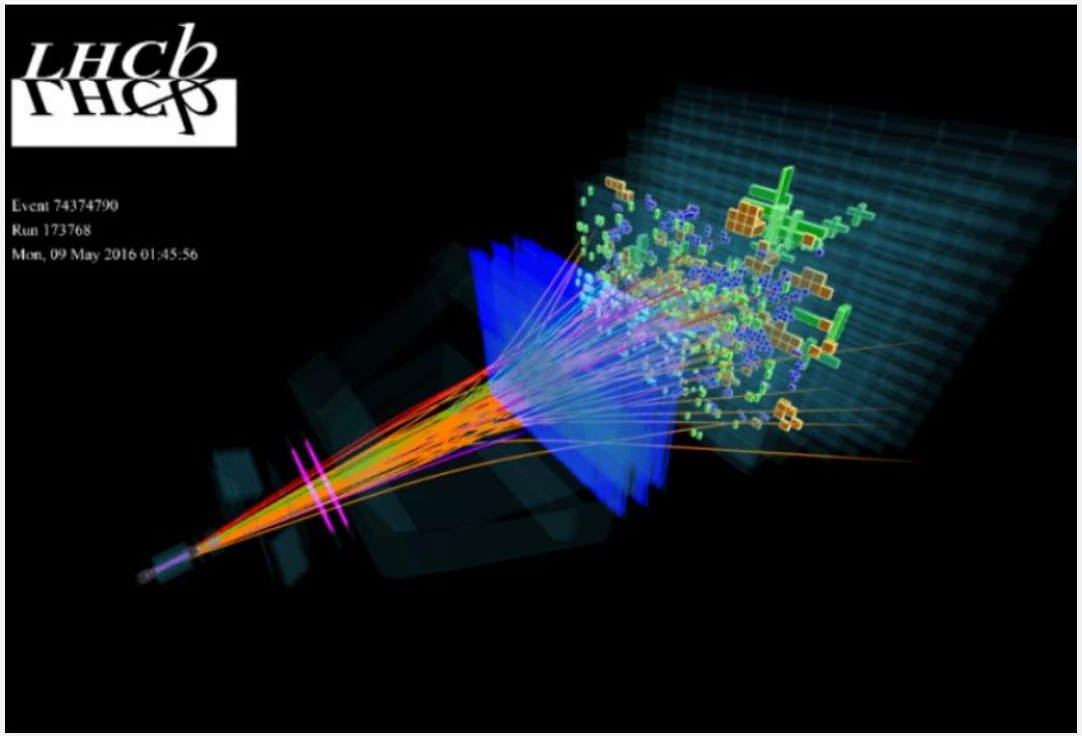


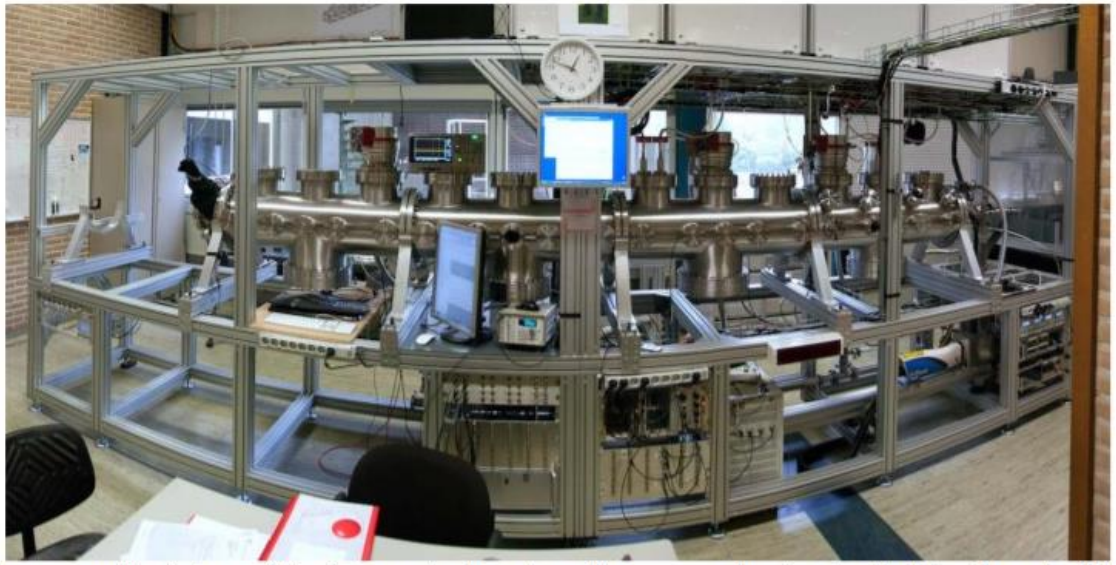
Why look for physics beyond the Standard Model (SM)?

- Extensions to the SM attempt to fill these knowledge gaps.
  - Grand Unified Theories, String Theory, SUSY, …
- These extensions predict new physical phenomena beyond the SM.
  - Variation of fundamental constants (VFC)
  - Violation of fundamental symmetries (*CP, P, T*)
- (non) discovery of these phenomena allows to discriminate between extensions or new theories.

Why look for physics beyond the SM with atoms and molecules?

- Accelerator research (LHCb, T2K, etc.)
- **Table-top experiments**





A panoramic picture of the four meter long traveling-wave decelerator that has been built in Groningen. It is in use for decelerating packets of the heavy diatomic molecule SrF, which is a prototypical system for the investigation of broken symmetries.

Why look for physics beyond the SM with atoms and molecules?

- **Table-top experiments: promising alternative to high energy research**
  - Versatile, sensitive to different phenomena
    - Parity violation
    - EDMs (electron, hadronic)
    - Variation of fundamental constants
    - Dark matter
    - ..
  - Various enhancement effects→ high sensitivity
  - Small scale
  - (Relatively) inexpensive

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Search for new physics with atoms and molecules

M. S. Safronova, D. Budker, D. DeMille, Derek F. Jackson Kimball, A. Derevianko, and Charles W. Clark
Rev. Mod. Phys. **90**, 025008 – Published 29 June 2018

How can (atomic and molecular) theory be of use?

- Insight into effect on molecular properties
- Identification of promising candidates for measurements
  - High sensitivity
  - Experimental considerations (stability, laser-coolability, etc.)
- Practical parameters for experiments
- Parameters for the interpretation of the results

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For use in experiments:

- Reliable predictions based on high accuracy calculations
- Preference for *ab initio* methods (predictive power)
- Possibility of assigning uncertainties

Choice of computational method becomes important

COMPUTATIONAL METHODS

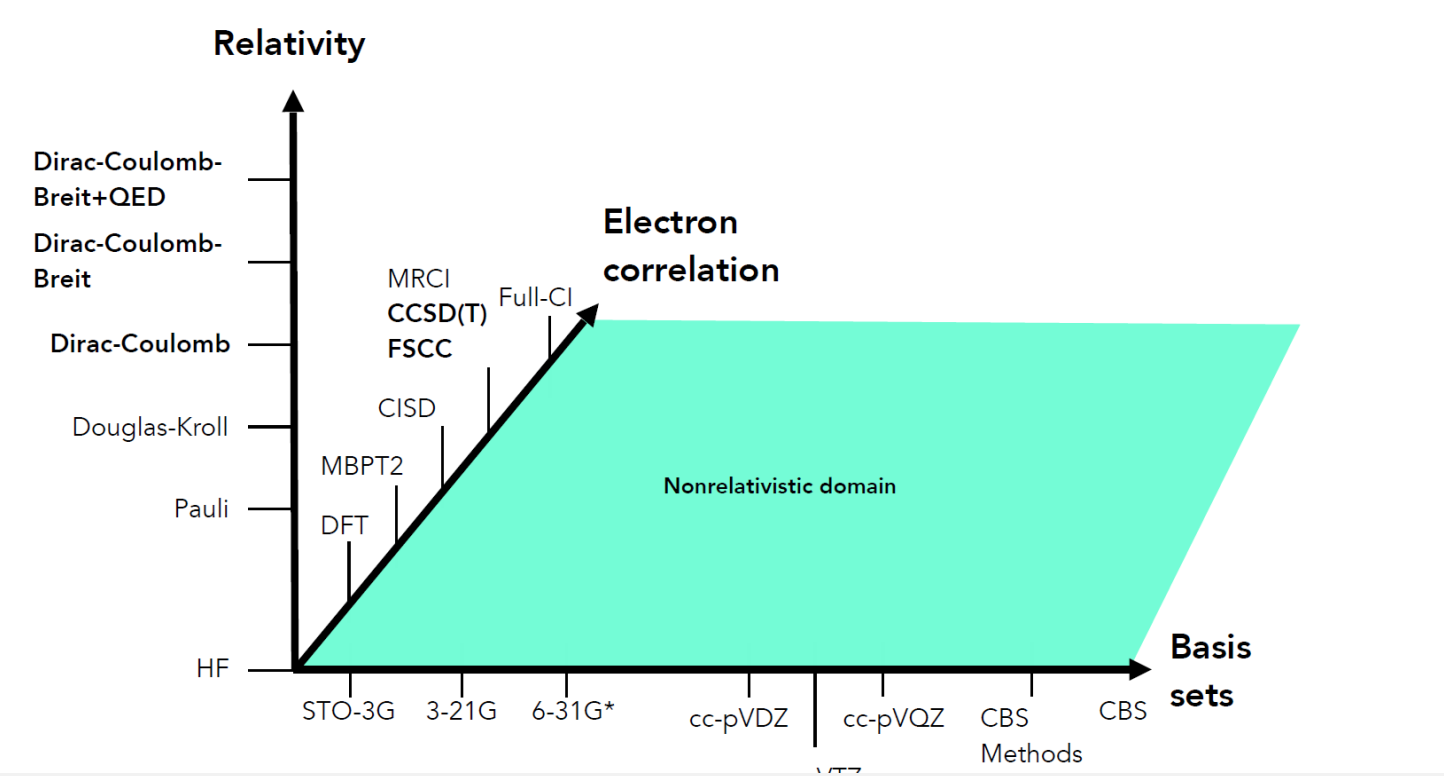
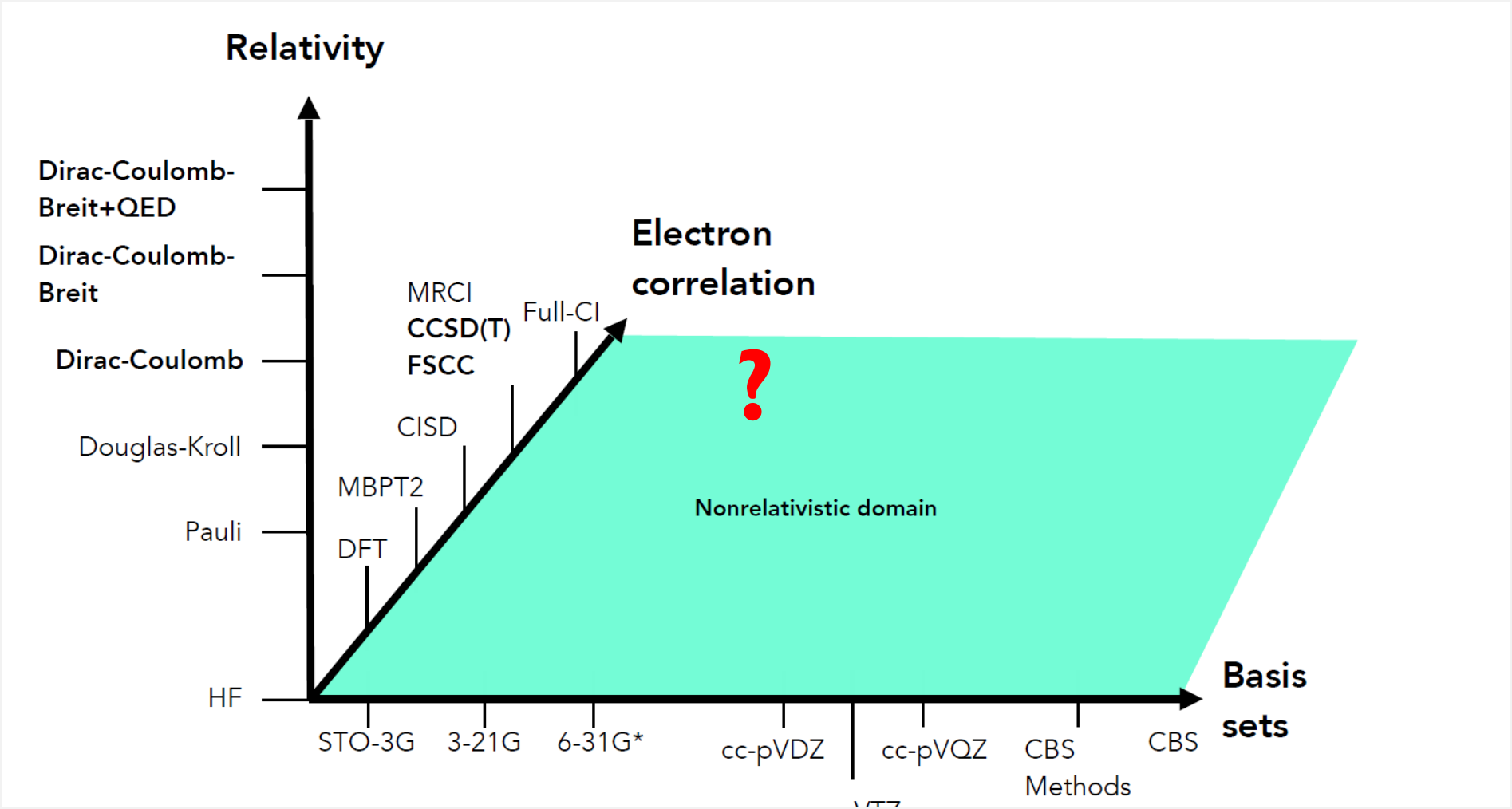


Figure courtesy of P. Schwerdtfeger


Relativity
Dirac-Coulomb-Breit+QED
Dirac-Coulomb-Breit
Dirac-Coulomb
Douglas-Kroll
Pauli
HF
Electron correlation
MRCI
CCSD(T)
FSCC
Full-CI
CISD
MBPT2
DFT
?
Nonrelativistic domain
Basis sets
STO-3G
3-21G
6-31G*
cc-pVDZ
cc-pVQZ
CBS
CBS Methods

What do we want to calculate?

