university of groningen

COMENIUS UNIVERSITY BRATISLAVA

QUANTUM CHEMISTRY AND EDMS

NIKHEF WORKSHOP: THEORY MEETS EXPERIMENT

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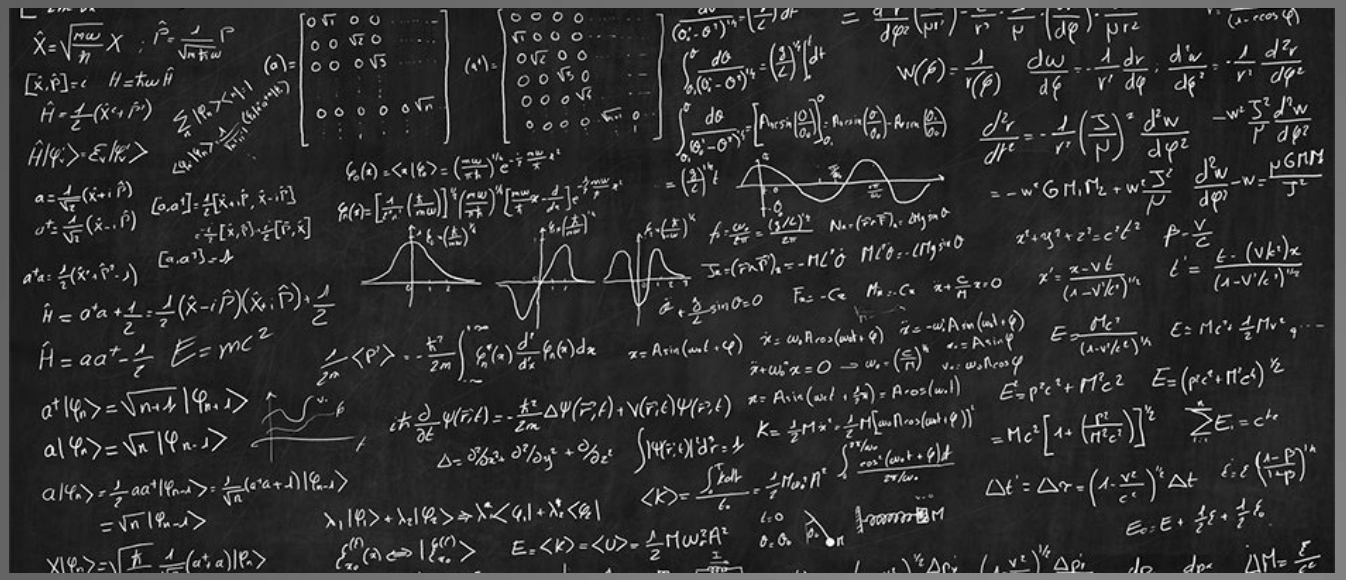
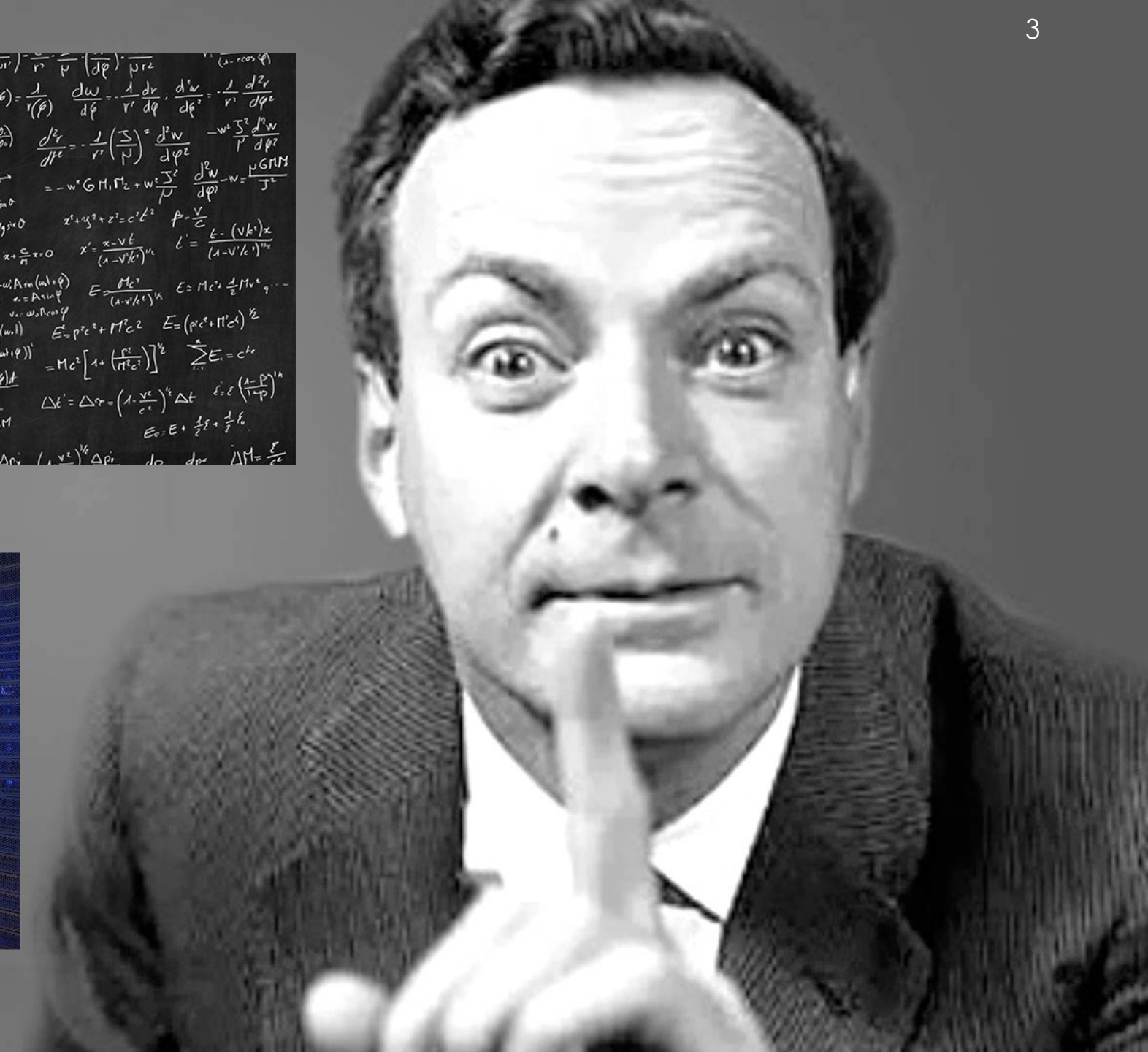
Intro

Why bother with theory?

- experiments are challenging and expensive
- small amounts of unstable, short-lived elements
- unprecedented sensitivity needed to detect the tiny effects of new physics
- special precautions are required (hazardous materials)
- practical considerations do not apply to theory
- alongside specially developed experimental techniques, theoretical support becomes crucial

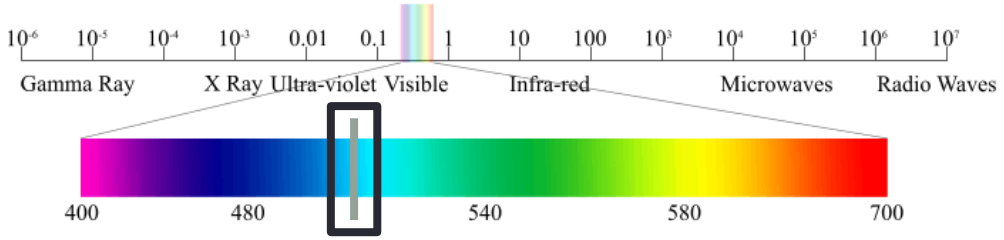




Where does theory fit?

- Identification of promising candidates for precision measurements
  - practical considerations (stability, laser-coolability, etc.)
  - high sensitivity to desired effect

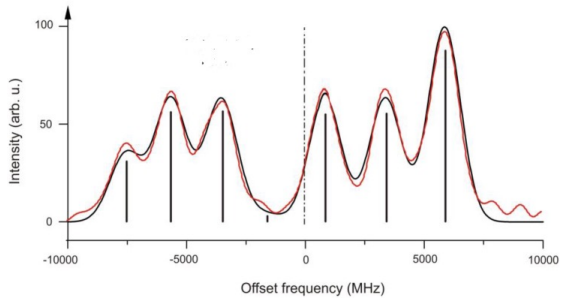
- Reliable predictions for planning the experiment

