



university of
 groningen



COMENIUS
UNIVERSITY
BRATISLAVA

(SOME) MOLECULAR SEARCHES FOR NEW PHYSICS

INT-24-1 PROGRAM

Lukáš F. Pašteka

Overview

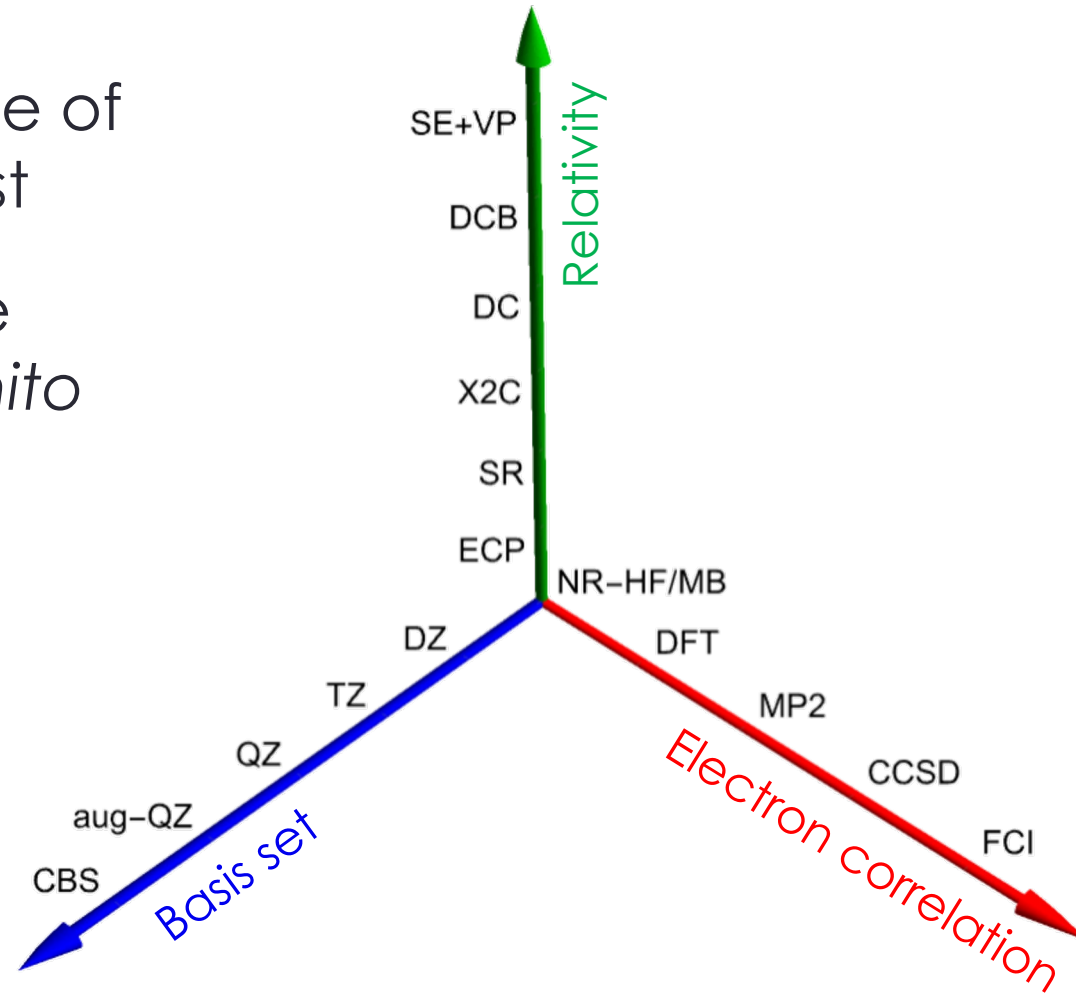
- Computational methods
- NL-eEDM related applications
- PV in chiral molecules
- Molecular searches for VFC