- Coupling parameters describing the effect of $P(T)$-violating phenomena (or variation of constants) on electronic structure
  - Relativistic in nature, hence relativistic methods
- Atomic and molecular parameters needed in experiments
  - (usually) heavy (radioactive) systems, hence relativistic methods
- High accuracy
  - State-of-the-art treatment of correlation, large basis sets
- Uncertainty estimates
  - Robust, transparent methods

Relativistic coupled cluster

- Based on the 4c Dirac Hamiltonian
- Accurate, size-consistent

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

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

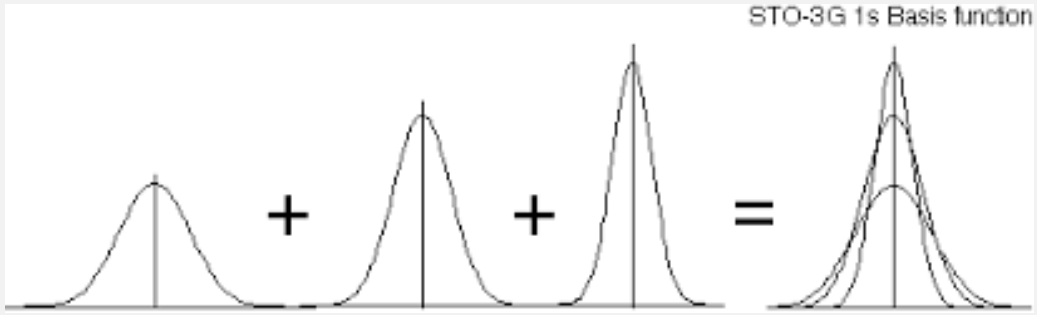
- **FSCC** – multireference Fock space coupled cluster

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

Use the suitable method, or both in complementary manner.

Basis sets

- Sets of (Gaussian) functions that are used to represent the electronic WF.
- Atom specific, different basis sets for different properties



$g = x^{\ell}\, y^{m}\, z^{n}\, e^{-\alpha r^2}$

'exponent' α

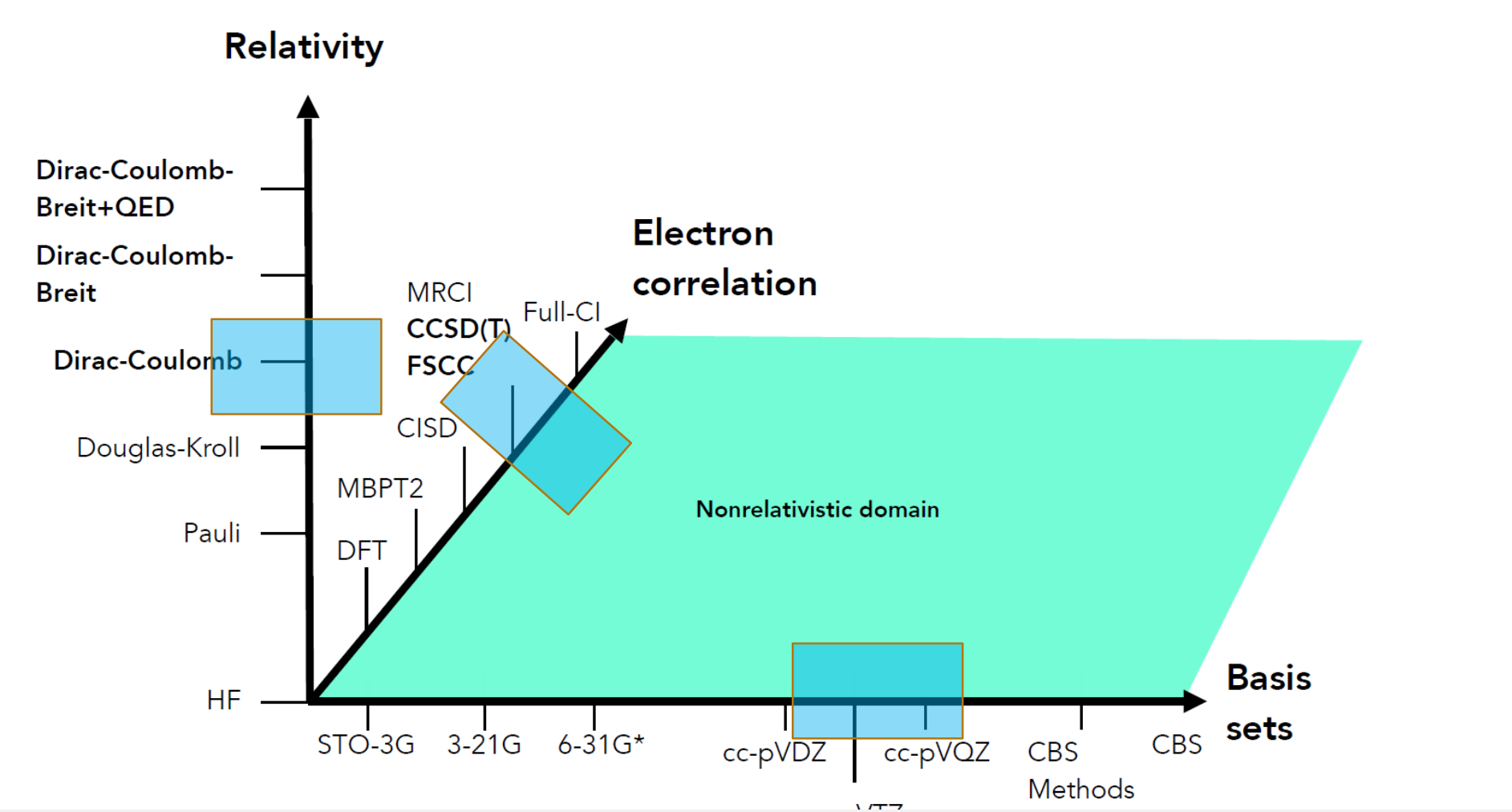
Gaussian type orbital

type of function:
$\ell = m = n = 0$ for s type
ℓ or m or n = 1 for p type
etc.

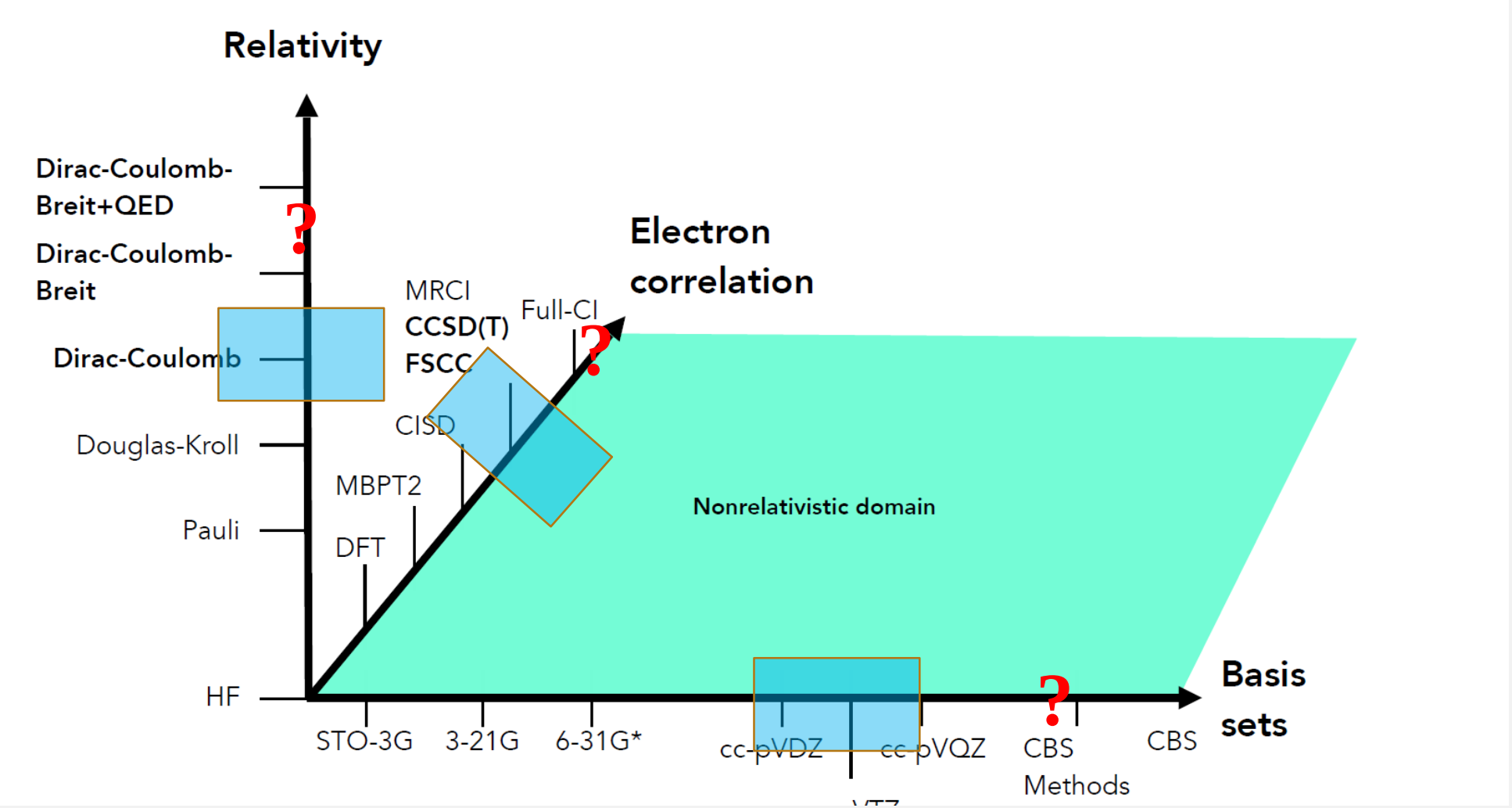
- Dyall's relativistic basis sets; augmented and extended to convergence

(K.G. Dyall, Theor. Chem Acc. 2002, 2004, 2006, 2007, 2009, 2011,2012, etc.)

Relativistic coupled cluster



How do we assign uncertainties?



Software

- Tel Aviv atomic computational package (TRAFS-3C)

Tel-Aviv Relativistic Atomic Fock-Space coupled cluster code, written by E.Eliav and U.Kaldor, with contributions from Y. Ishikawa, A. Landau, A. Borschevsky and H. Yakobi.

- DIRAC18 computational package

DIRAC, a relativistic *ab initio* electronic structure program, release DIRAC18 (2018)

and:

- MRCC code of Kallay et al., www.mrcc.hu (higher excitations)
- CFOUR package, http://www.cfour.de (geometry optimisation of polyatomic molecules)

What can we calculate?