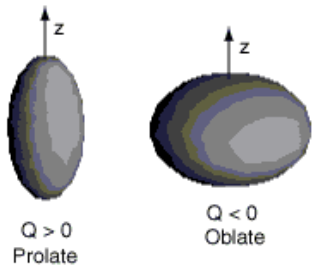


- Extraction of data from measurements

HFS

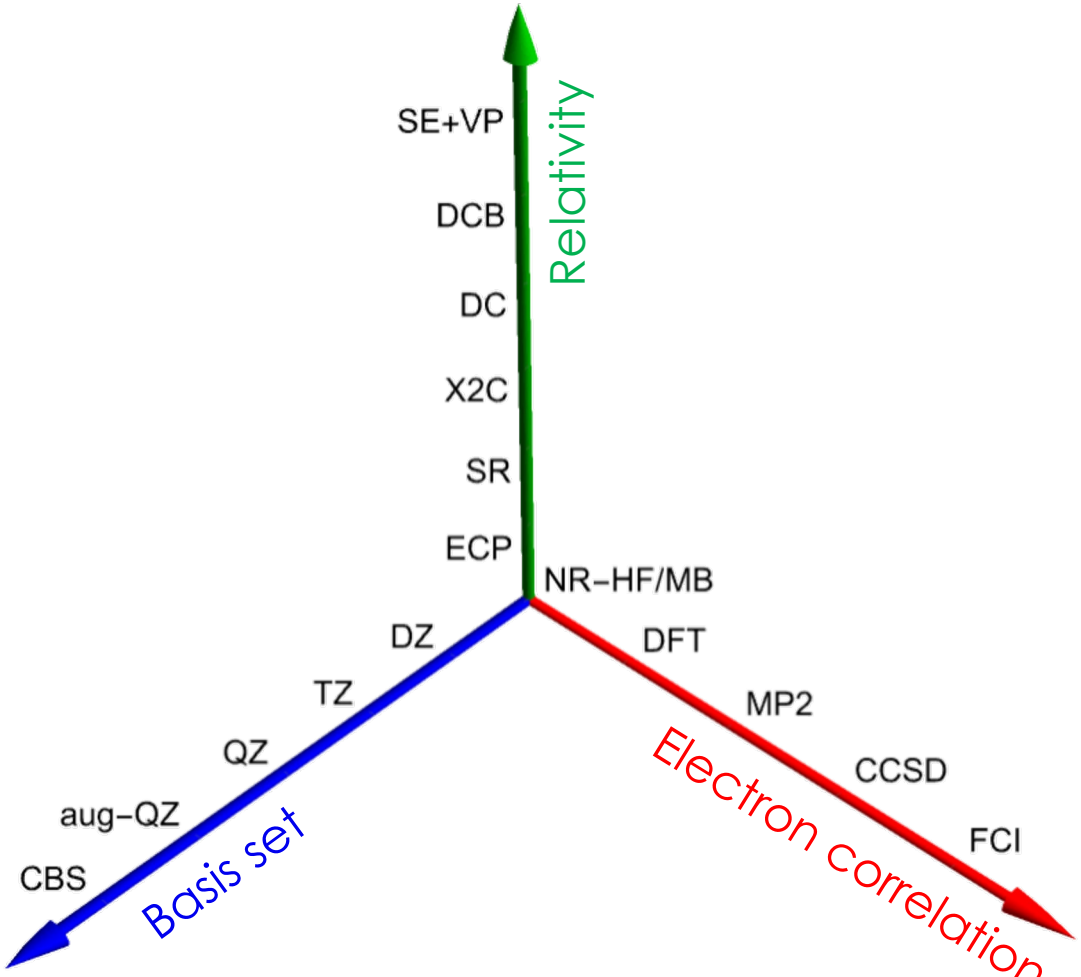
$B = eQ_s q$





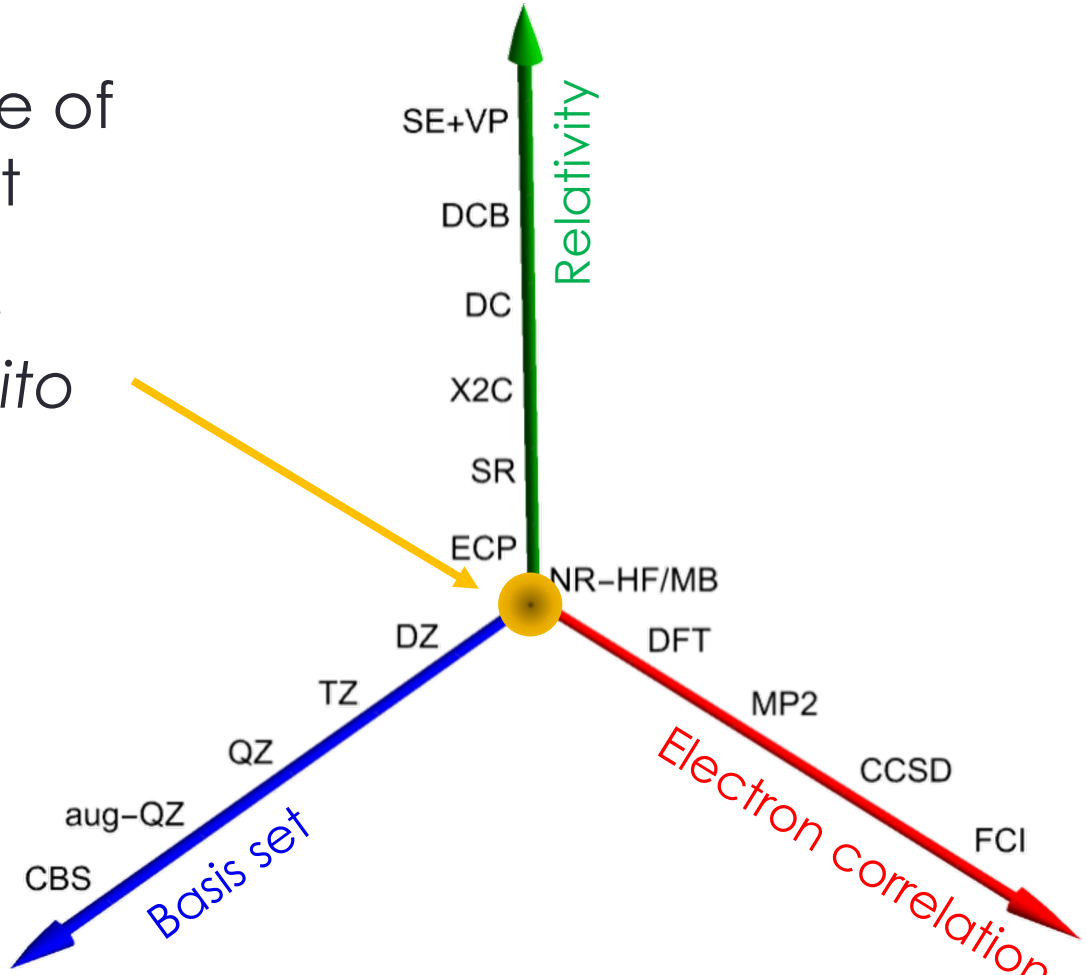
Computational methods
a general idea

Computational methods



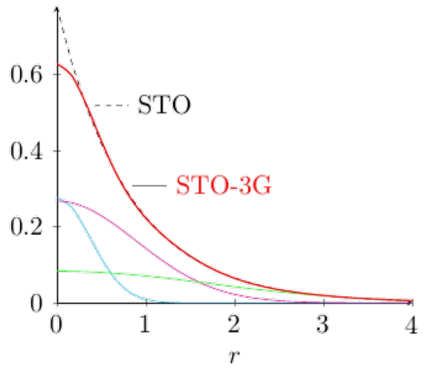
Computational methods

- systematic increase of accuracy and cost
- starting point is the cheapest still *ab inito* method
- computation is a balancing act

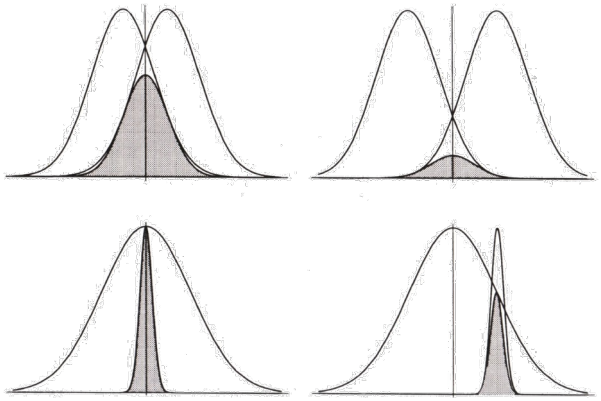


Computational methods

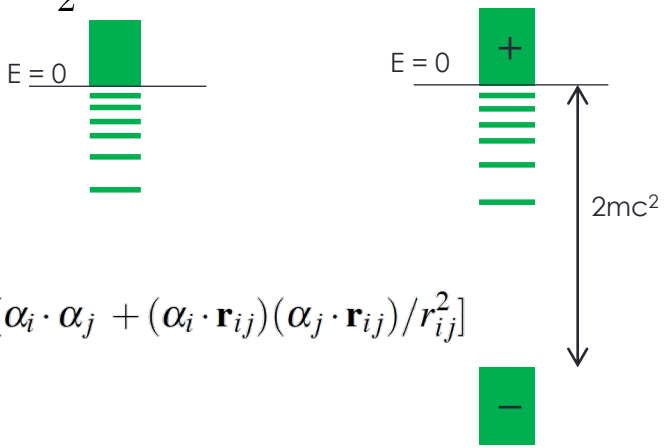
- vector space
- 1-electron expansion
- MO-LCAO
- atom and property specific
- Gaussian (radial) basis sets



$$G_{nlm}(r,\theta,\psi) = N_n \underbrace{r^{n-1}e^{-\alpha r^2}}_{\text{radial part}} \underbrace{Y_l^m(\theta,\psi)}_{\text{angular part}}$$



- i.e. Hamiltonian $H = \sum_i h_i + \sum_{i<j} h_{ij}$
- Schrödinger → Dirac → beyond
- $h_i = -\frac{1}{2}\nabla^2 + V_n \rightarrow h_i = c\alpha \cdot \mathbf{p} + \beta c^2 + V_n$



$$h_C = 1/r_{ij}$$

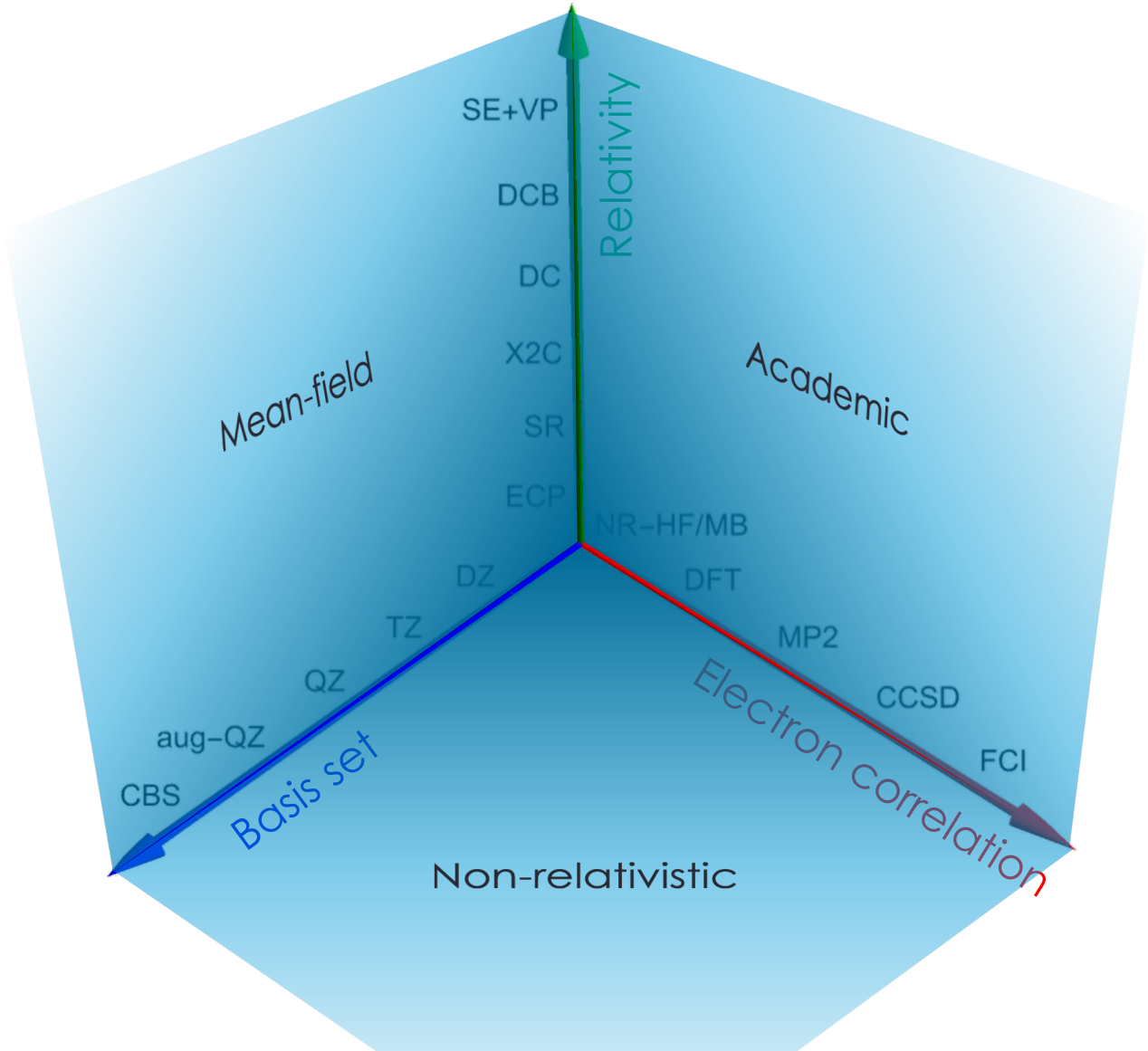
$$h_B = -\frac{1}{2r_{ij}}[\alpha_i \cdot \alpha_j + (\alpha_i \cdot \mathbf{r}_{ij})(\alpha_j \cdot \mathbf{r}_{ij})/r_{ij}^2]$$

- *N*-electron expansion (SD /CSF)
- post-HF methods
  - MP perturbation theory
  - configuration interaction $\psi = \sum_I C_I \Phi_I$
  - coupled cluster

$$\psi = \exp(T)\Phi$$

$$T = T_1 + T_2 + T_3 + \ldots + T_N$$

Computational methods

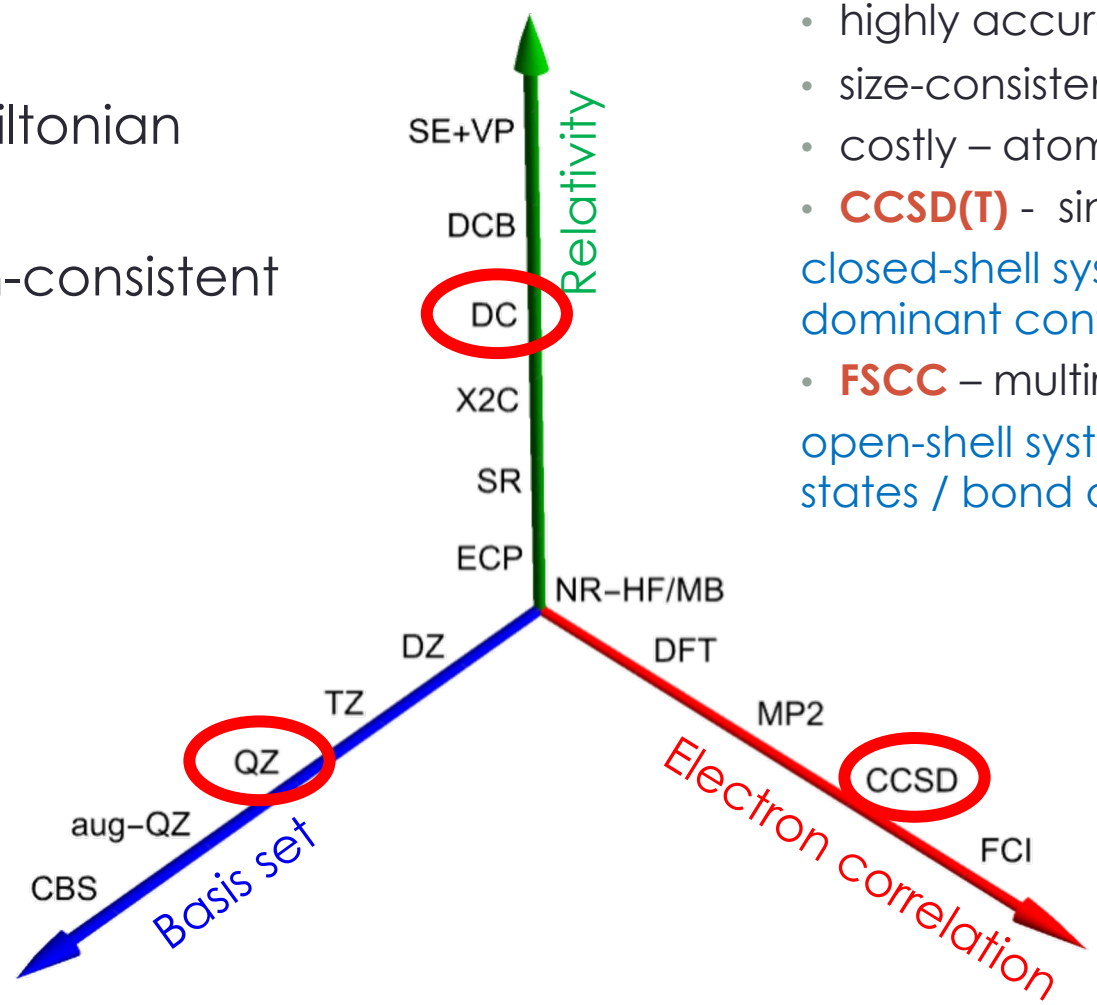


The right tool for the job

- Coupling parameters of *P*(*T*)-violating phenomena, variation of fundamental constants, …
  - relativistic in nature → relativistic methods
- Atomic and molecular parameters needed in experiments
  - heavy systems → relativistic methods
- High accuracy
  - state-of-the-art treatment of correlation + large basis sets
- Uncertainty estimates
  - robust and systematic methodology