- Atomic properties: energies, IPs, EAs, spectra, hyperfine structure parameters, polarisabilities
- Molecular properties: geometries, spectroscopic constants, electronic structure, Franck-Condon Factors (FCFs), transition strengths
- Specific properties:
  - W_d, W_s (eEDM experiments)
  - W_A (NSD-PV, nuclear anapole moments)
  - W_M (nuclear magnetic quadrupole moments)
  - Sensitivity to variation of α
  - ...
- CCSD(T), FSCC (applicable to different systems/states)
- Expected accuracy: ~10 meV for energies
- Systematic investigation of effect of computational parameters and uncertainty evaluation

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- ✗ FSCC is limited to systems with up to two valence electrons/holes
- ✗ Some properties not (yet) available, e.g. Schiff moment sensitivity factors

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APPLICATIONS

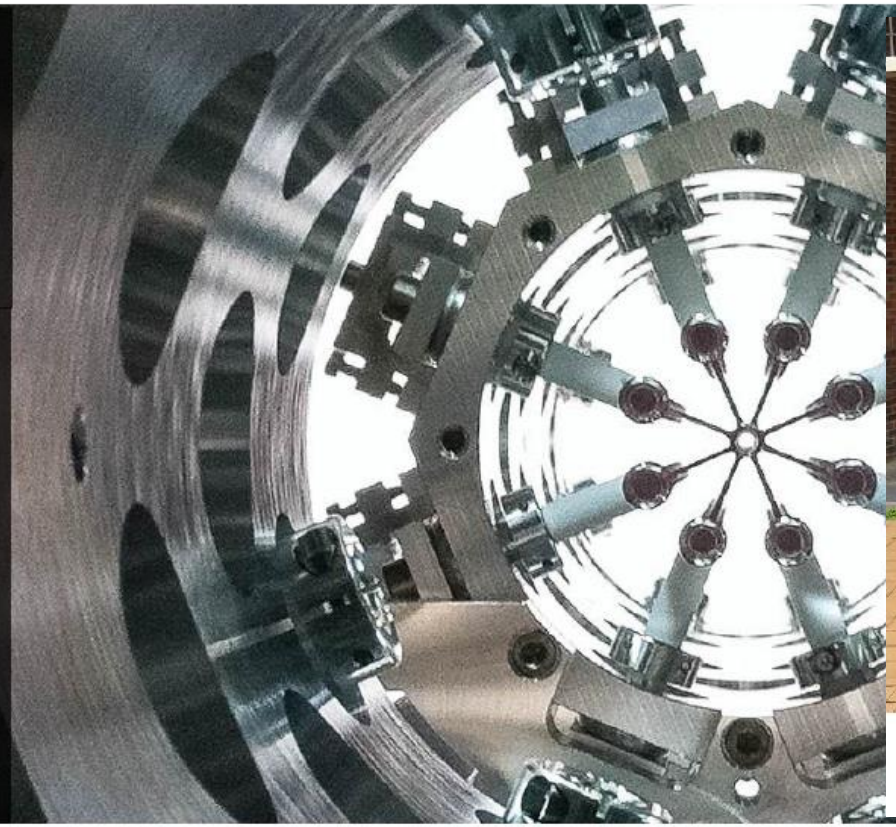
- Search for eEDM in BaF molecules:
  - Laser cooling scheme
  - Sensitivity to eEDM: new method + uncertainty evaluation
  - Sanity check: HFS constants in BaF
- Same methods, new stuff:
  - IP of RaF
  - Polyatomic molecules

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

Scientific staff:
- Anastasia Borschevsky
- Rick Bethlem
- Steven Hoekstra
- Klaus Jungmann
- Rob Timmermans
- Wim Ubachs
- Lorenz Willmann

PhD students:
- Parul Aggarwal
- Alexander Boeschoten
- Kevin Esajas
- Pi Haase
- Yongliang Hao
- Virginia Marshall
- Thomas Meijknecht
- Maarten Mooij
- Anno Touwen
- Artem Zapara

Postdocs
- Malika Denis
- Yanning Yin



NL-*e*EDM collaboration

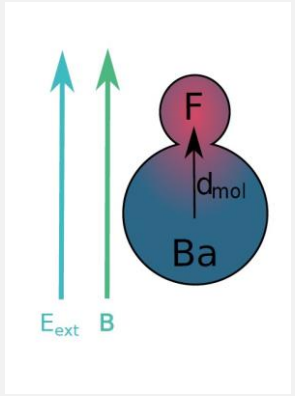
university of groningen
van swinderen institute for particle physics and gravity

Nikhef
Dutch National Institute for (astro)Particle Physics

VU VRIJE UNIVERSITEIT AMSTERDAM

Electron EDM

- Standard Model prediction: ~10^{-38} e*cm
- SM extensions predict much larger values
- Measurement will provide signal of new physics



- Use a molecule!
- YbF, ThO, HfF^+,…
- Upper limit 10^{-29} e*cm, with ThO*

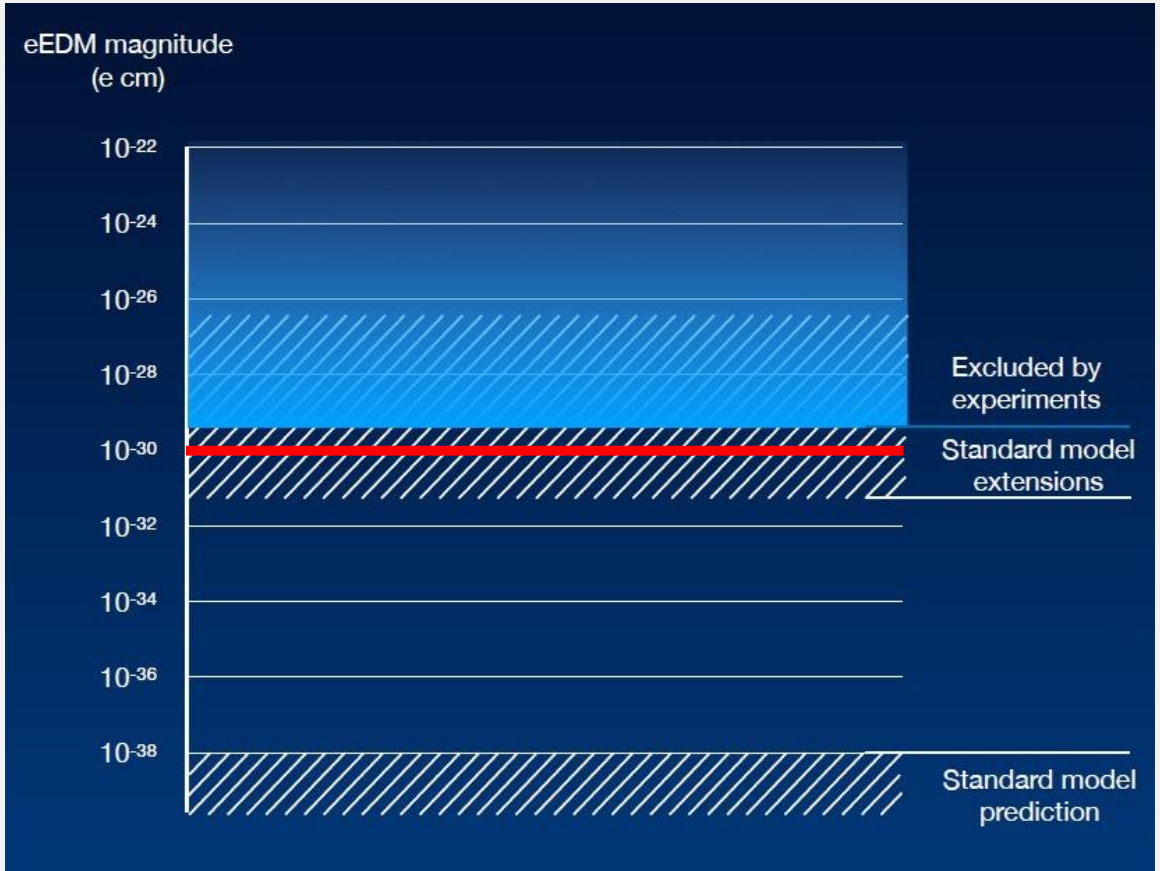
Improved limit on the electric dipole moment of the electron

ACME Collaboration

Nature **562**, 355–360(2018) | Cite this article

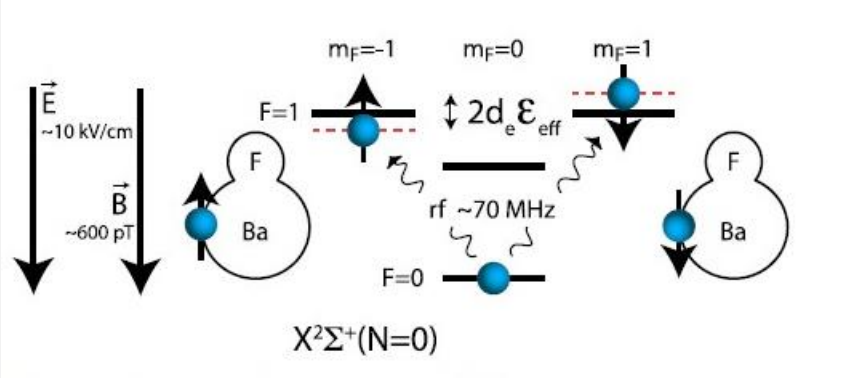
17k Accesses | **191** Citations | **360** Altmetric | Metrics

- … and **BaF**
  - Experimental advantages (laser cooling, Stark deceleration)

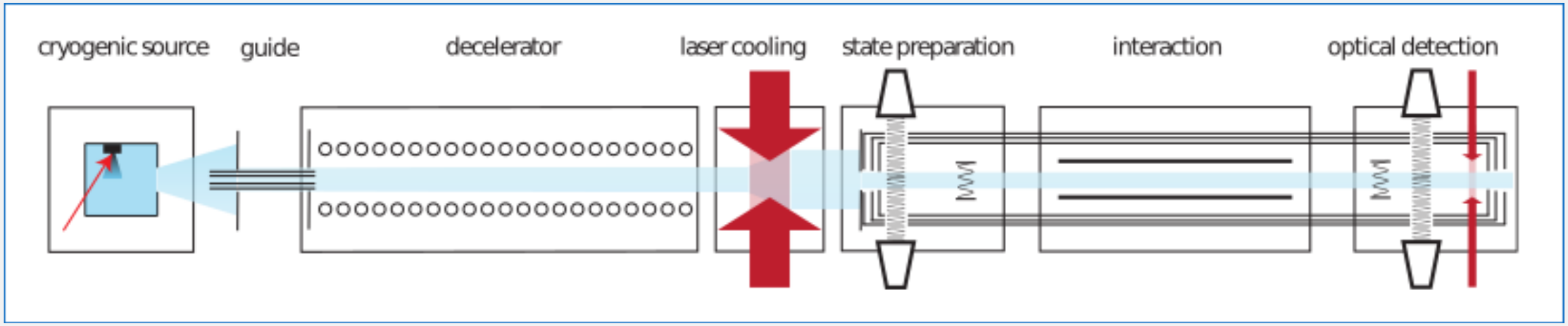


The experiment:

- The EDM signal is detectable through a difference in the total accumulated phase for the parallel and the antiparallel orientation of the external magnetic and the electric fields.



$$\sigma_d = \frac{1}{2|P|W_d\langle \mathbf{S}\cdot\mathbf{n}\rangle \tau\sqrt{N}}$$



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Eur. Phys. J. D (2018) 72: 197
https://doi.org/10.1140/epjd/e2018-90192-9

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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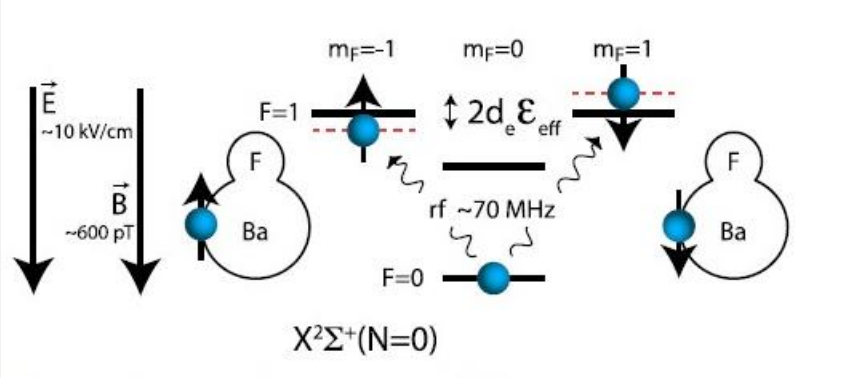
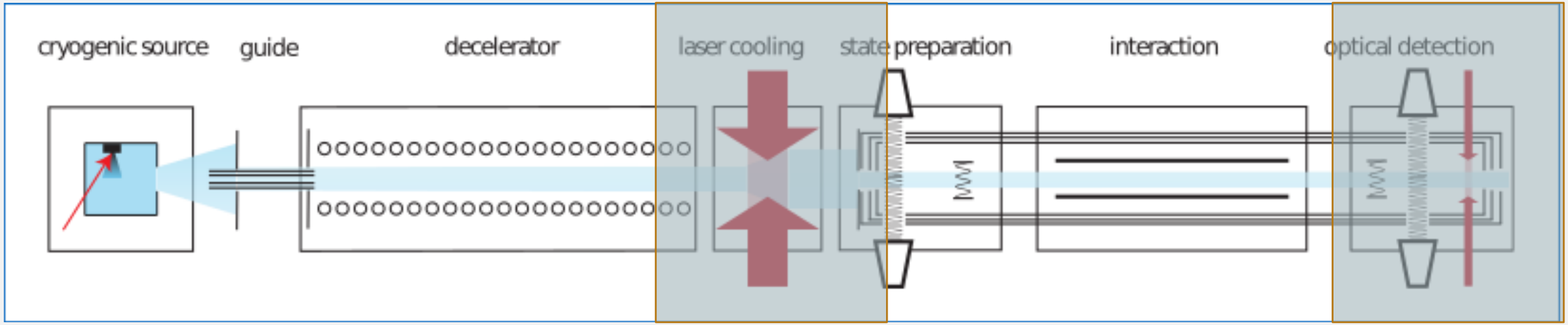


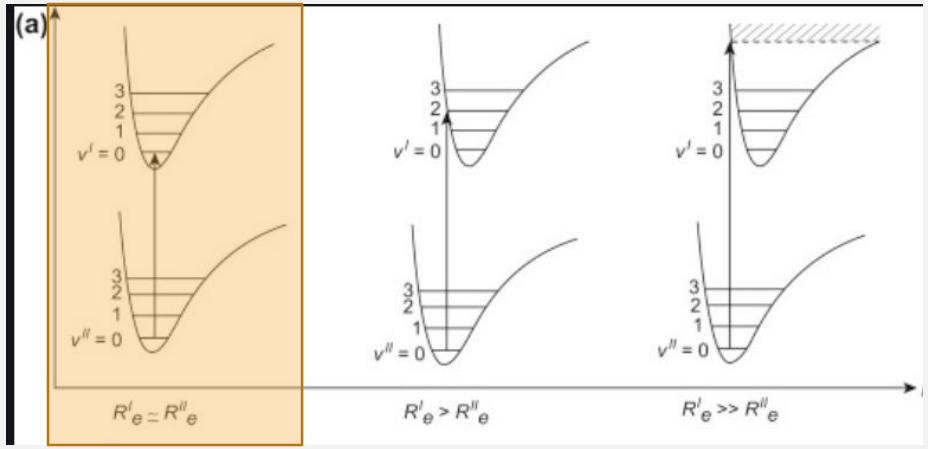
$$\sigma_d = \frac{1}{2|P|W_d\langle \mathbf{S}\cdot\mathbf{n}\rangle \tau\sqrt{N}}$$

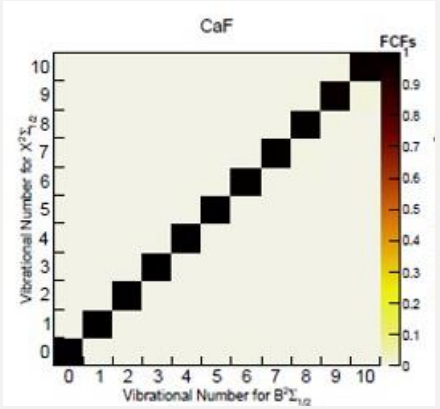
$E_{eff}=2W_d$



Laser cooling:

- Using light to slow transverse motion of the molecules
- We need to identify the optimal cooling scheme (transition):
  - Short lifetime (efficient cooling)
  - Diagonal Frank-Condon factors (FCFs), to avoid leaks

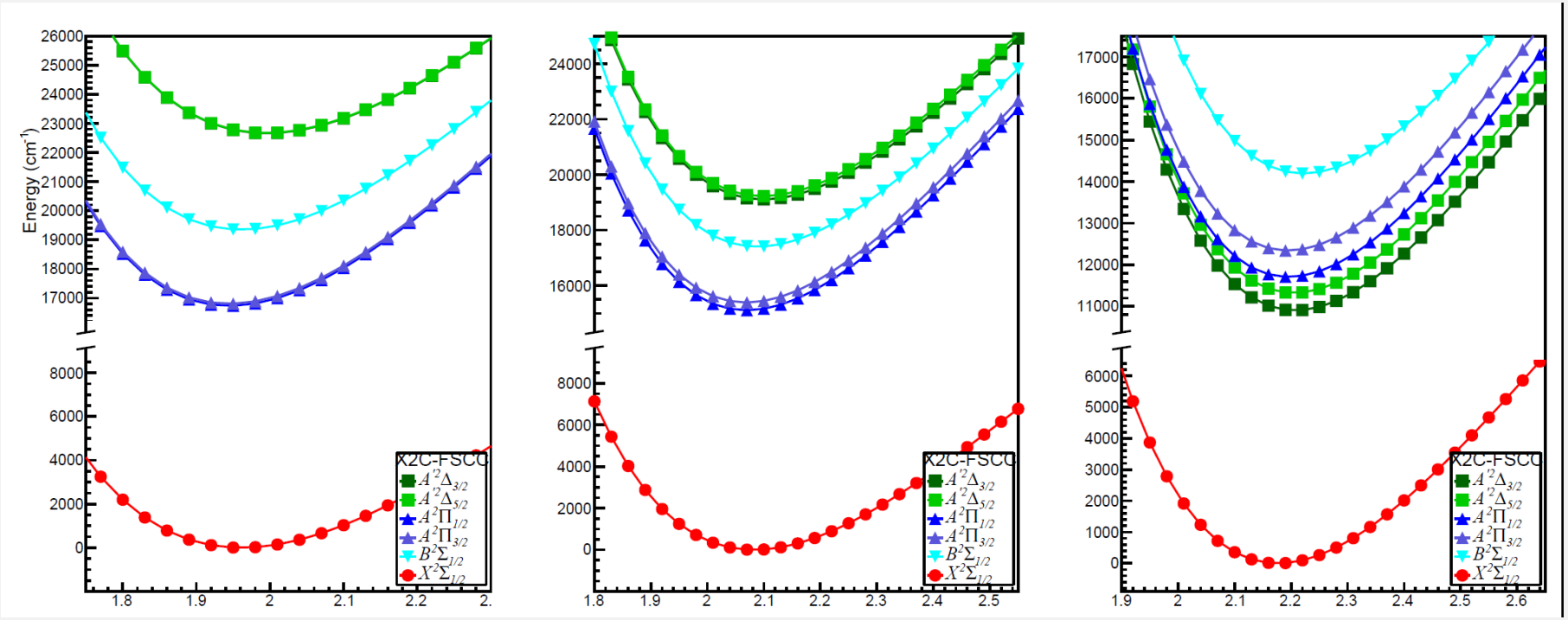




- Needed: potential energy curves, spectroscopic constants, FCFs, transition dipole moments, etc.

Laser cooling:

Relativistic FSCC calculations for the 6 lowest electronic states of CaF, SrF, and BaF

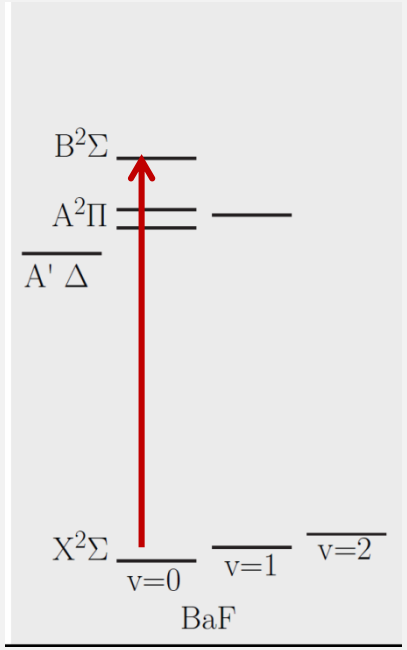


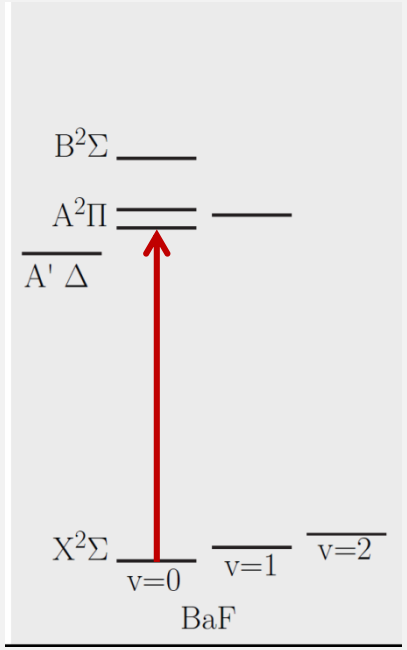
Laser cooling:

- Two possible cooling schemes:

$X\ ^2\Sigma_{1/2} \rightarrow B\ ^2\Sigma_{1/2}$ (CaF)

$X\ ^2\Sigma_{1/2} \rightarrow A\ ^2\Pi_{1/2}$ (CaF and SrF)





- Use calculated FCFs (measure of overlap of vibrational wavefunctions) to determine the appropriate scheme
- Diagonal FCFs→ efficient cooling

Laser cooling:

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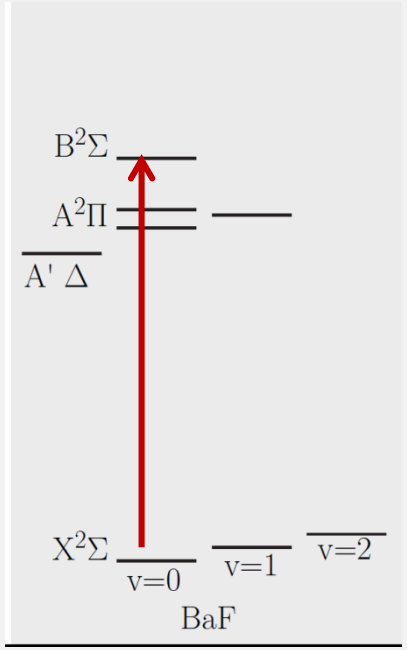

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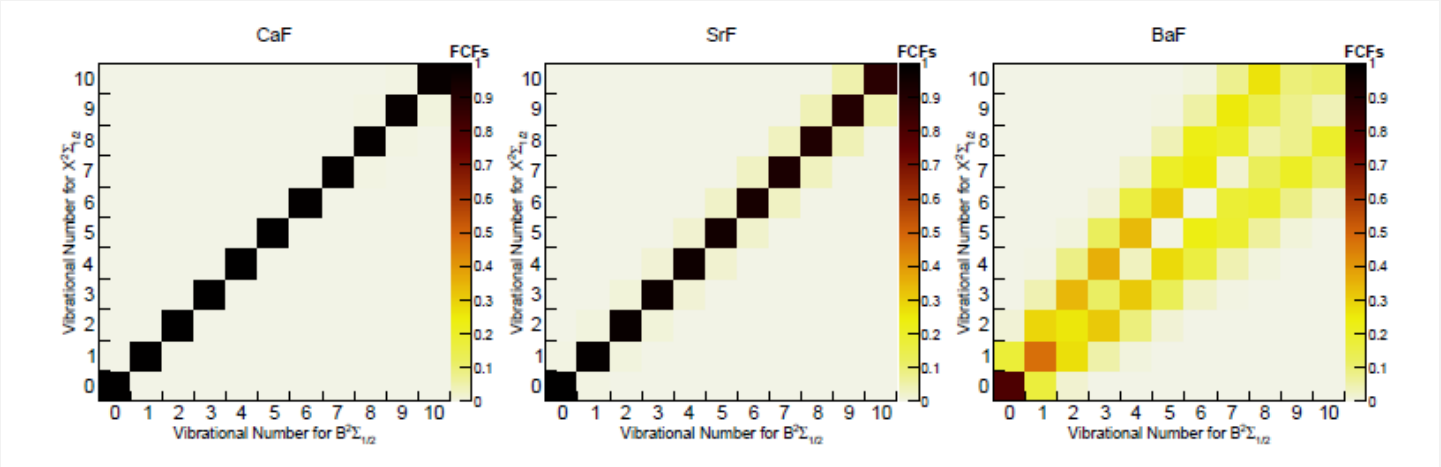

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Nope ☹

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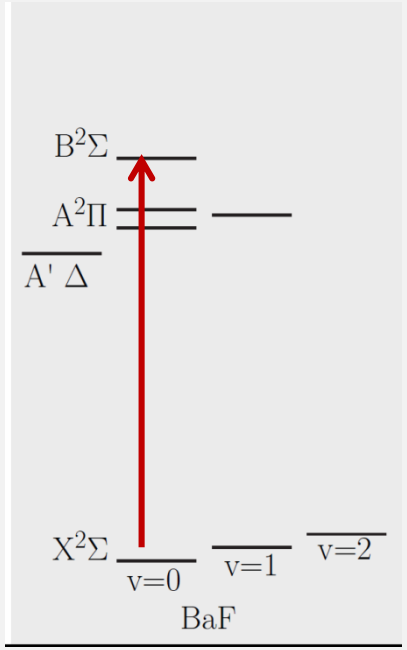

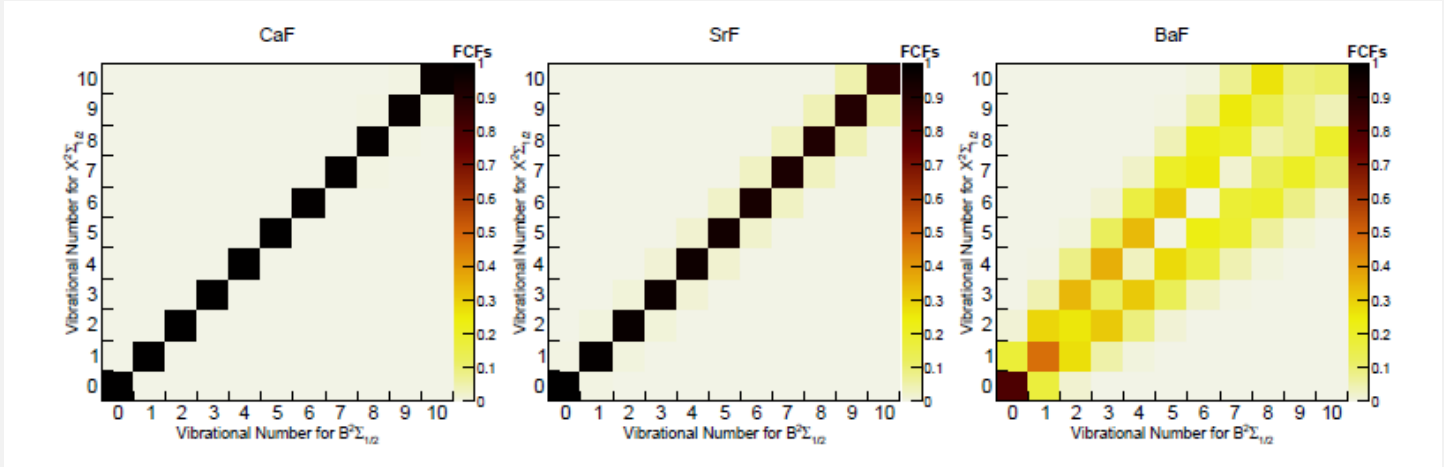

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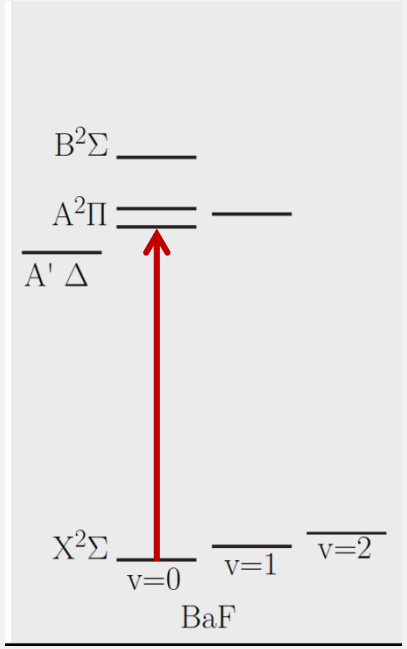