Golden standard

- 4c Dirac-Coulomb Hamiltonian
- large flexible correlation-consistent basis sets
  - CBS extrapolation



- Coupled-Cluster
  - highly accurate
  - size-consistent
  - costly – atoms & small molecules
  - **CCSD(T)** - single reference CC

  closed-shell systems / systems with one dominant configuration (e.g. BaF, $X\ ^2\Sigma$)
  - **FSCC** – multireference Fock-space CC

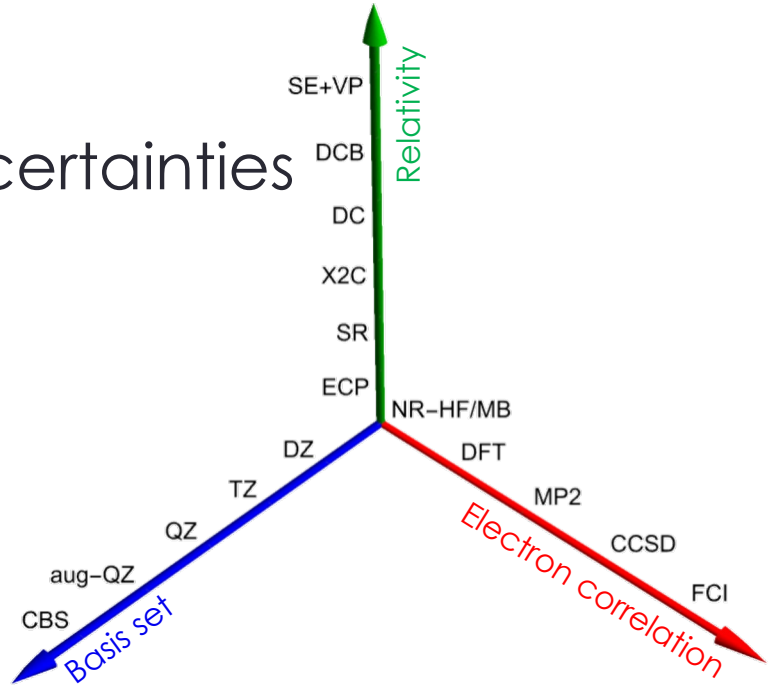
  open-shell systems / spectrum of excited states / bond dissociation

What can we calculate

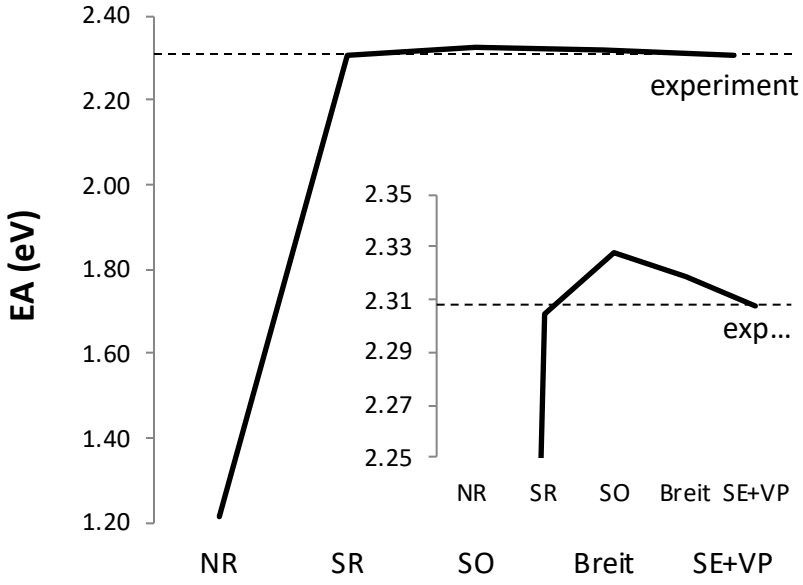
- Atomic properties
  - energies, IPs, EAs, spectra, HFS parameters, polarizabilities, …
- Molecular properties
  - geometries, spectroscopic constants, laser cooling schemes, …
- Properties for interpretation of precision measurements:
  - W_d, Ws (eEDM experiments)
  - W_A (NSD-PV, nuclear anapole moments)
  - W_M (NMQ moments)
  - E_{PV} (parity-violating energy shifts)
  - sensitivity to a-variation
- Expected accuracy
  - ~ 10 meV for energies, ~ 5 % for properties
  - can do better
- Systematic improvement and uncertainty evaluation

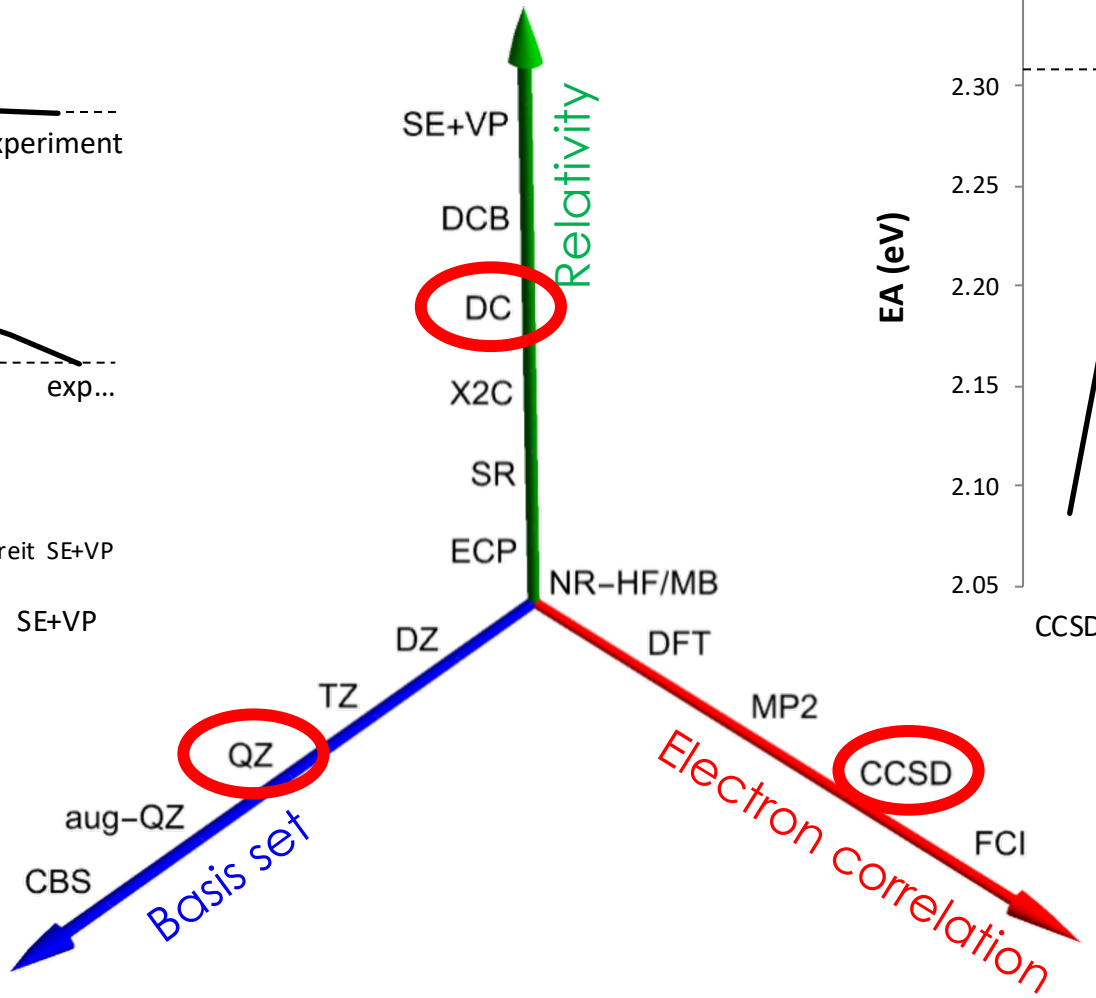
Uncertainty estimation

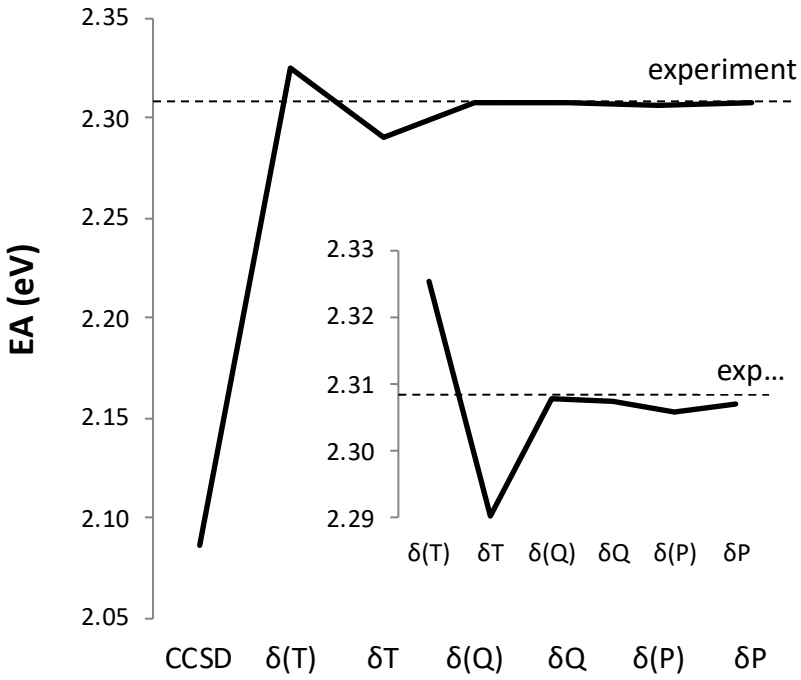
- Calculate the same property in a lighter homologue (and compare to experiment)
- Calculate a different property in the same atom/molecule (and compare to experiment)
- Perform a computational investigation to assign uncertainties based on method incompleteness