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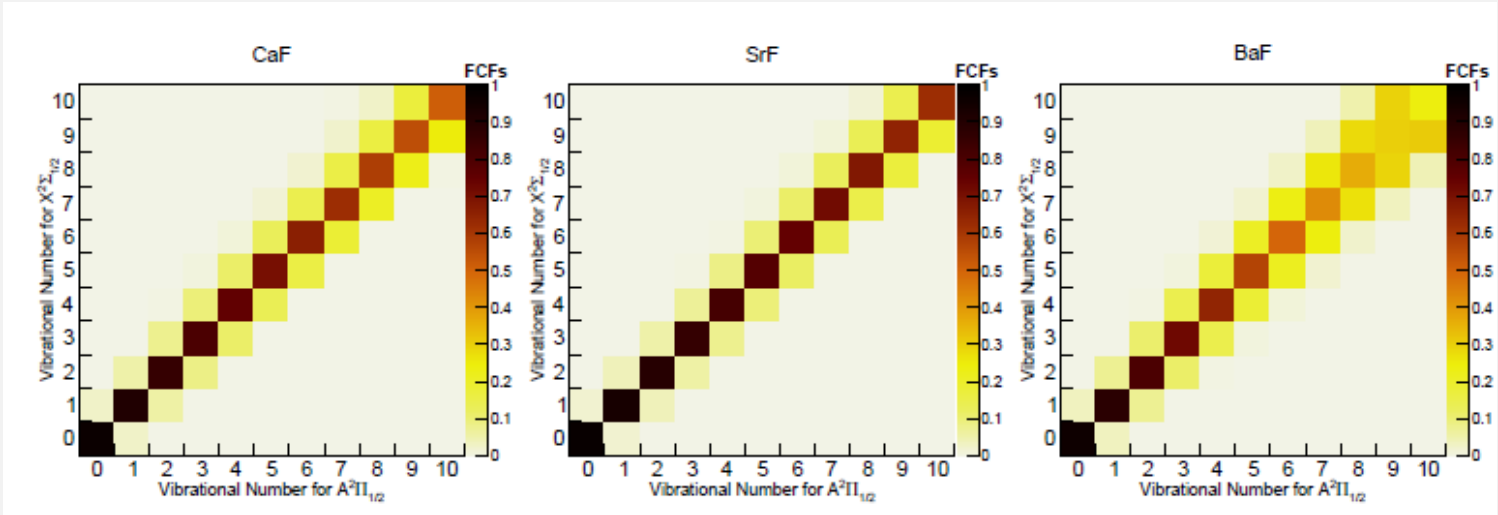

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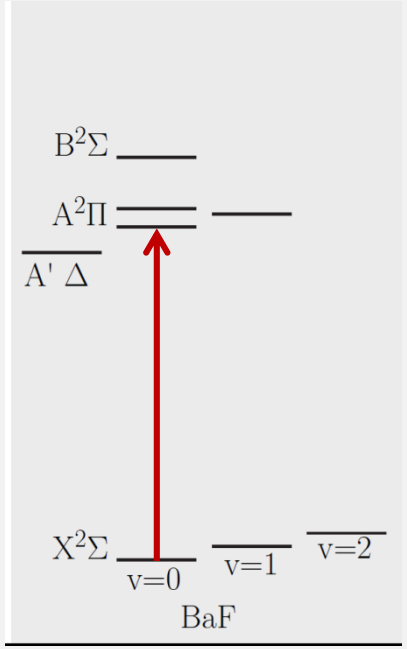
Yes! ☺



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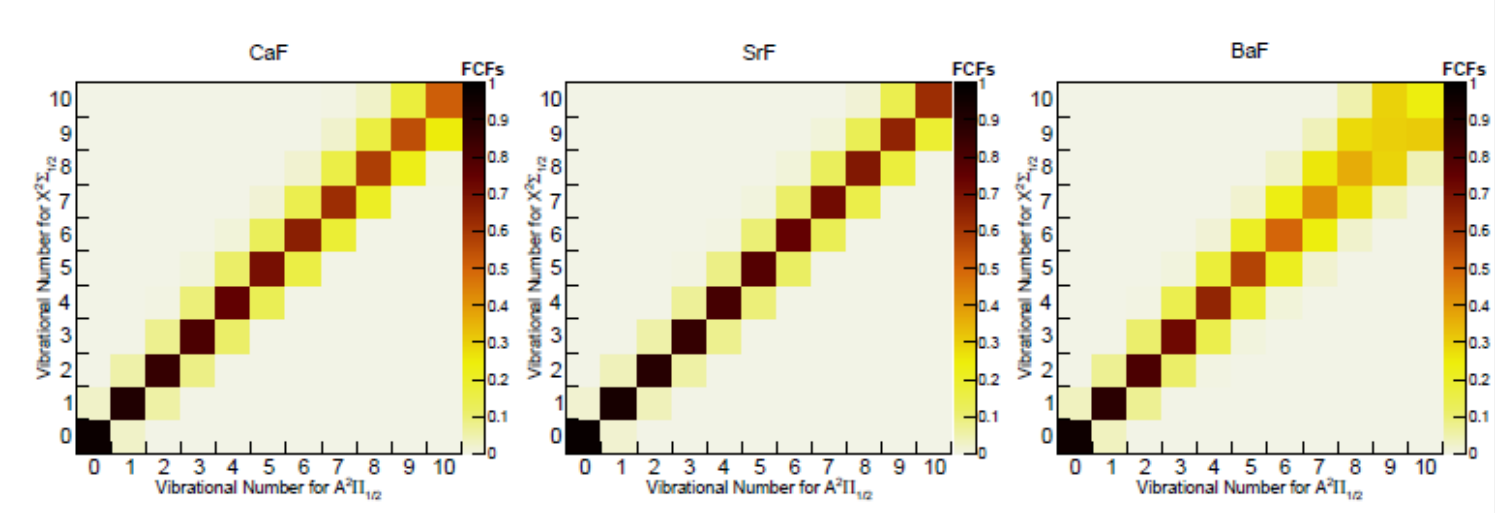
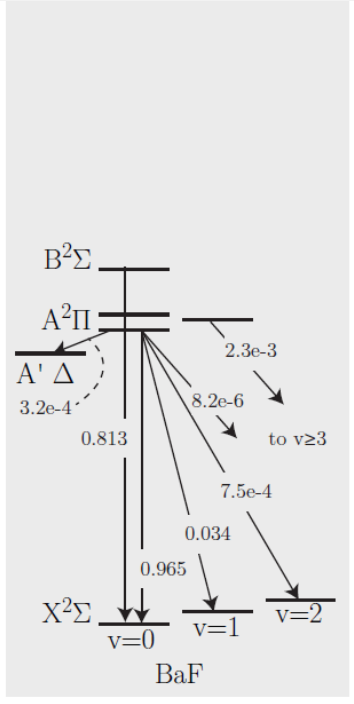
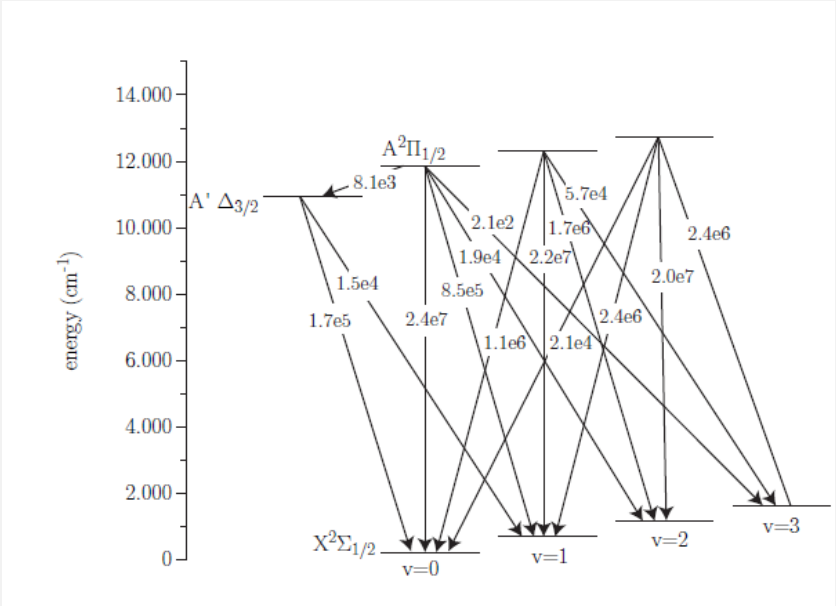


Cooling scheme:

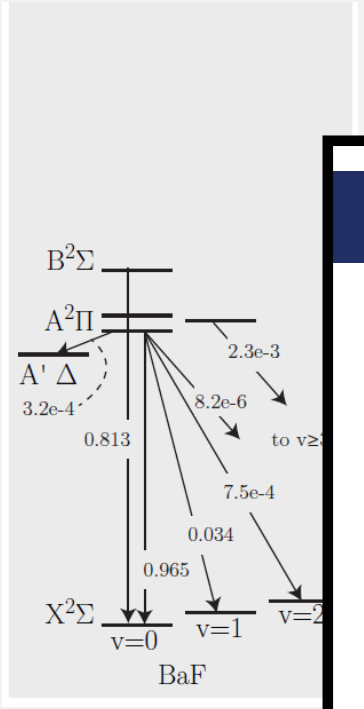




Yongliang Hao

Transition	Repump	CaF	SrF	BaF
$X-A$	no repump	25	36	19
	$v=1$ repump	7.9×10^2	1.6×10^3	6.4×10^2
	$v=2$ repump	2.2×10^4	6.2×10^4	2.1×10^3
	Δ repump			7.6×10^4
$X-B$	no repump	4.0×10^3	1.9×10^2	3.4
	$v=1$ repump	4.1×10^3	3.8×10^4	43

Cooling scheme:



The Journal of Chemical Physics ARTICLE scitation.org/journal/jcp

High accuracy theoretical investigations of CaF, SrF, and BaF and implications for laser-cooling

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Yongliang Hao,[1,2] Lukáš F. Pašteka,[3] Lucas Visscher,[4] Parul Aggarwal,[1,2] Hendrick L. Bethlem,[5] Alexander Boeschoten,[1,2] Anastasia Borschevsky,[1,2,a)] Malika Denis,[1,2] Kevin Esajas,[1,2] Steven Hoekstra,[1,2] Klaus Jungmann,[1,2] Virginia R. Marshall,[1,2] Thomas B. Meijknecht,[1,2] Maarten C. Mooij,[5] Rob G. E. Timmermans,[1,2] Anno Touwen,[1,2] Wim Ubachs,[5] Lorenz Willmann,[1,2] Yanning Yin,[1,2] and Artem Zapara[1,2] (NL-*e*EDM Collaboration)

14.000

$X = B$	no repump	4.0×10	1.9×10	3.4
	$v = 1$ repump	4.1×10^3	3.8×10^4	43

Interpreting the experiment

$$\hat{H}^{\mathrm{P,T}} = (W_d d_e + W_s k_s)\hat{\mathbf{S}} \cdot \hat{\mathbf{n}}$$

d_e- electron EDM, κ_s - *S-PS* electron-nucleon interaction

W_d, W_s- molecule (and state) specific enhancement factors; depend on electronic structure and must come from theory.

$$\Delta E = (W_d d_e + W_s \kappa_s) < \hat{S} \cdot \hat{n} > (E_{\mathrm{ext}})$$

Interpreting the experiment

$$\hat{H}^{\mathrm{P,T}} = (W_d d_e + W_s k_s)\hat{\mathbf{S}} \cdot \hat{\mathbf{n}}$$

$$\Delta E = (W_d d_e + W_s \kappa_s) < \hat{S} \cdot \hat{n} > (E_{\mathrm{ext}})$$

d_e- electron EDM, κ_s - *S-PS* electron-nucleon interaction

Electric dipole moments: A global analysis

Timothy Chupp and Michael Ramsey-Musolf
Phys. Rev. C **91**, 035502 – Published 6 March 2015

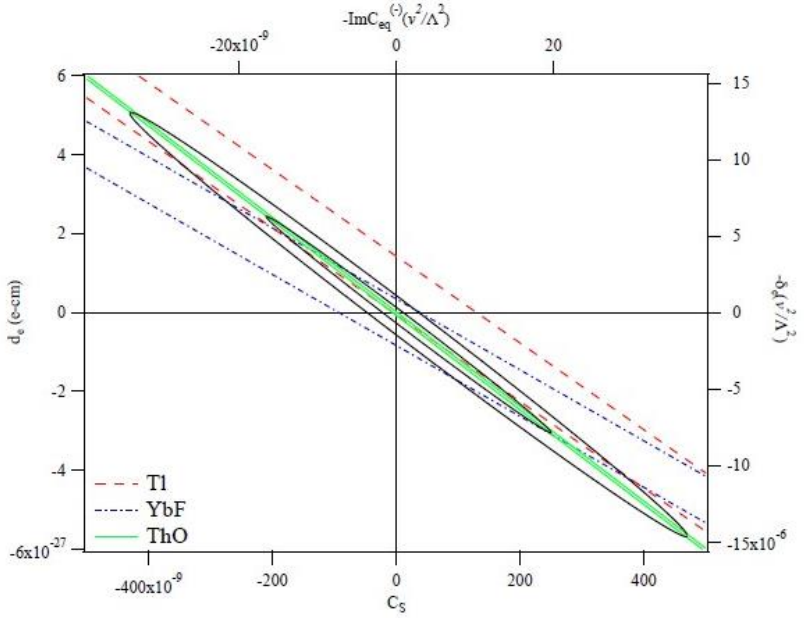


FIG. 1: Electron edm d_e as a function of C_S from the experimental results in Tl, YbF and ThO. Also shown are 68% and 95% error ellipses representing the best-fit for the paramagnetic systems and including $d_A(^{199}\mathrm{Hg})$ as discussed in the text. Also shown are the constraints on the dimensionless Wilson coefficients δ_e and $\mathrm{Im}\, C_{eq}^{(-)}$ times the squared scale ratio $(v/\Lambda)^2$.

Investigations of optimal combinations of molecules:

- K. Gaul, S. Marquardt, T. Isaev, and R. Berger, Phys. Rev. A **99**, 032509 (2019)
- A . Sunaga, M. Abe, V. S. Prasannaa, T. Aoki, and M. Hada, J. Phys. B **53**, 015102 (2019)

Interpreting the experiment

$$\hat{H}^{\mathrm{P,T}} = (W_d d_e + W_s k_s)\hat{\mathbf{S}} \cdot \hat{\mathbf{n}}$$

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

$$W_d = \frac{1}{d_e} \langle \psi_\Omega | H^{\mathrm{EDM}} | \psi_\Omega \rangle$$

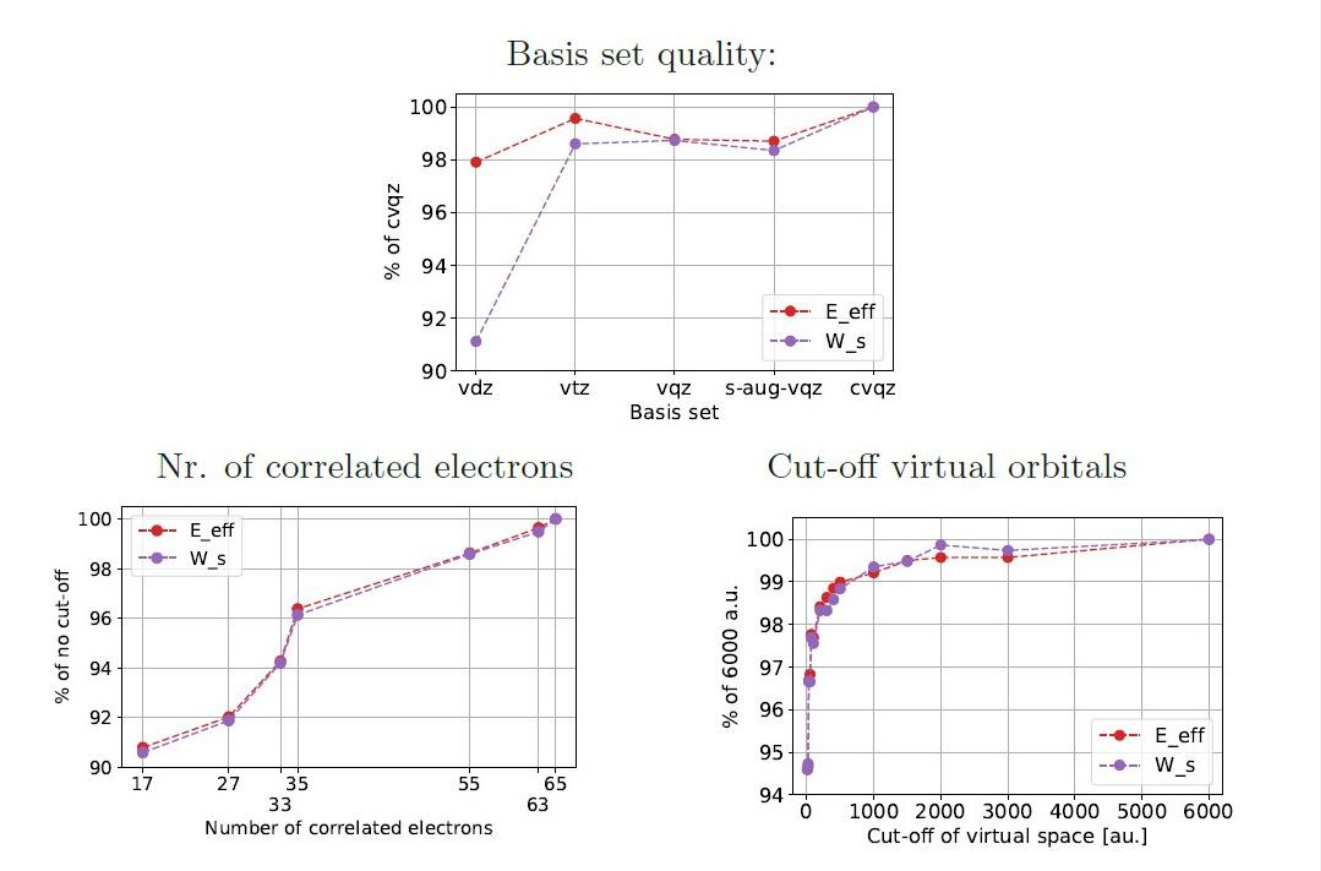
$$H_S = i\frac{G_F}{\sqrt{2}} Z\kappa_s \sum_{i=1}^{n} \gamma^0\gamma^5\rho_A(r_i)$$

$$W_S = \frac{1}{\kappa_s} \frac{1}{\Omega} \langle \psi_\Omega | H_S | \psi_\Omega \rangle$$

- Use relativistic CCSD(T) to calculate W_d and W_s.
- Systematically improve the calculation up to convergence
- Perform an extensive computational study to estimate uncertainties

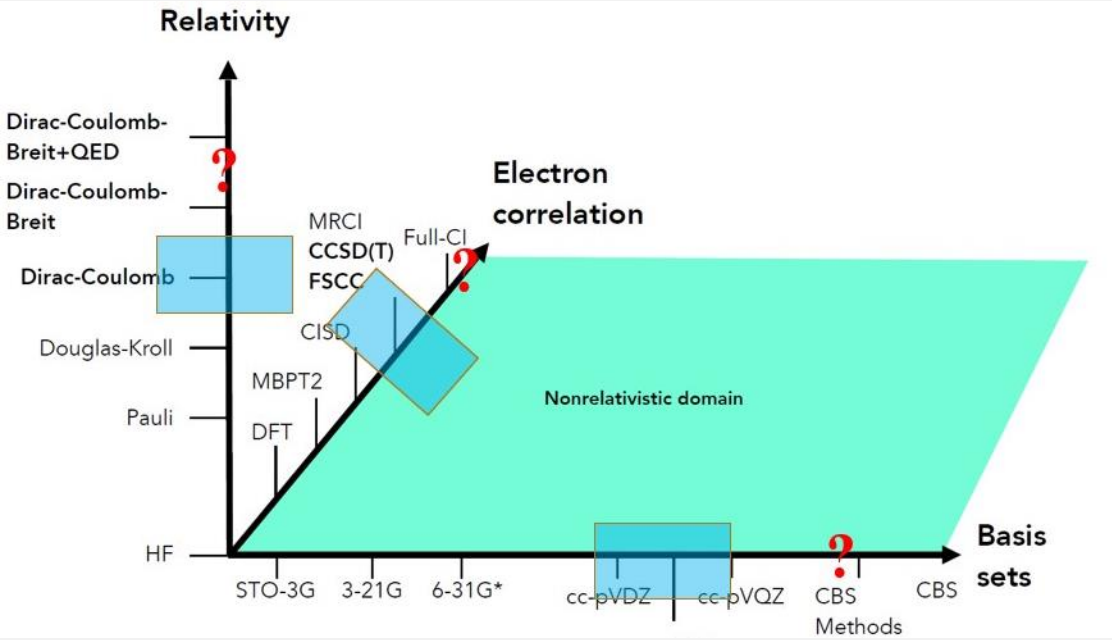
Interpreting the experiment

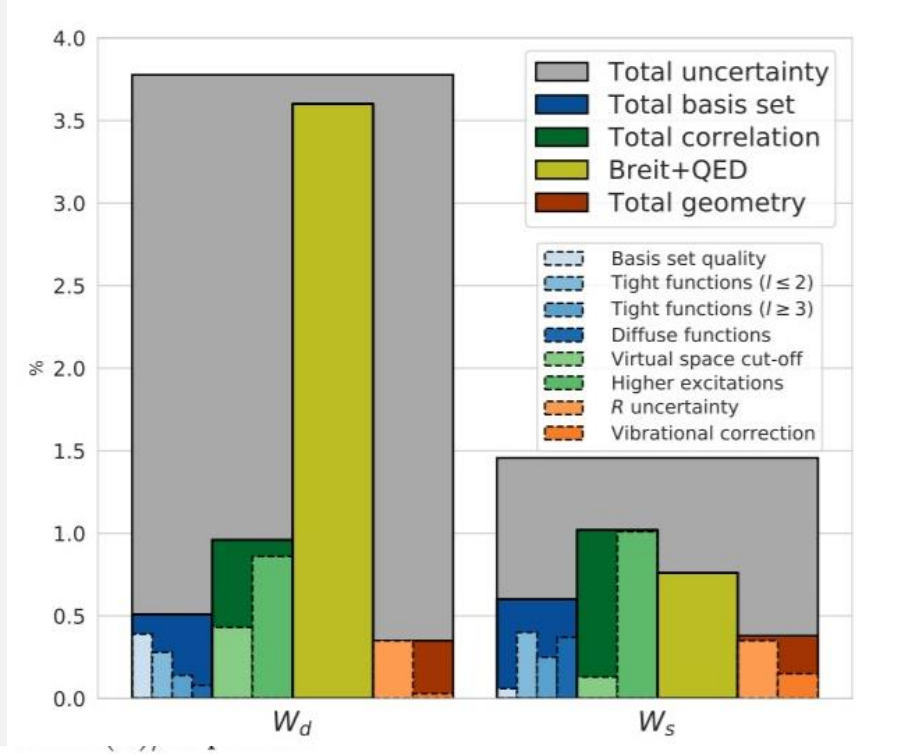
- Use relativistic CCSD(T) to calculate W_d and W_s.
- Systematically improve the calculation up to convergence



Interpreting the experiment

- Use relativistic CCSD(T) to calculate W_d and W_s in BaF
- Systematically improve the calculation up to convergence
- Perform an extensive computational study to estimate uncertainties