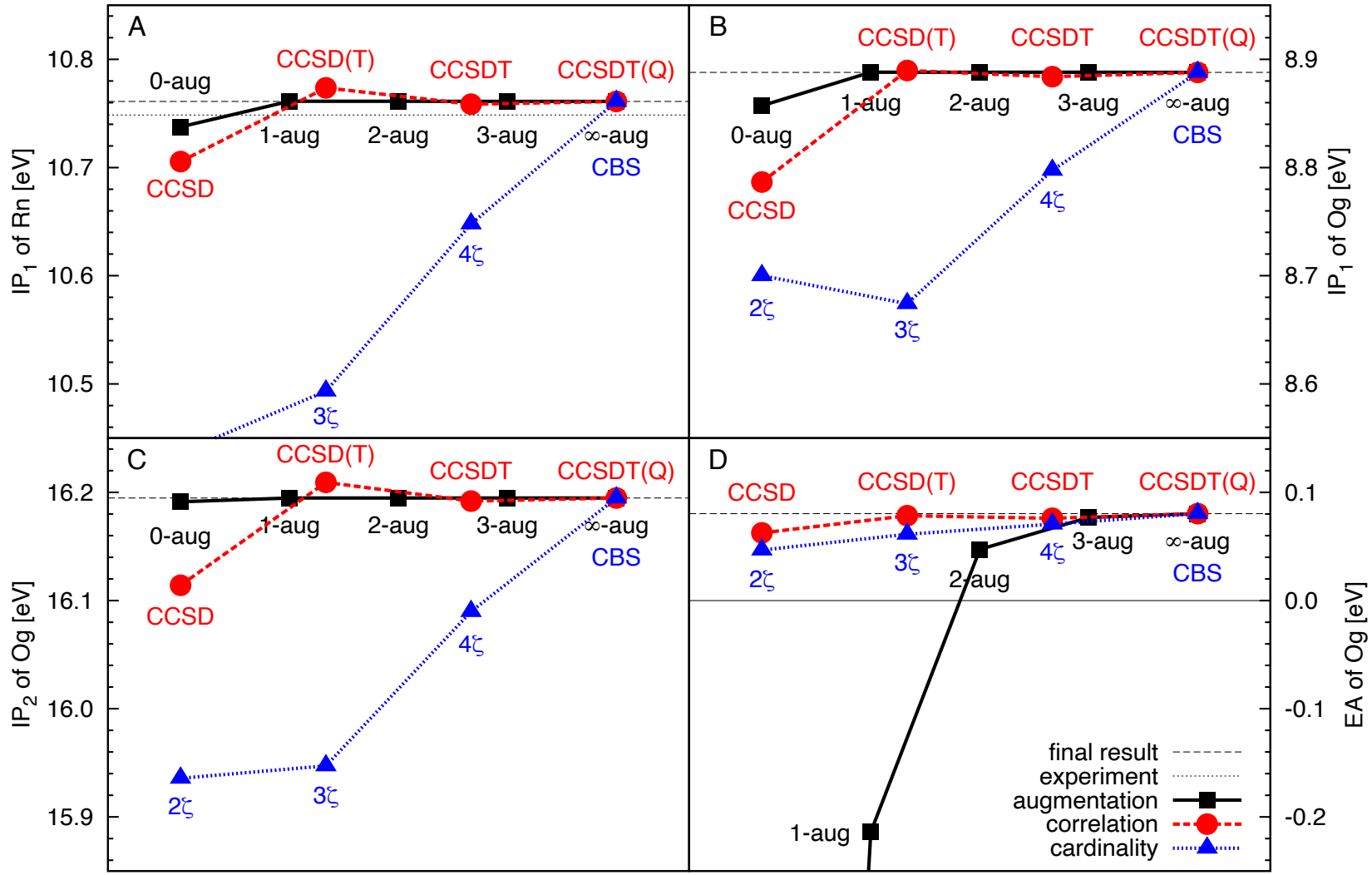
Uncertainty estimation







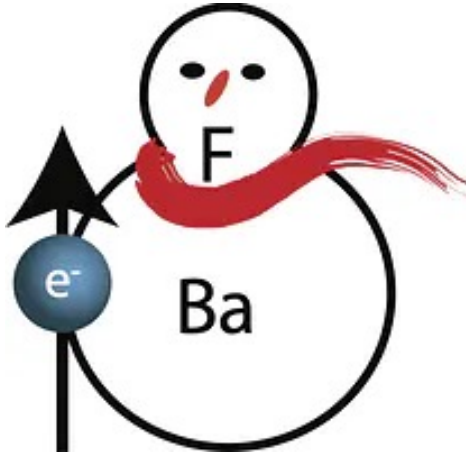
Uncertainty estimation – IP/EA of Rn/Og



In service to NL-eEDM

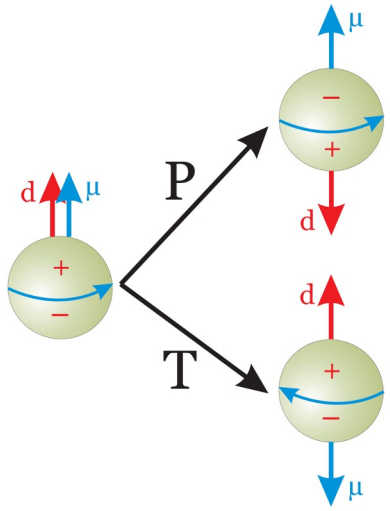
Selected applications

- BaF (and friends)
  - coupling constants
  - laser cooling
  - IPs
- Polyatomic molecules
  - $BaCH_3$
  - $YbCH_3$
  - BaOH



Anastasia Borschevsky

P,T-odd properties



Total electronic angular momentum projection

$$\Omega = \mathbf{J}_e \cdot \mathbf{n}$$

$$H_{sr}^{\mathcal{P},\mathcal{T}-\mathrm{odd}} = \left(W_\mathrm{s} k_\mathrm{s} + W_\mathrm{d} d_\mathrm{e}\right) \Omega$$

Electron electric dipole moment (eEDM)

$\mathcal{P},\mathcal{T}$-odd scalar pseudoscalar (S-PS) neutral-current electron-nucleon interaction constant

Kriplovich, Nauka (1981), English trans. G&B (1991)
Kozlov, Zh. Eksp. Teor. Fiz. 89, 1933 (1985)
Dimitriev et al, Phys. Lett. A 167, 280 (1992)

W_d/W_s parameters

$$H_{sr}^{\mathcal{P},\mathcal{T}-\mathrm{odd}} = (W_\mathrm{s}\, k_\mathrm{s} + W_\mathrm{d}\, d_\mathrm{e})\, \Omega$$

$$W_\mathrm{s} = \frac{1}{\Omega\, k_\mathrm{s}} \langle \Psi^{(0)} | H^{\mathrm{S-PS}} | \Psi^{(0)} \rangle$$

$$W_\mathrm{d} = \frac{1}{\Omega\, d_\mathrm{e}} \langle \Psi^{(0)} | H^{\mathrm{eEDM}} | \Psi^{(0)} \rangle$$

$$H^{\mathrm{S-PS}} = \frac{\imath G_\mathrm{F} k_\mathrm{s}}{e\sqrt{2}} \sum_{i,k} \rho_k(\mathbf{r}_i) \gamma^0 \gamma^5$$

$$H^{\mathrm{eEDM}} = -d_\mathrm{e} \sum_i \gamma^0 \boldsymbol{\Sigma} \cdot \mathbf{E}(\mathbf{r}_i)$$

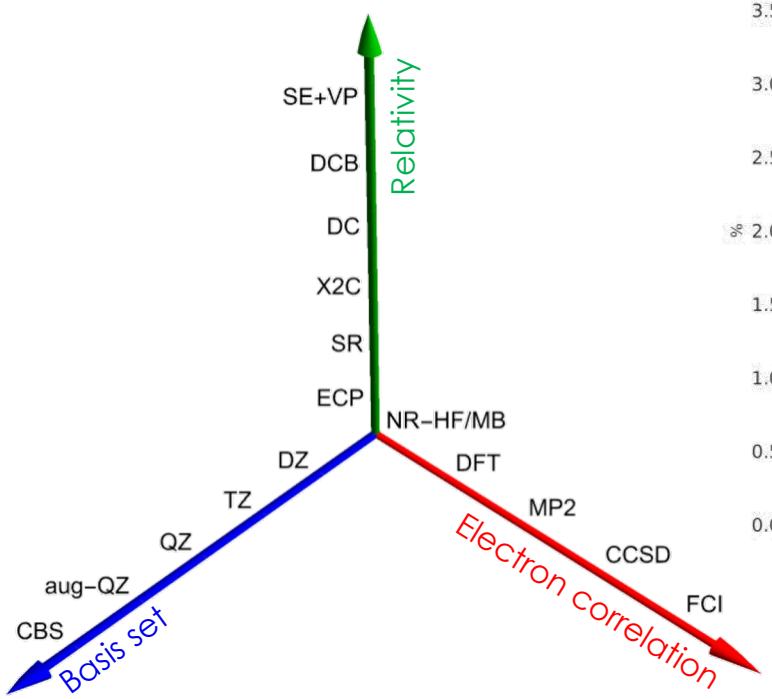
$$W_{\mathrm{s(d)}} = \frac{1}{\Omega} \frac{dE\left(\lambda_{k_\mathrm{s}(d_\mathrm{e})}\right)}{d\lambda_{k_\mathrm{s}(d_\mathrm{e})}}\bigg|_{\lambda_{k_\mathrm{s}(d_\mathrm{e})}=0}$$

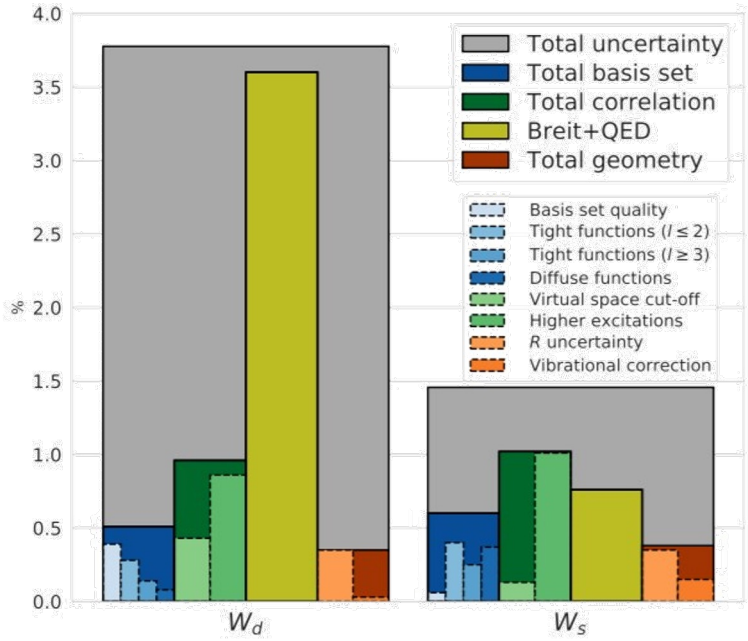
$$E(\lambda_p) = \langle 0 | H_0 + \lambda_p H_p | 0 \rangle$$

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

BaF: W_d/W_s parameters

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

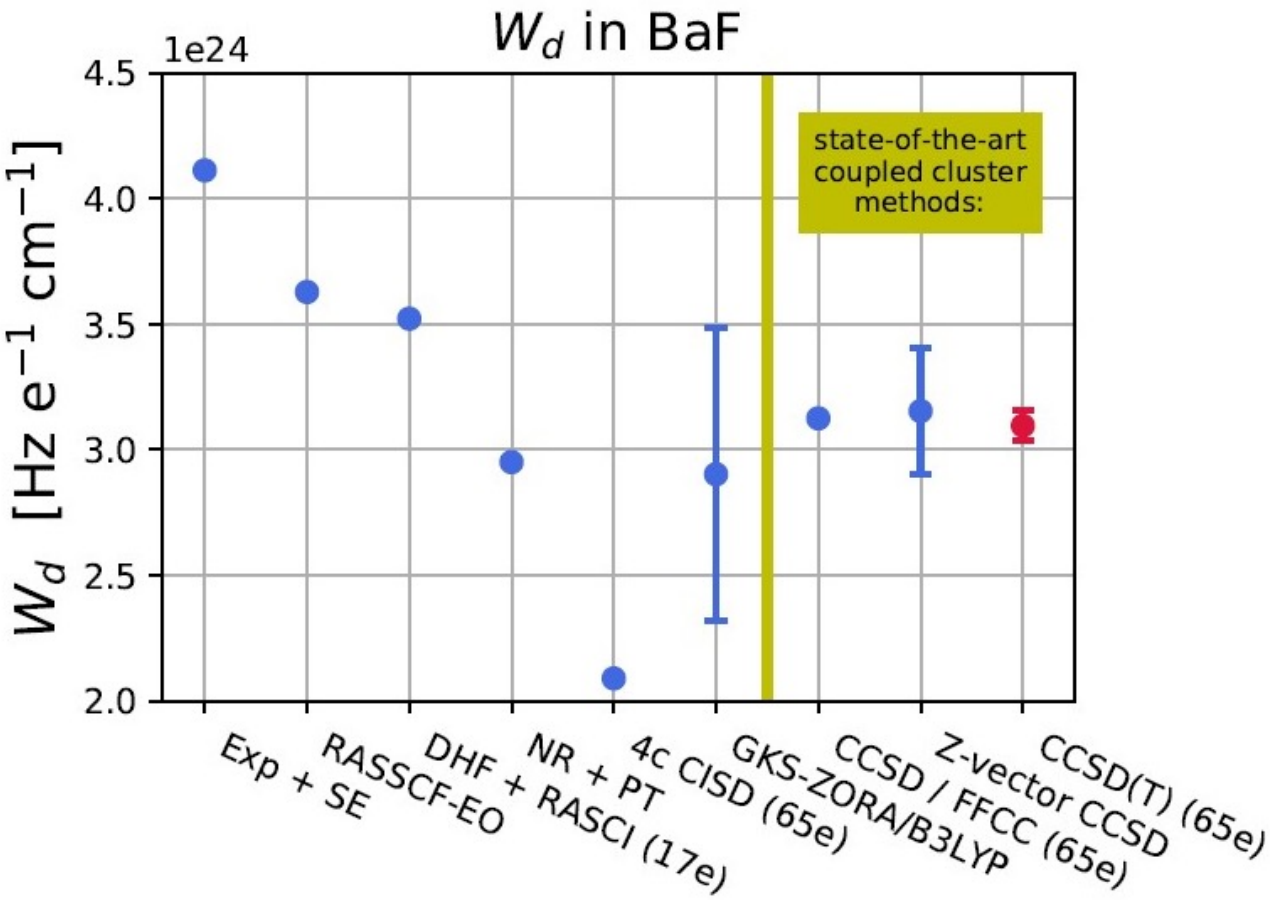
Haase et al., J. Chem. Phys. 155, 034309 (2021)

BaF: W_d/W_s parameters

- Final recommended values

BaF	W_d^* $[\frac{10^{24}\text{Hz}}{\text{e cm}}]$	W_s [Hz]
DC CCSD(T)	3.13 ± 0.24	8.29 ± 0.12

Pi Haase



Haase et al., J. Chem. Phys. 155, 034309 (2021)