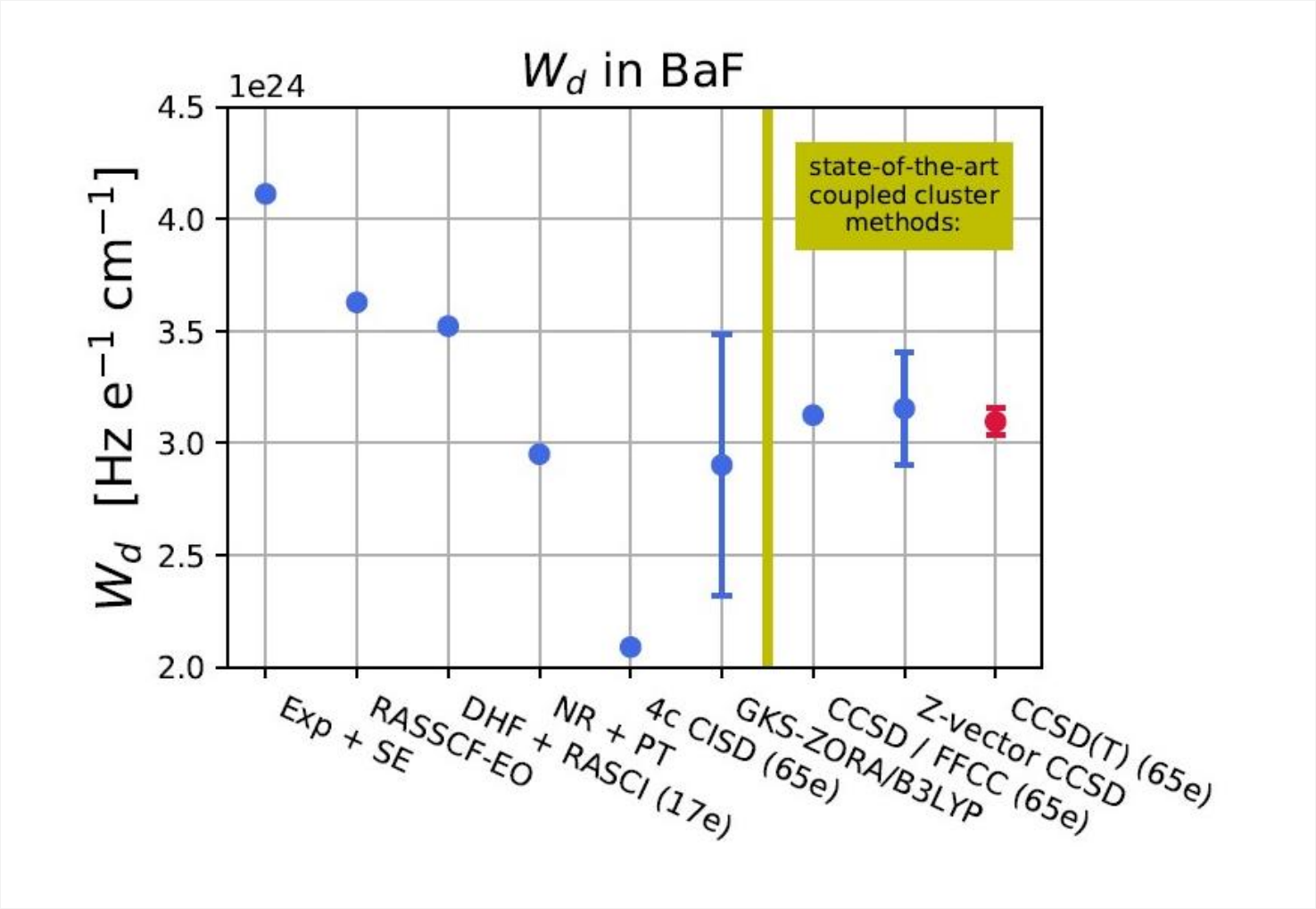
Source	Estimation scheme	δW_d	δW_s
Basis set			
Quality	(vqz - vtz)/2	0.012	0.005
Diffuse funct.	s-aug-vqz - vqz	0.002	0.031
Tight funct. $l \leq 2$	(s, p, d)	0.009	0.033
Tight funct. $l \geq 3$	aeqz - cvqz	0.004	0.021
Correlation			
Virtual space cut-off	6000 a.u - 2000 a.u.	0.014	0.011
Higher excitations	(CCSD−T - CCSD+T)·2	0.027	0.084
Relativity			
Breit+QED	(DC+ΔG - DC)·2	0.113	0.064
Geometry			
R uncertainty	R - (R - δR) (aetz)	0.011	0.029
Vibrational effects	R_e - v_0 (aetz)	0.001	0.013
Total			
sum	$\sqrt{\Sigma_i \delta_i^2}$	0.119	0.122
%		3.79	1.47

Interpreting the experiment

- Final recommended values:

BaF	W_d^* $[\frac{10^{24}\text{Hz}}{\text{e cm}}]$	W_s [Hz]
DC CCSD(T)	3.13 (3.8%)	8.29 (1.5%)

Pi Haase



Interpreting the experiment

- Final recommended values:

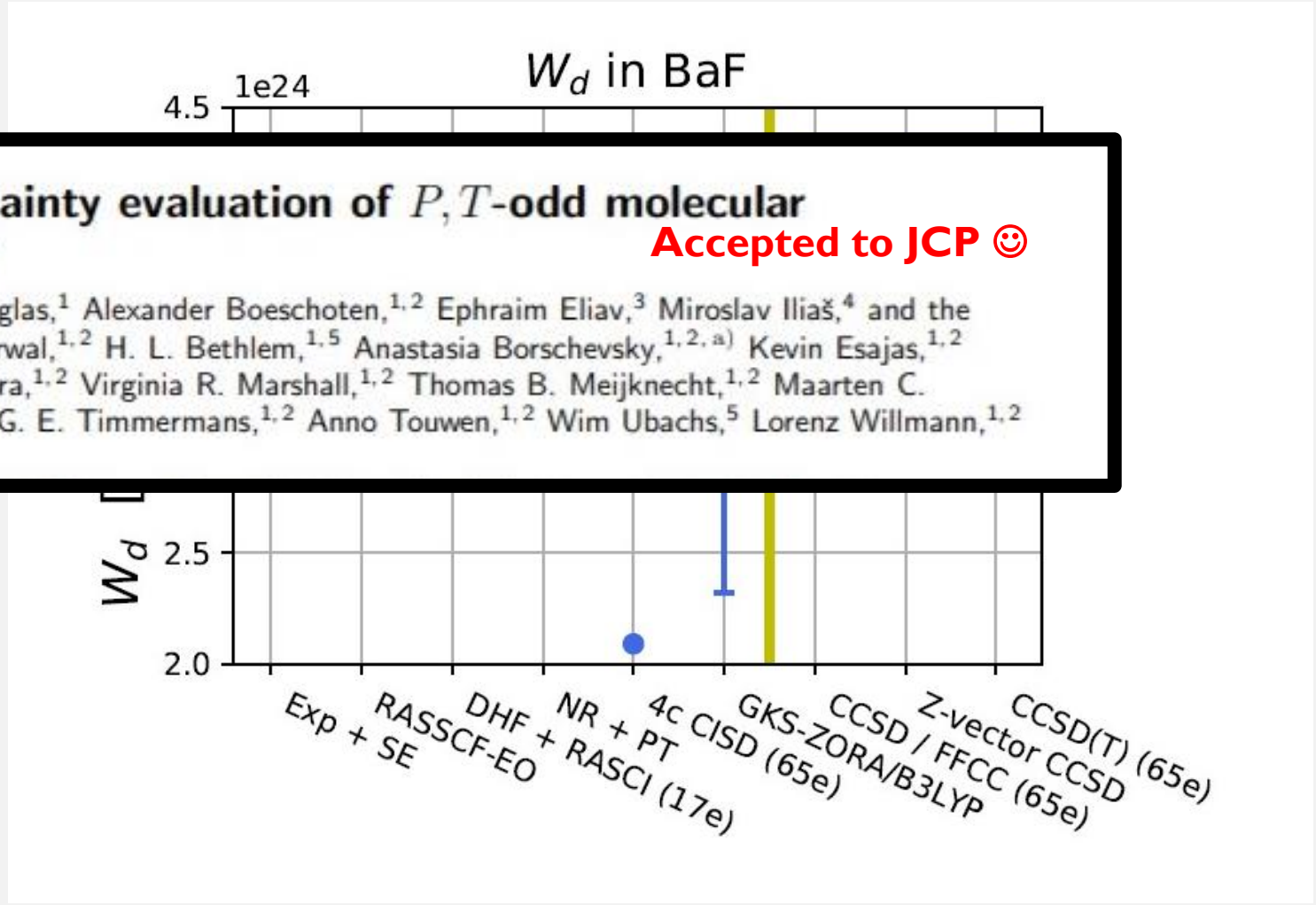
Ba	
DC CCS	

Systematic study and uncertainty evaluation of P,T-odd molecular enhancement factors in BaF

Accepted to JCP ☺

Pi A. B. Haase,[1,2] Diewertje J. Doeglas,[1] Alexander Boeschoten,[1,2] Ephraim Eliav,[3] Miroslav Iliaš,[4] and the eEDM collaboration:,[1,2] Parul Aggarwal,[1,2] H. L. Bethlem,[1,5] Anastasia Borschevsky,[1,2,a)] Kevin Esajas,[1,2] Yongliang Hao,[1,2,b)] Steven Hoekstra,[1,2] Virginia R. Marshall,[1,2] Thomas B. Meijknecht,[1,2] Maarten C. Mooij,[2,5] Kees Steinebach,[1,c)] Rob G. E. Timmermans,[1,2] Anno Touwen,[1,2] Wim Ubachs,[5] Lorenz Willmann,[1,2] and Yanning Yin[1,2,d)]

Pi Haase



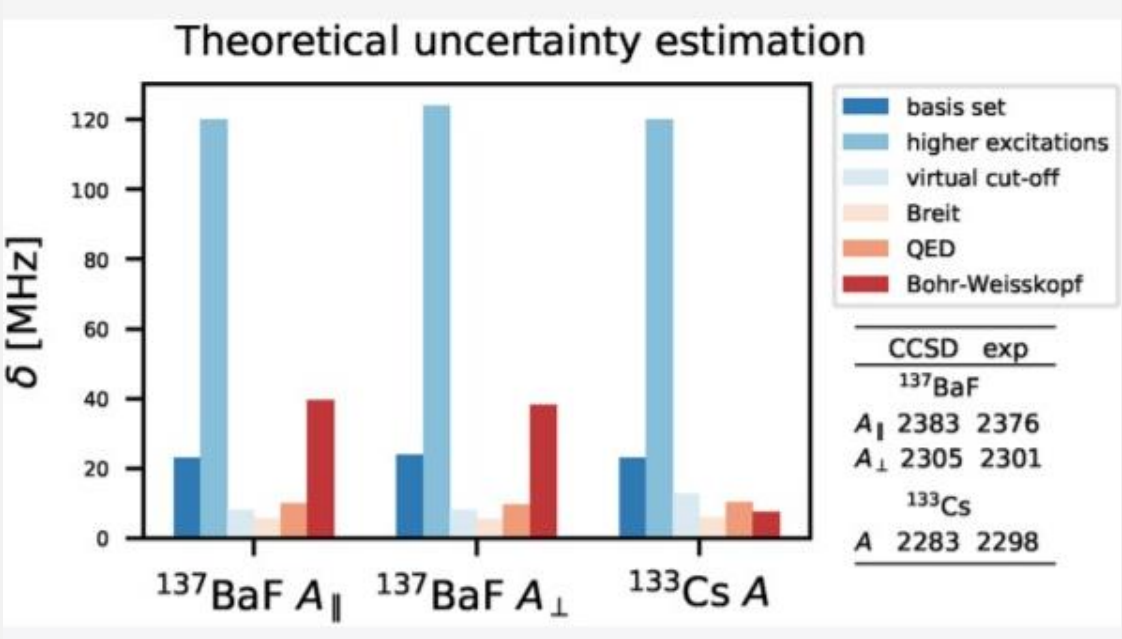
Interpreting the experiment

BaF	W_d^* $[\frac{10^{24}\text{Hz}}{\text{e cm}}]$	W_s [Hz]
DC CCSD(T)	3.13 (3.8%)	8.29 (1.5%)

- Is the uncertainty estimate realistic?
- Use a similar property, where comparison to experiment is possible, as a sanity check
- Magnetic hyperfine structure constants

Table 8. $A_\parallel$ and $A_\perp$ of ^{137}Ba in BaF (MHz)

	^{137}BaF			
method	$A_\parallel$	%(exp)	$A_\perp$	%(exp)
GRECP SCF-EO[90]	2264	−4.71	2186	−5.00
GRECP RASSCF-EO[90]	2272	−4.38	2200	−4.39
DF RASCI[91]	2240	−5.72	2144	−6.82
DF MBPT[91]	2314	−2.61	2254	−2.04
DC CCSD (this work)	2383(129)	0.29	2305(132)	0.17
exp[77]	2376(12)		2301(9)	



Interpreting the experiment

- Is the uncertainty estimate realistic?

Pi Haase

THE JOURNAL OF PHYSICAL CHEMISTRY A

ACS AUTHORCHOICE

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Article

Hyperfine Structure Constants on the Relativistic Coupled Cluster Level with Associated Uncertainties

Pi A. B. Haase,* Ephraim Eliav, Miroslav Iliaš, and Anastasia Borschevsky

Cite This: *J. Phys. Chem. A* 2020, 124, 3157–3169

Read Online

NEW STUFF

IP of RaF

Laser-cooled RaF as a promising candidate to measure molecular parity violation

T. A. Isaev, S. Hoekstra, and R. Berger
Phys. Rev. A **82**, 052521 – Published 24 November 2010

Article | Open Access | Published: 27 May 2020

Spectroscopy of short-lived radioactive molecules

R. F. Garcia Ruiz, R. Berger, [...]X. F. Yang

Nature **581**, 396–400 (2020) | Cite this article

Approaching meV level for transition energies in the radium monofluoride molecule RaF and radium cation Ra^+ by including quantum-electrodynamics effects

J. Chem. Phys. **154**, 201101 (2021); https://doi.org/10.1063/5.0053659

Leonid V. Skripnikov[a)]

PHYSICAL REVIEW LETTERS

Highlights Recent Accepted Collections Authors Refe

Accepted Paper

Isotope shifts of radium monofluoride molecules

Phys. Rev. Lett.