Uncertainty estimation

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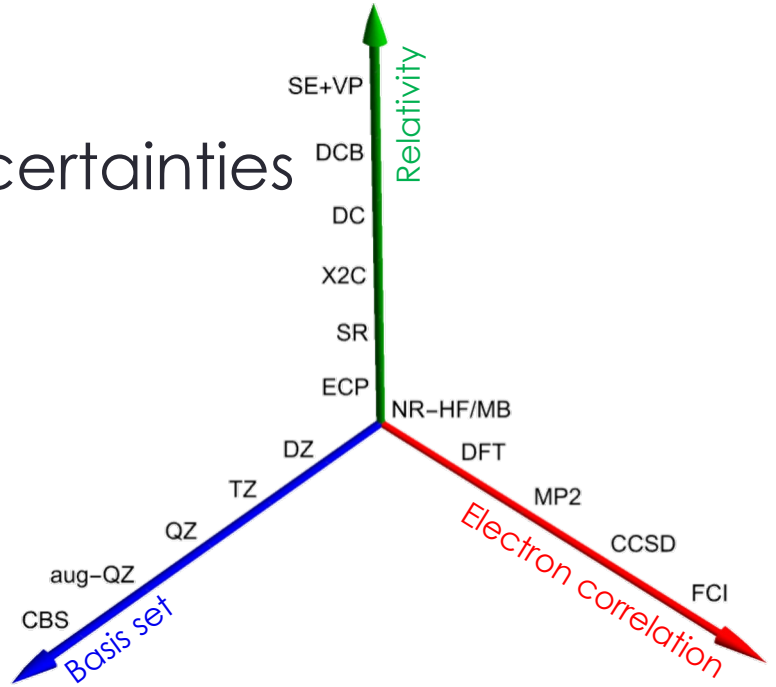


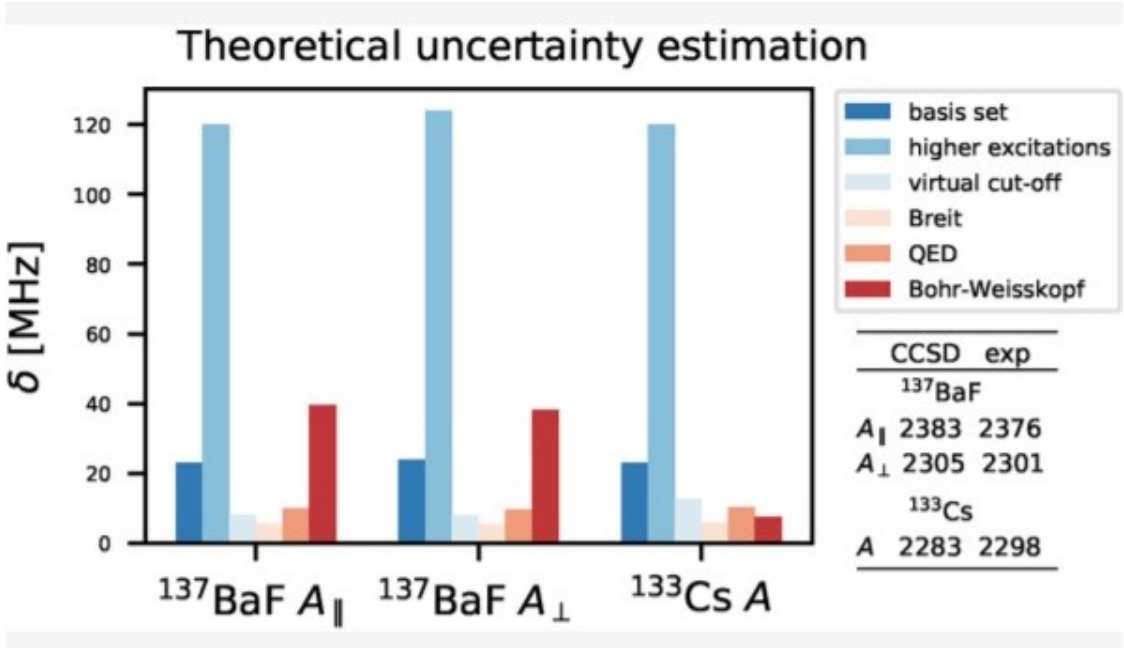
BaF: Magnetic HFS constants

- A proxy property for W_d/W_s parameters

BaF	W_d^* $[\frac{10^{24}\text{Hz}}{\text{e cm}}]$	W_s [Hz]
DC CCSD(T)	3.13 ± 0.24	8.29 ± 0.12

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

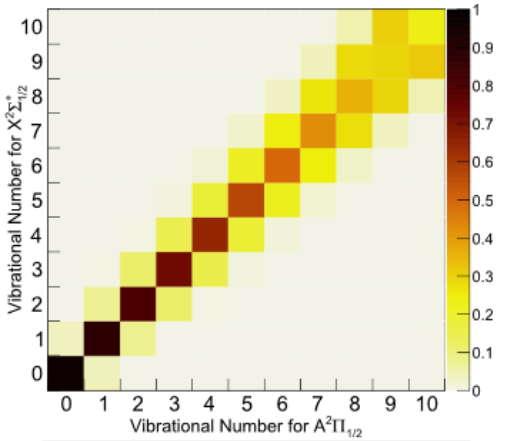
	^{137}BaF			
method	$A_\parallel$	%(exp)	$A_\perp$	%(exp)
GRECP SCF-EO[90]	2264	−4.71	2186	−5.00
GRECP RASSCF-EO[90]	2272	−4.38	2200	−4.39
DF RASCI[91]	2240	−5.72	2144	−6.82
DF MBPT[91]	2314	−2.61	2254	−2.04
DC CCSD (this work)	2383(129)	0.29	2305(132)	0.17
exp[77]	2376(12)		2301(9)	

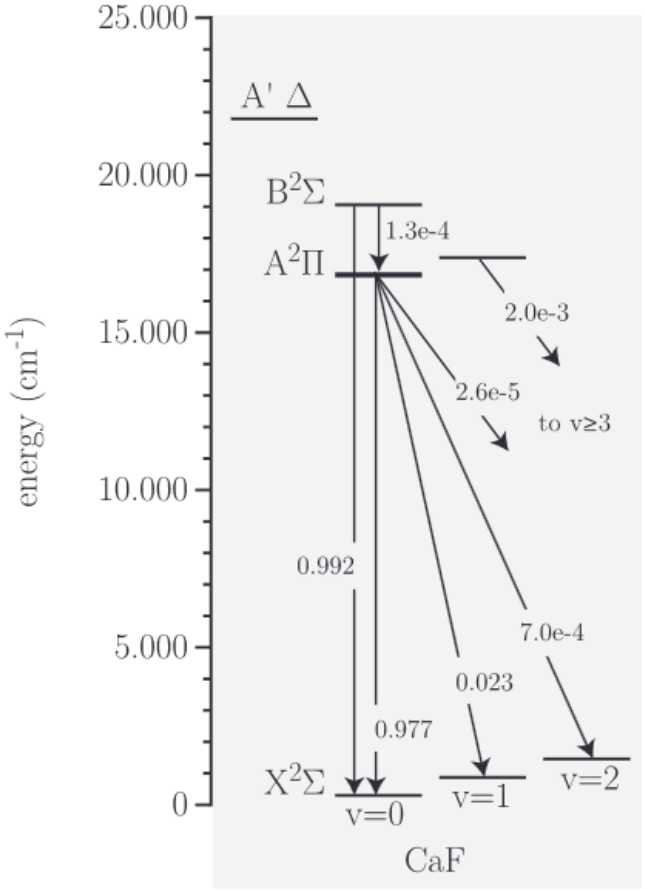


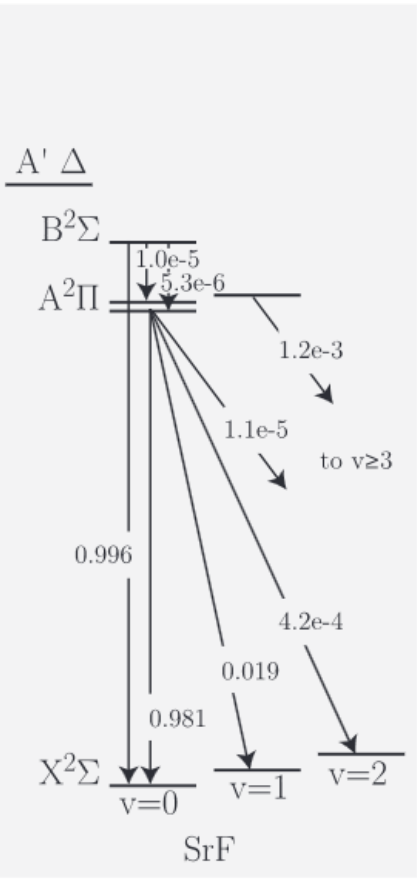
Haase et al., J. Phys. Chem. A 124, 3157 (2020)

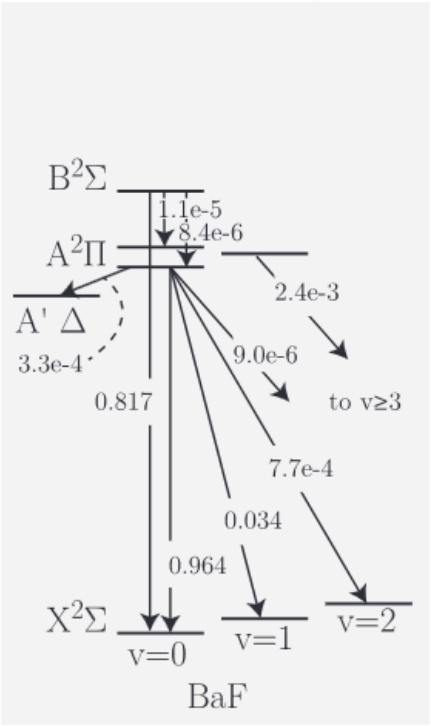
MF cooling schemes

- Yongliang Hao





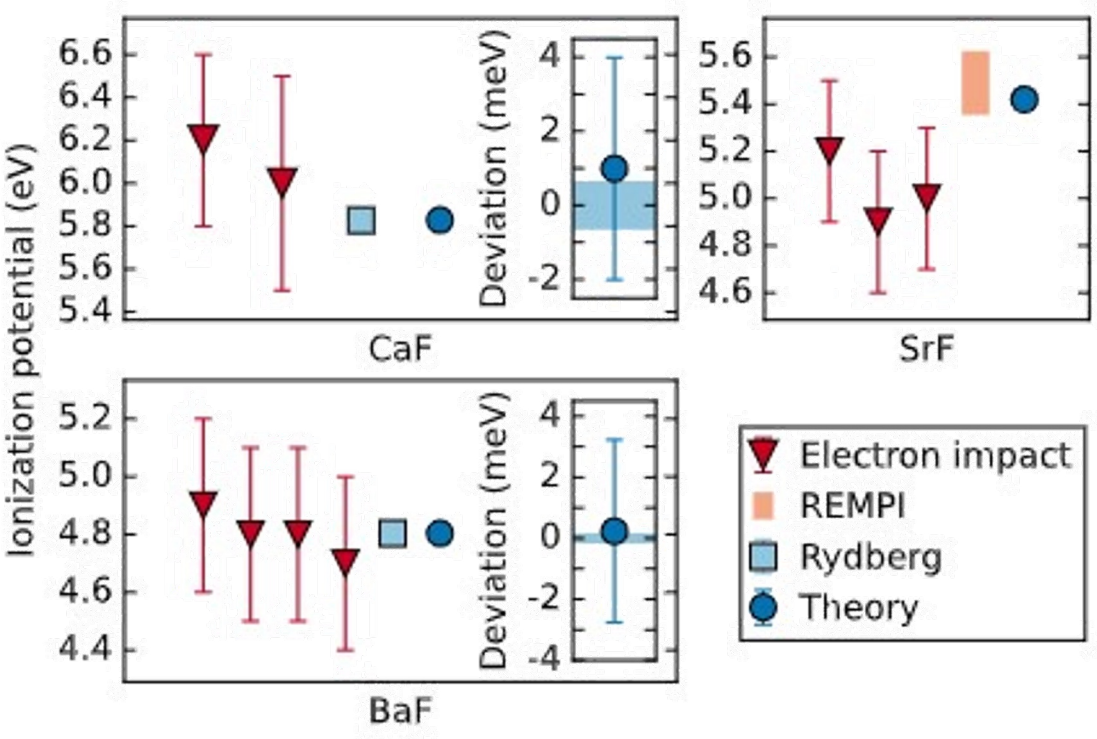




Hao et al., J. Chem. Phys. 151, 034302 (2019)

Ionization potentials of MF

- Excellent agreement for CaF and BaF
- For SrF, new IP measurements would be useful



Aleksandra Kuyberis

TABLE VI: Recommended theoretical IP of MF (M = Ca, Sr, Ba) [eV] with uncertainties.