S. M. Udrescu et al.

Accepted 19 May 2021

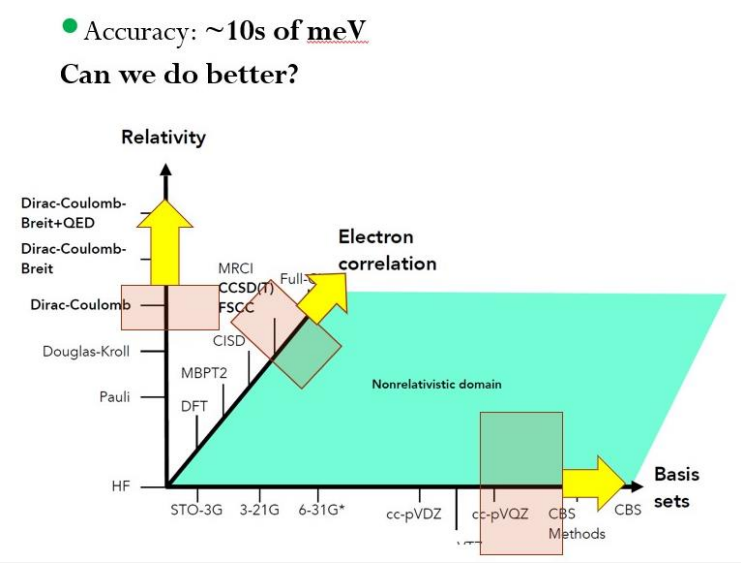
Nuclear magnetization distribution effect in molecules: Ra^+ and RaF hyperfine structure

J. Chem. Phys. **153**, 114114 (2020); https://doi.org/10.1063/5.0024103

Leonid V. Skripnikov[1,2,a)]

IP of RaF

- Aim for highest accuracy: 4c CCSD(T)+higher order corrections

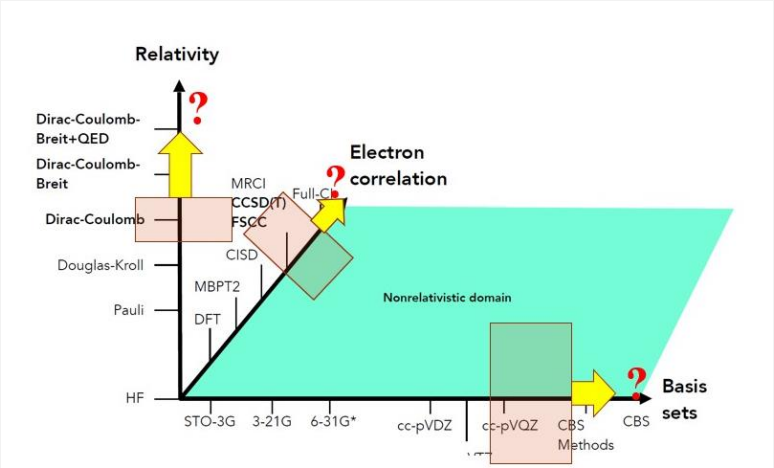


Method/contribution	IP (eV)	Contribution (eV)
4c-CCSD (s-cv4z)	4.926	
4c-CCSD(T) (s-cv4z)	4.972	0.046
4c-CCSD(T) (CBS)	4.978	0.006
4c-CCSDT (CBS)	4.980	0.002
4c-CCSDT (CBS)+Breit*	4.982	0.002
4c-CCSDT (CBS)+Breit+QED*	4.970	-0.012
Correction for final active space	4.977	0.007
Final prediction	**4.977**	

*Obtained for Ra^+

IP of RaF

- Uncertainty evaluation



Type	Source	IP (eV)	How?
Basis set	Extrapolation error	0.003	(CBS- s-cv4z)/2
	Diffuse functions	0.001	(d-v4z – sv4z)/2
	Basis type	0.003	v3z vs. ae3z
Relativity	Higher order QED	0.005	Δlamb/2
Correlation	Correlation space	0.002	all e- vs. 35 e
	Higher excitations	0.001	(T-(T))/2
Total uncertainty		**0.010**	

IP of RaF

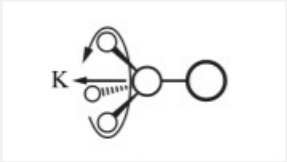
- Final recommended value for adiabatic IP: **4.977+/- 0.010**
- Waiting for experimental confirmation (or disproof)

Aleksandra Kiuberis

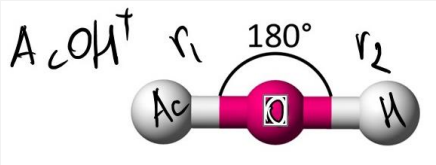
Polyatomic molecules

- On Monday we learned: polyatomic molecules are awesome
- We agree

- Molecules to investigate:



  - $BaCH_3, YbCH_3$: symmetric top molecules
  - $AcOH^+$: linear system



- Could be used in experiments to measure eEDM (but also NMQM, or anapole moments, etc.)
- Investigate sensitivity to eEDM

Polyatomic molecules

- For polyatomic molecules computational costs play an important role
- Two step process:
  - Geometry optimisation: scalar relativistic approach, pseudopotentials, CCSD(T)
  - Calculations of sensitivity parameters: 4c-CCSD(T)/FSCC, error estimate
- Makes the calculations feasible

Polyatomic molecules

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- Two step process:
  - **Geometry optimisation: scalar relativistic approach, pseudopotentials, CCSD(T)**
  - Calculations of sensitivity parameters: 4c-CCSD(T)/FSCC, error estimate
- Makes the calculations feasible

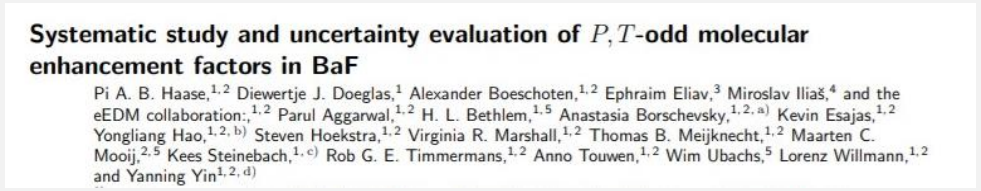
Molecule	*M*—C(Å)	C—H(Å)	*M*CH (°)
$BaCH_3$	2.55	1.10	113
$YbCH_3$	2.39	1.09	112

SR-CCSD(T) level of theory with ANO-RCC-PV*n*Z basis set; $n = 5$ for $BaCH_3$ and $n = 4$ for $YbCH_3$.

r_1	2.057
r_2	0.957

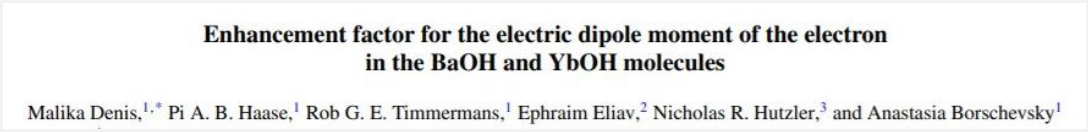
Polyatomic molecules

- For polyatomic molecules computational costs play an important role
- Two step process:
  - Geometry optimisation: scalar relativistic approach, pseudopotentials, CCSD(T)
  - **Calculations of sensitivity parameters: 4c-CCSD(T)/FSCC, error estimate**
- Makes the calculations feasible



Systematic study and uncertainty evaluation of P,T-odd molecular enhancement factors in BaF

Pi A. B. Haase,[1,2] Diewertje J. Doeglas,[1] Alexander Boeschoten,[1,2] Ephraim Eliav,[3] Miroslav Iliaš,[4] and the eEDM collaboration:,[1,2] Parul Aggarwal,[1,2] H. L. Bethlem,[1,5] Anastasia Borschevsky,[1,2,a)] Kevin Esajas,[1,2] Yongliang Hao,[1,2,b)] Steven Hoekstra,[1,2] Virginia R. Marshall,[1,2] Thomas B. Meijknecht,[1,2] Maarten C. Mooij,[2,5] Kees Steinebach,[1,c)] Rob G. E. Timmermans,[1,2] Anno Touwen,[1,2] Wim Ubachs,[5] Lorenz Willmann,[1,2] and Yanning Yin[1,2,d)]



Enhancement factor for the electric dipole moment of the electron in the BaOH and YbOH molecules

Malika Denis,[1,*] Pi A. B. Haase,[1] Rob G. E. Timmermans,[1] Ephraim Eliav,[2] Nicholas R. Hutzler,[3] and Anastasia Borschevsky[1]

	W_d [GV/cm]
$BaCH_3$	**3.45 (4.5%)**
BaF*	3.31 (3.8%)
BaOH**	3.21 (3.2 %)
$YbCH_3$	**14.0 (3.6 %)**
YbF**	11.8
YbOH**	11.7 (4.3%)
$AcOH^+$	**27.8**

Polyatomic molecules

- For polyatomic molecules computational co… important role
- Two step process:
  - Geometry optimisation: scalar relativistic… opotentials, CCSD(T)
  - **Calculations of sensitivity para… SD(T)/FSCC, error estimate**

Preliminary Values

Aleksandra Kiuberis

	W_d [GV/cm]
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$AcOH^+$	**27.8**

Yuly Andrea Chamorro Mena

P,T-odd molecular

Ephraim Eliav,[3] Miroslav Iliaš,[4] and the
stasia Borschevsky,[1,2,a)] Kevin Esajas,[1,2]
Thomas B. Meijknecht,[1,2] Maarten C.
ouwen,[1,2] Wim Ubachs,[5] Lorenz Willmann,[1,2]

ole moment of the electron
molecules

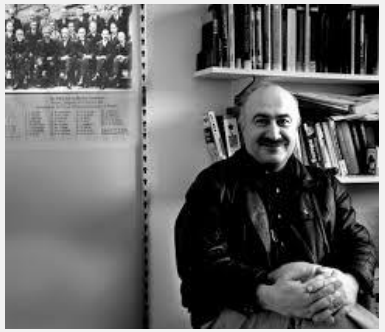
er,[3] and Anastasia Borschevsky[1]

CONCLUSIONS

- State of the art high accuracy computational approach
- Versatile method: many possible applications
- Reliable predictions, uncertainty estimates possible
- Close collaborations with experimental groups

- These are very exciting times!

TEL AVIV UNIVERSITY
אוניברסיטת תל-אביב



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SYDNEY • AUSTRALIA

Victor Flambaum

Peter Schwerdtfeger

CTCP
Centre *for* Theoretical
Chemistry *and* Physics

RELATIVISTIC COUPLED CLUSTER

- Based on the 4c Dirac Hamiltonian
- Exponential wave operator:

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

- S is the excitation operator:

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

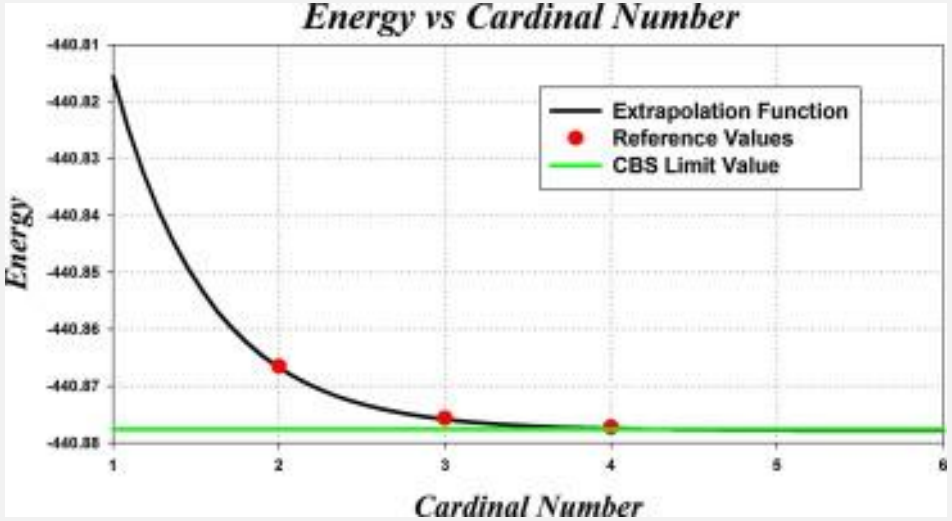
- CC energy equations:

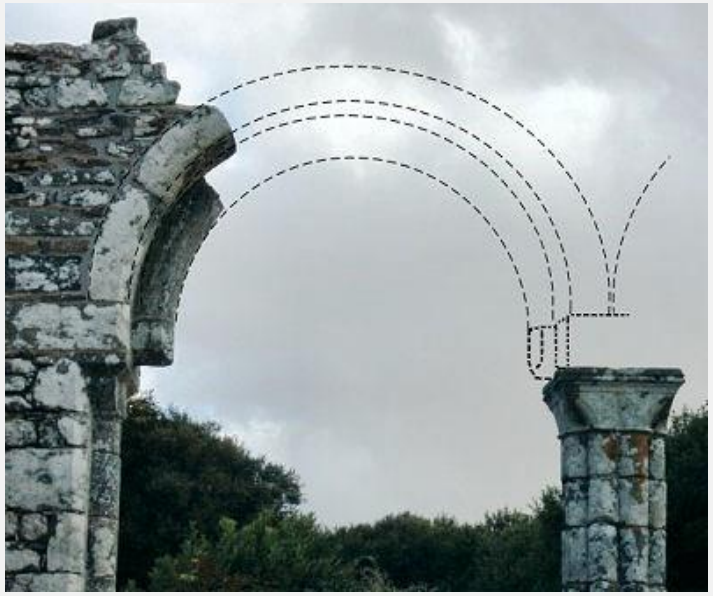
$$\langle \Phi_0 | (H - E_{\mathrm{CCSD}}) \exp(S_1 + S_2) | \Phi_0 \rangle = 0$$

- Accurate, all-order in PT, size-extensive, and size-consistent

Reaching meV accuracy

Complete basis set limit extrapolation





V. Vasilyev, http://sf.anu.edu.au/~vvv900/cbs