IP	CaF	SrF	BaF
Adiabatic	5.821(3)	5.415(1)	4.800(3)
Adiabatic+ZPE	5.828(3)	5.420(1)	4.804(3)
Experiment[a]	5.8270(6)	5.36–5.62	4.80377(1)

[a]-CaF[69], SrF[70] and BaF[39]

Kyuberis et al., Phys. Rev. A asap (2024)

Uncertainty estimation

- Calculate the same property in a lighter homologue (and compare to experiment)

- Calculate a different property in the same atom/molecule (and compare to experiment)

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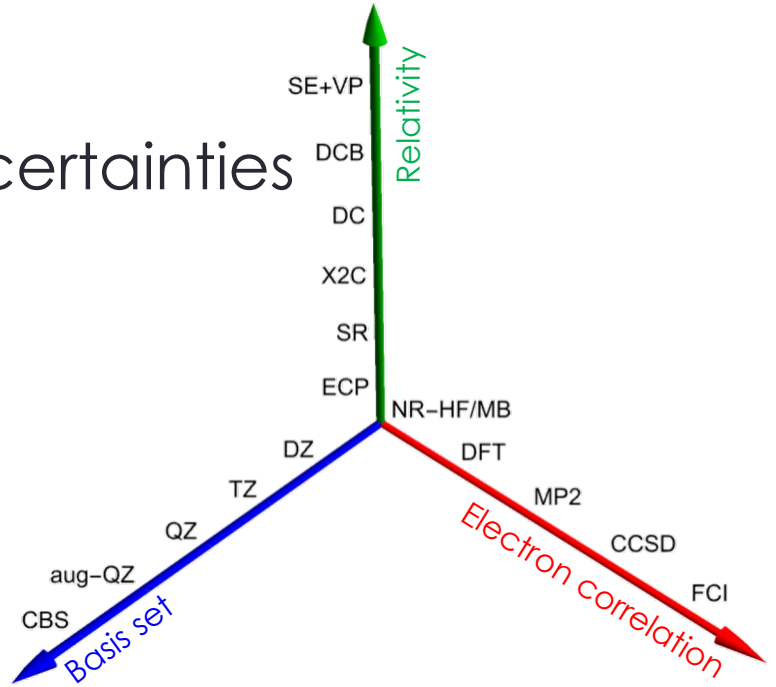
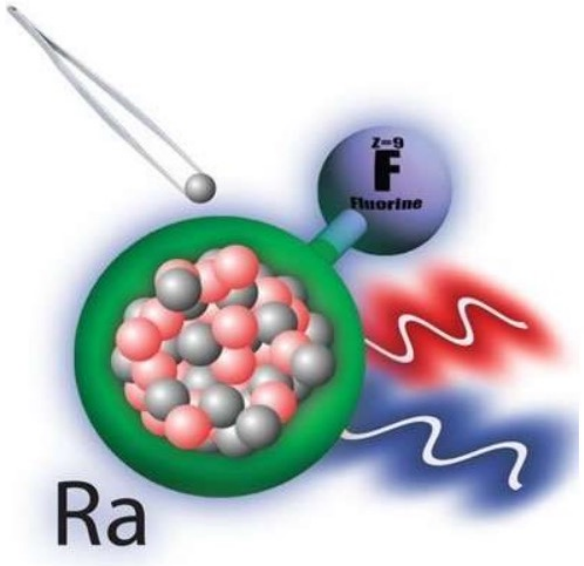


Ionization potential of RaF

- a promising candidate for precision measurements
- Many (high-impact) experimental studies
- Spectra, isotope shifts
- New measurements: IP
- Theory before experiment



87. "Precision spectroscopy and laser cooling scheme of a radium-containing molecule".
S.M. Udrescu, S. Wilkins, A. Breier, M. Athanasakis-Kaklamanakis, **R.F. Garcia Ruiz** et a
Nature Physics (2023).

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Spectroscopy of short-lived radioactive molecules

R. F. Garcia Ruiz, R. Berger, J. Billowes, C. L. Binnersley, M. L. Bissell, A. A. Breier, A. J. Brinson, K. Chrysalidis, T. E. Cocolios, B. S. Cooper, K. T. Flanagan, T. F. Giesen, R. P. de Groote, S. Franchoo, F. P. Gustafsson, T. A. Isaev, Á. Koszorús, G. Neyens, H. A. Perrett, C. M. Ricketts, S. Rothe, L. Schweikhard, A. R. Vernon, K. D. A. Wendt, ... X. F. Yang + Show authors

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Isotope Shifts of Radium Monofluoride Molecules

S. M. Udrescu *et al.*
Phys. Rev. Lett. **127**, 033001 – Published 14 July 2021

Ionization potential of RaF

- Measurement
  - ionization threshold under multi-step laser excitation
  - both two-step and three-step ionization schemes.
- Theory
  - relativistic CC with higher order corrections

Method	IP (eV)
CBS-DC-CCSD	4.932
CBS-DC-CCSD(T)	4.983
+aug+ae.vs.cv	4.986
+ΔT	4.987
+Breit	4.985
+QED	4.979
Theoretical	4.979(9)
Experimental	4.972(4)

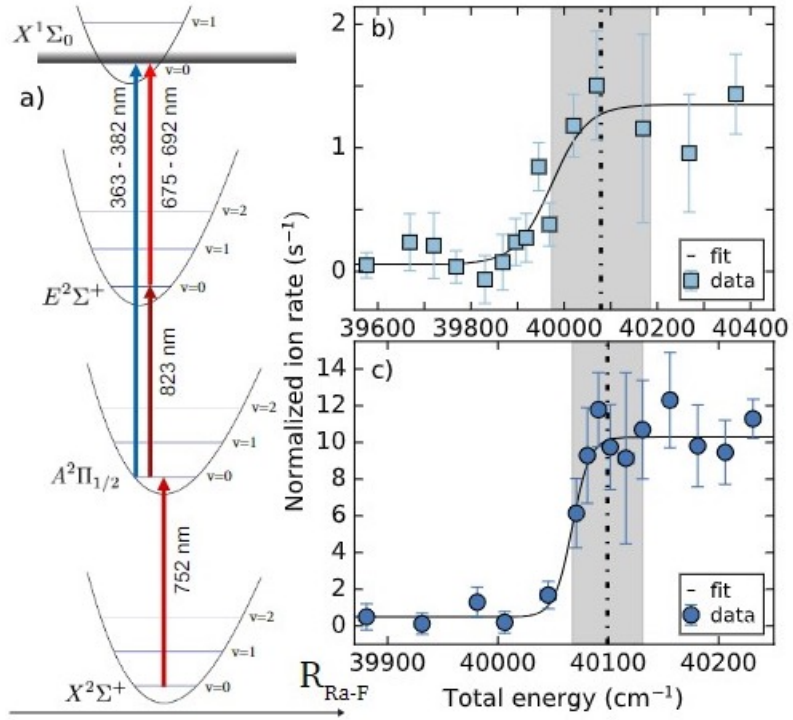
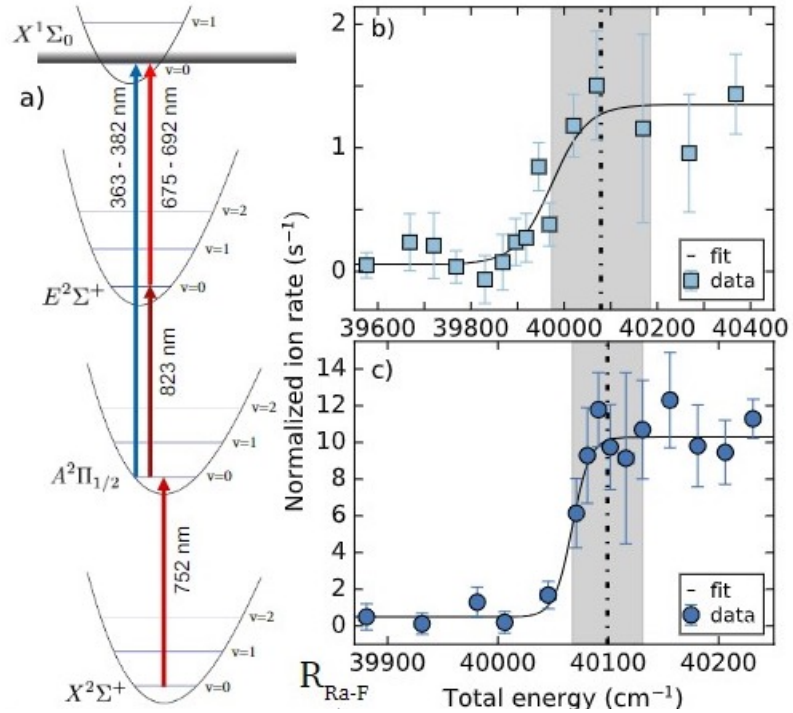


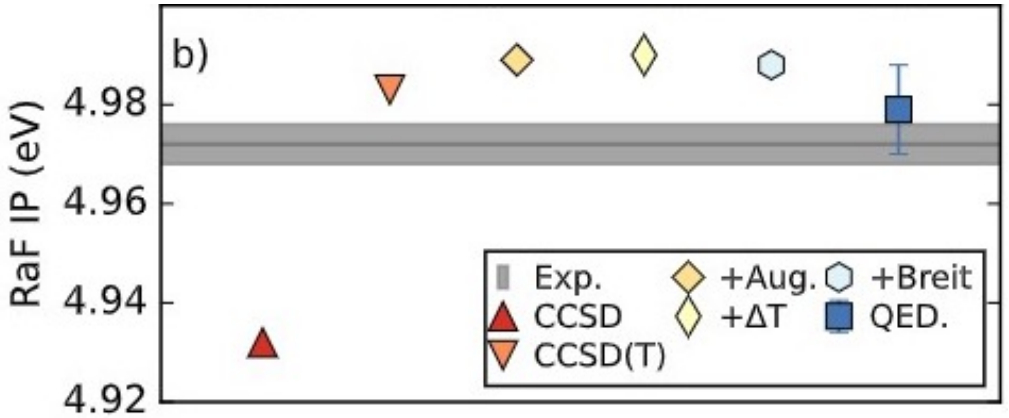
FIG. 1. **a)** The two-step and three-step ionization schemes used in the experiments. Power-normalized, background-subtracted ion count rate as a function of total photon energy in $^{226}Ra^{19}F$ for the **b)** two-step scheme and **c)** three-step scheme. The determined IPs are shown as vertical dashed-and-dotted lines with their 1σ uncertainties as gray bands.

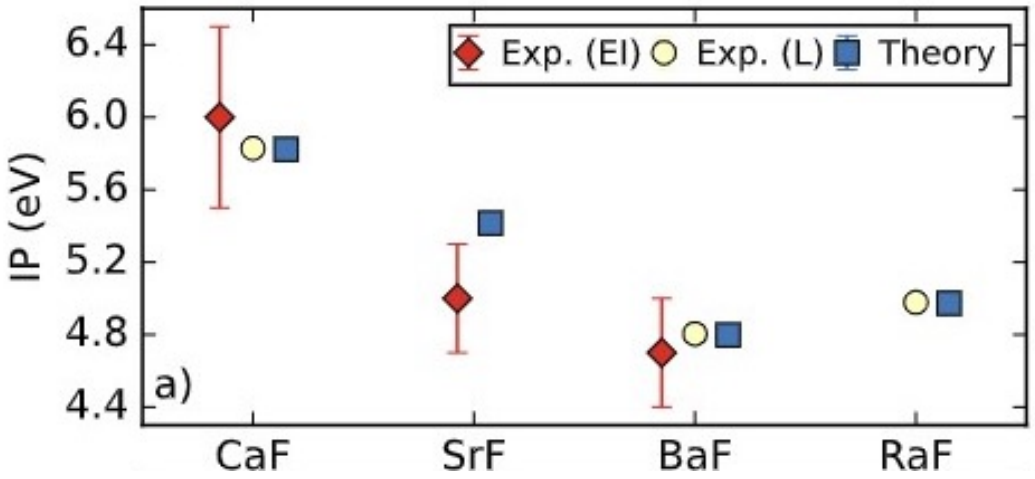
Wilkins et al., in prep. (2024)

Ionization potential of RaF

- Measurement
  - ionization threshold under multi-step laser excitation
  - both two-step and three-step ionization schemes.
- Theory
  - relativistic CC with higher order corrections

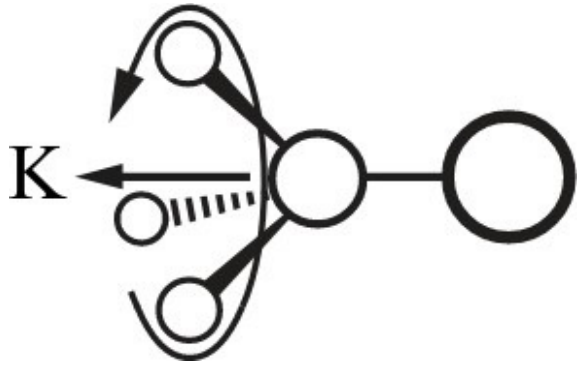






Wilkins et al., in prep. (2024)

Symmetric top molecules

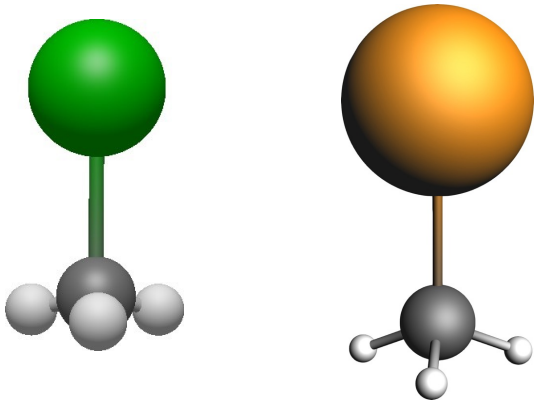


- $BaCH_3$ and $YbCH_3$
- long-lived close-lying opposite parity eigenstates (K-doublets)
- expected to be laser-coolable
- similar W_d/W_s parameters to other Ba/Yb containing molecules

Chamorro et al., Phys. Rev. A 106, 052811 (2022)

Symmetric top molecules

- $BaCH_3$ and $YbCH_3$

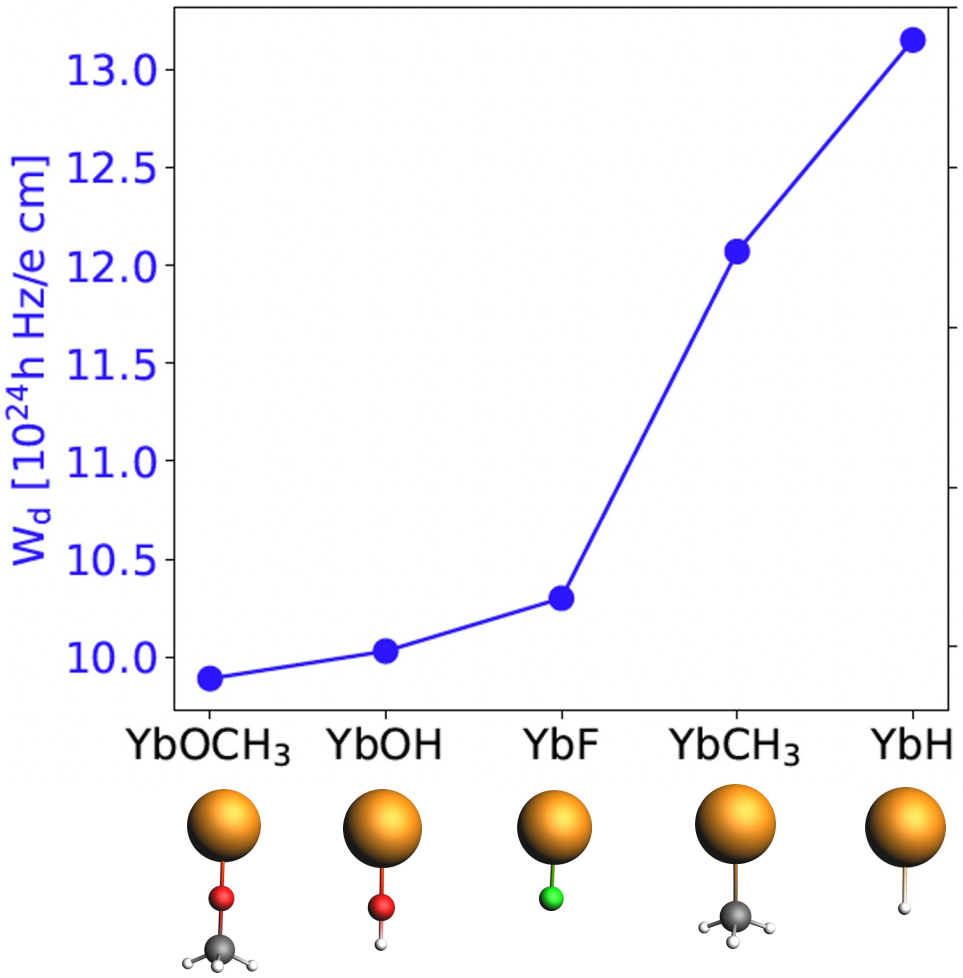


Yuly Chamorro

Molecule	Method	W_d ($10^{24}\frac{h\text{Hz}}{e\text{cm}}$)	W_s (hkHz)
$BaCH_3$	*DC-CCSD(T)*	*3.22 ± 0.12*	*8.42 ± 0.29*
$BaOCH_3$	X2C-CCSD(T)	3.05 [74]	
BaOH	DC-CCSD(T)	3.10 ± 0.15 [38]	
	ZORA-cGHF	3.32 ± 0.33 [39]	8.79 ± 0.88 [39]
	ZORA-cGKS	2.98 ± 0.30 [39]	7.91 ± 0.79 [39]
BaF	DC-CCSD(T)	3.13 ± 0.12 [37]	8.29 ± 0.12 [37]
$YbCH_3$	*DC-FSCC(0,1)*	*13.80 ± 0.35*	*50.16 ± 1.27*
$YbOCH_3$	X2C-CCSD(T)	11.60 [74]	
YbOH	DC-FSCC(0,1)	11.30 ± 0.5 [38]	
	ZORA-cHFS	11.40 ± 1.14 [39]	41.2 ± 4.12 [39]
	ZORA-cGKS	8.54 ± 0.85 [39]	30.8 ± 3.08 [39]
	DC-CCSD	11.47 ± 0.68 [75]	
YbF	DC-FSCC	11.39 [37]	

Chamorro et al., Phys. Rev. A 106, 052811 (2022)

Bonding effects



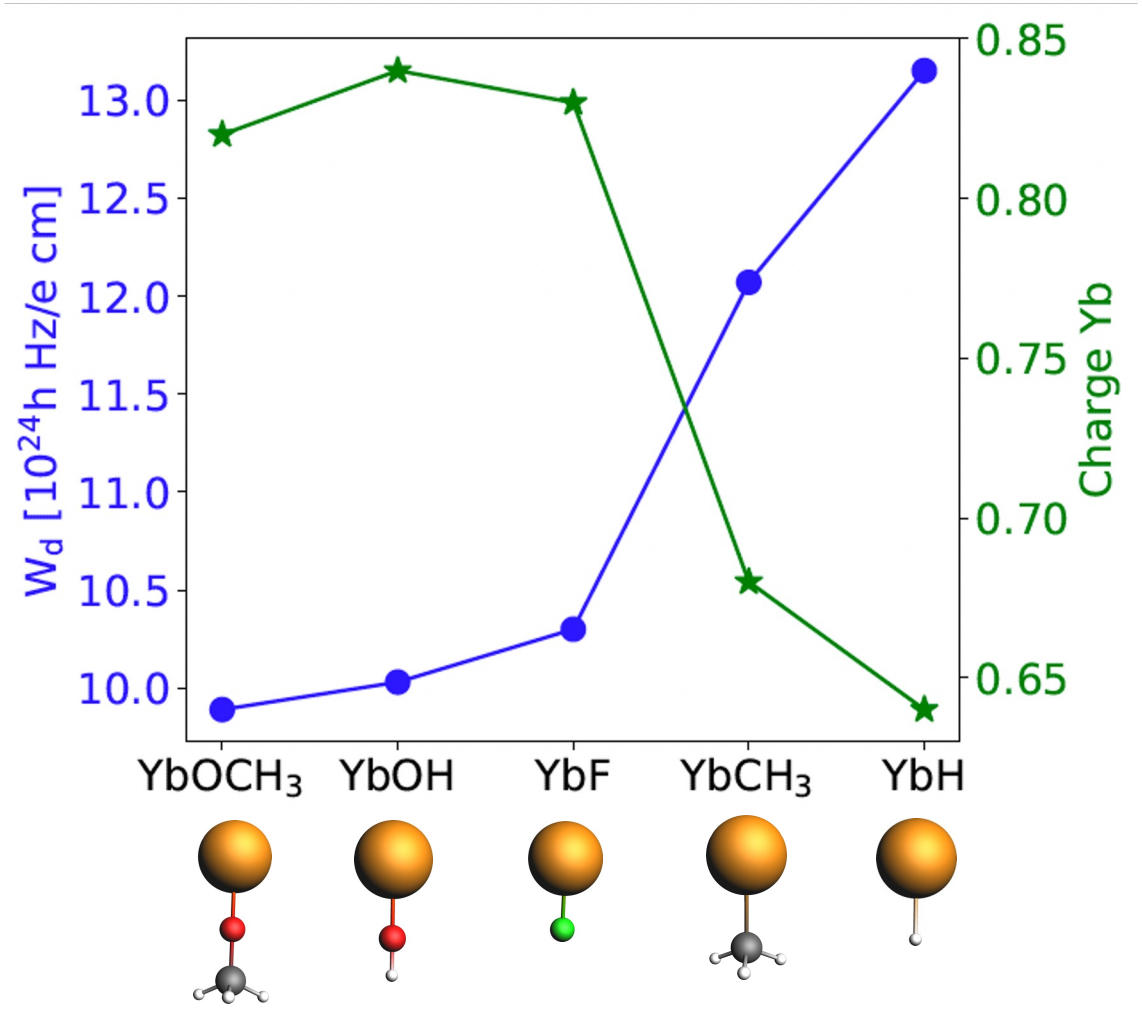
Chamorro et al., Phys. Rev. A 106, 052811 (2022)

Bonding effects

- smaller charge on Yb

↓

- less polar = more covalent



Chamorro et al., Phys. Rev. A 106, 052811 (2022)

Bonding effects

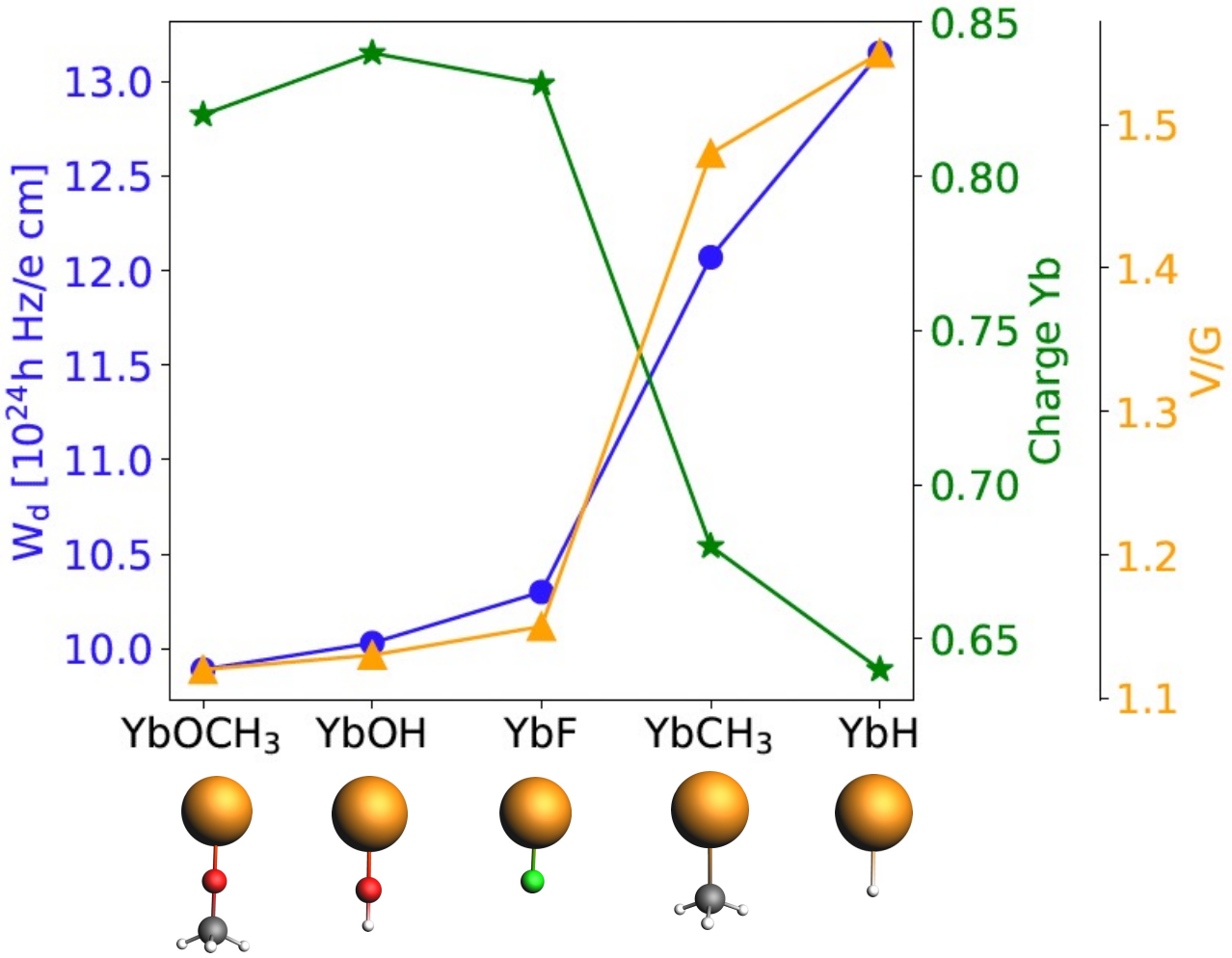
- smaller charge on Yb

↓

- less polar = more covalent

- V/G at BCP
  - measure of covalent character
  - <1 ionic, 1-2 polar, >2 covalent

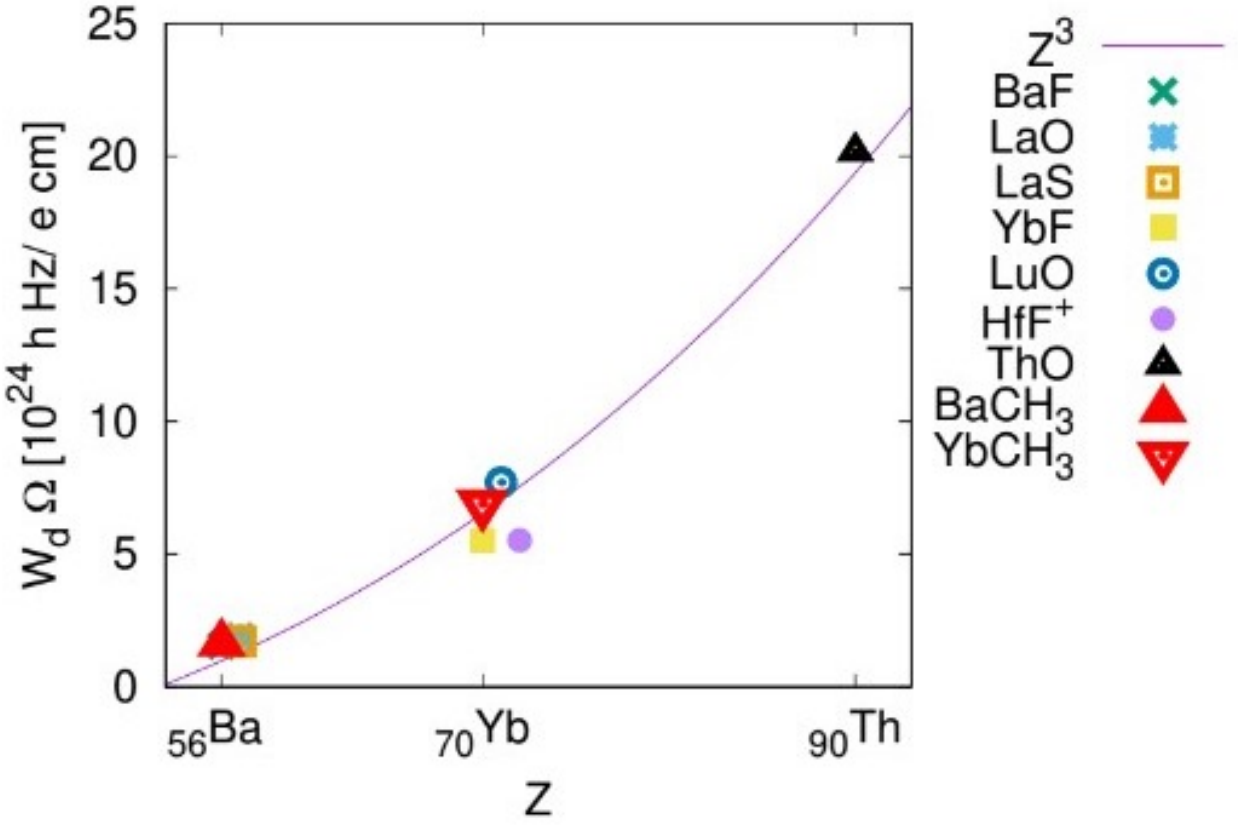
- downside – laser coolability



Chamorro et al., Phys. Rev. A 106, 052811 (2022)

Z scaling

- W_d scales with the atomic number Z^3
  - as predicted



Bouchiat, M. A., Bouchiat, C., J. Phys., France 35, 899-927 (1974)

Bouchiat et Bouchiat, J. Phys. France 35, 899 (1974)

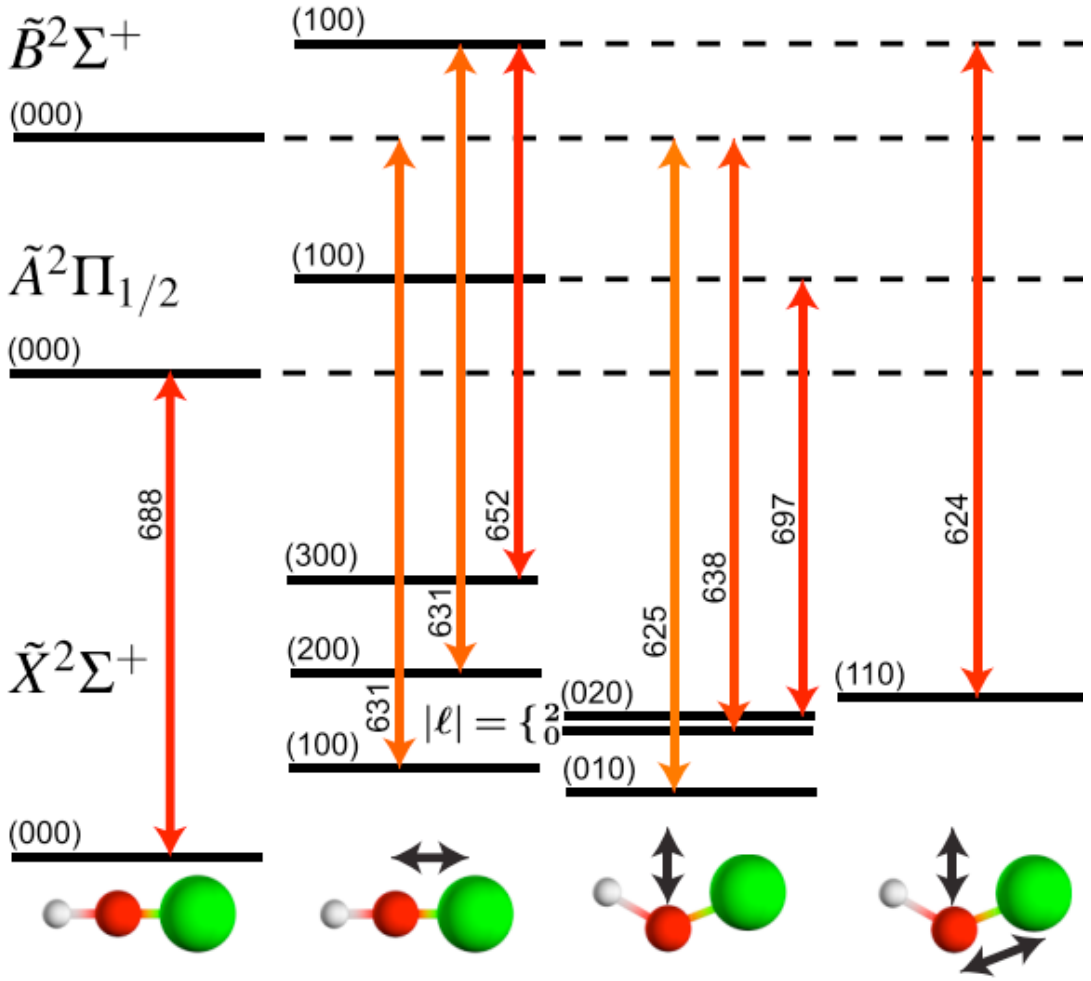
BaOH – work in progress

- bending mode lifetime
- cooling scheme

Radoslava Hlavacova

- polarizability and scattering tensors

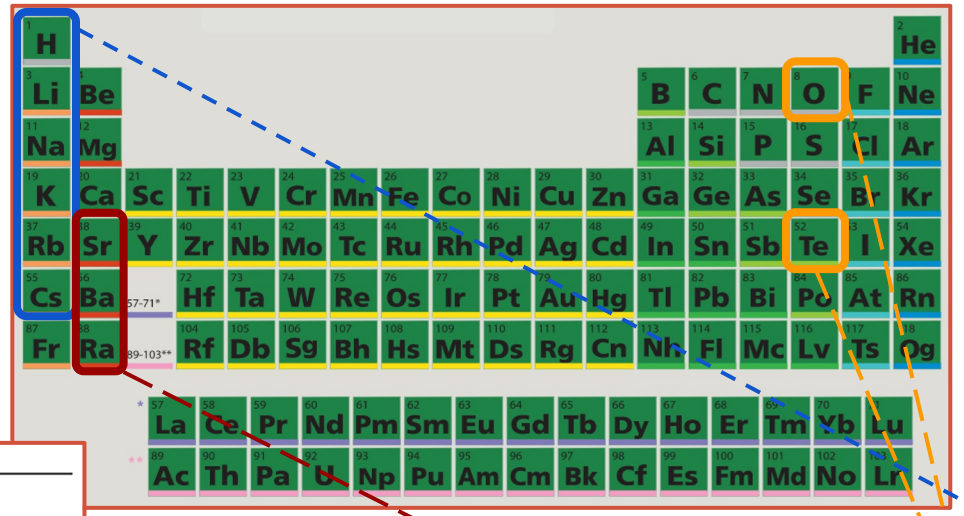
Eifion Prinsen

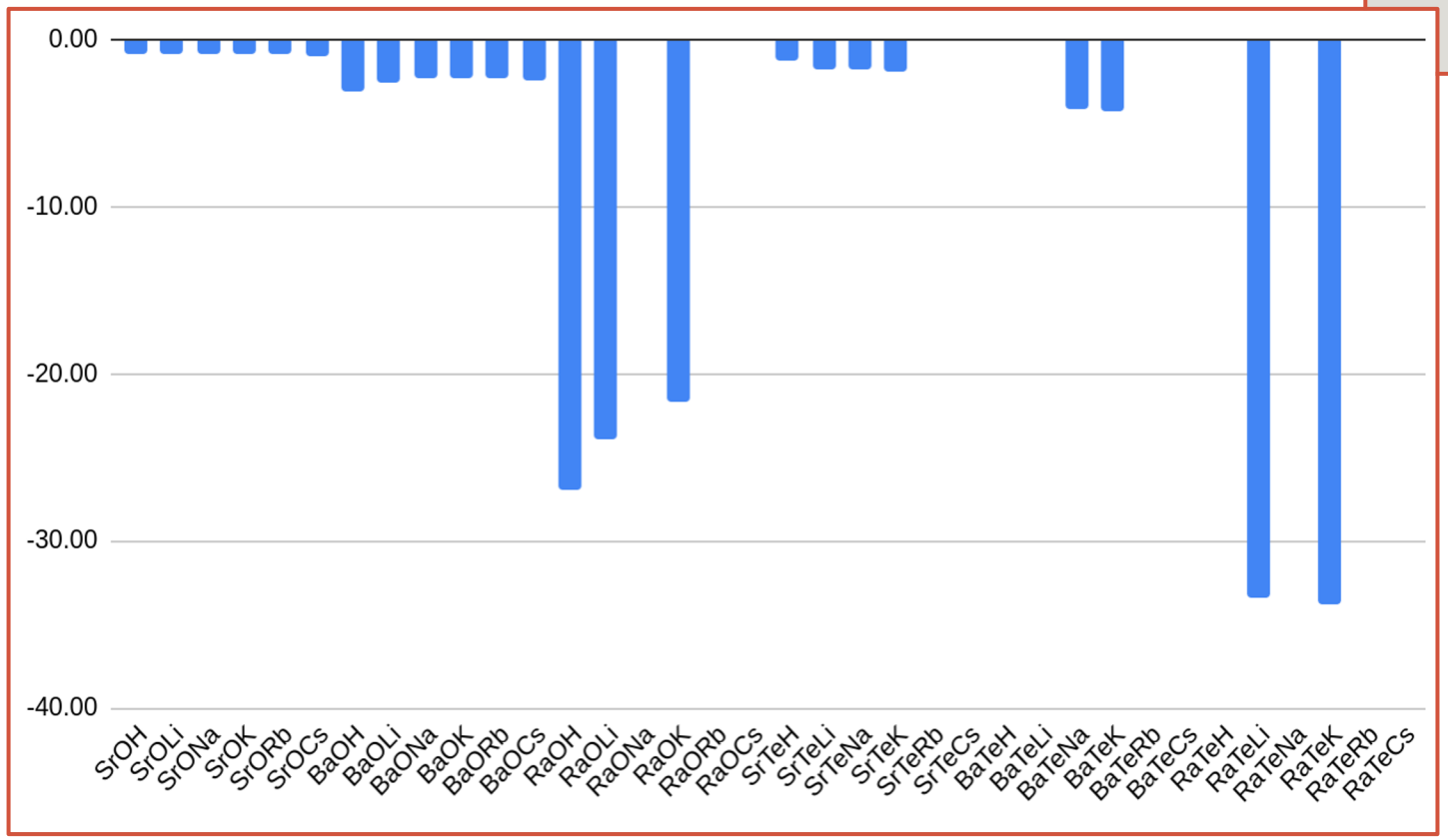


(this is fake news – actually SrOH)

Systematic investigations

- Trends and bonding





Agustin Aucar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