Computational methods a general idea



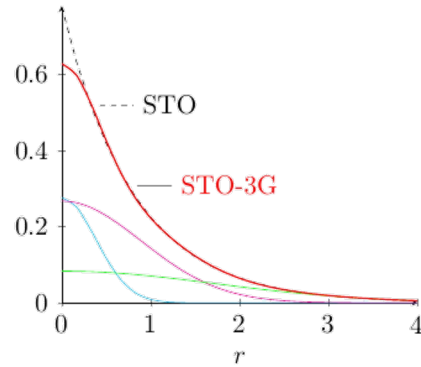
Computational methods

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

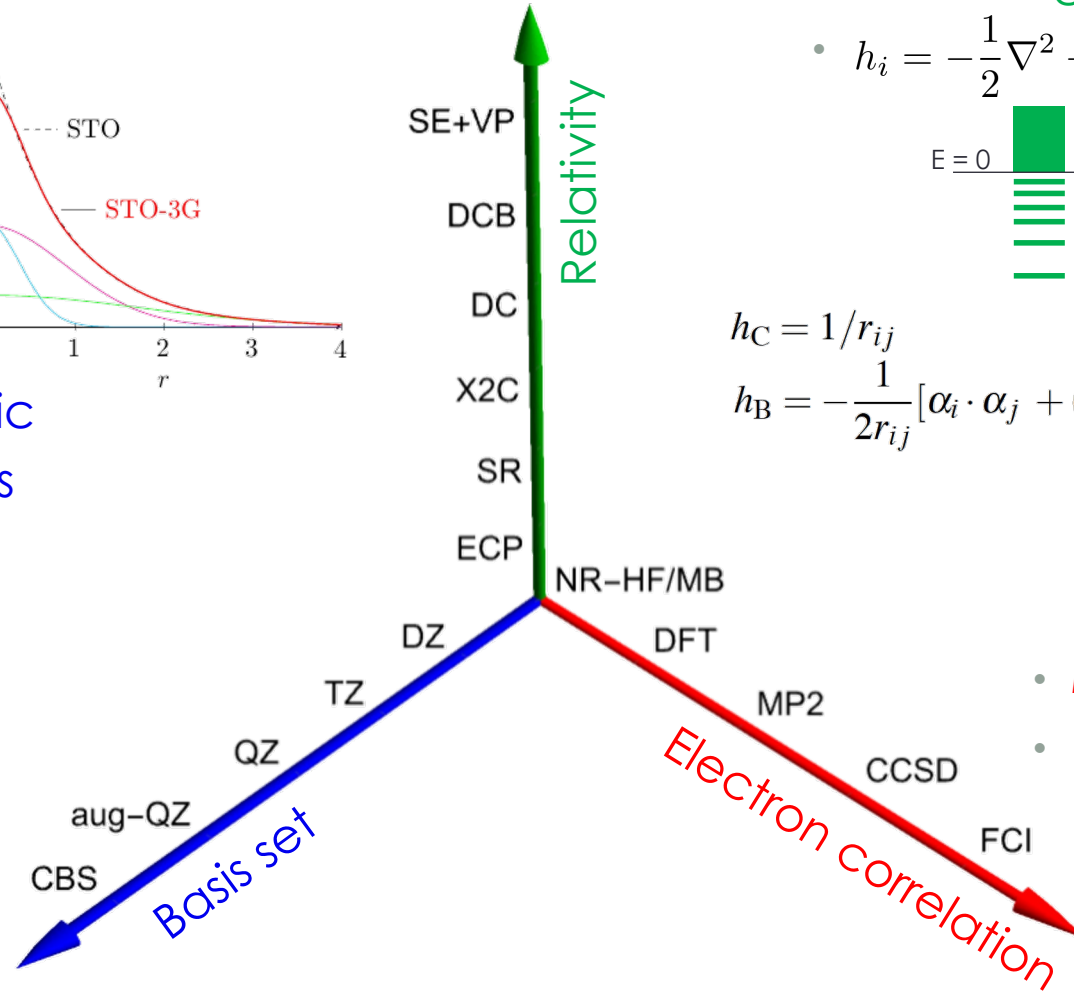
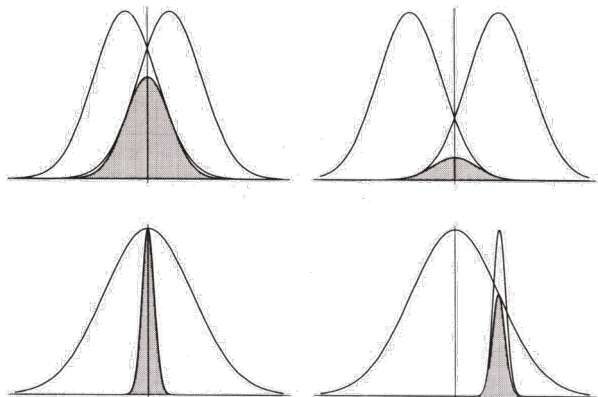


Computational methods

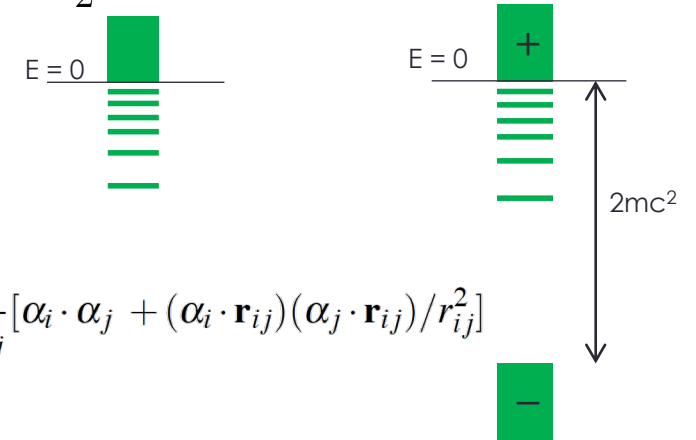
- vector space
- 1-electron expansion
- MO-LCAO
- atom and property specific
- Gaussian (radial) basis sets



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



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



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

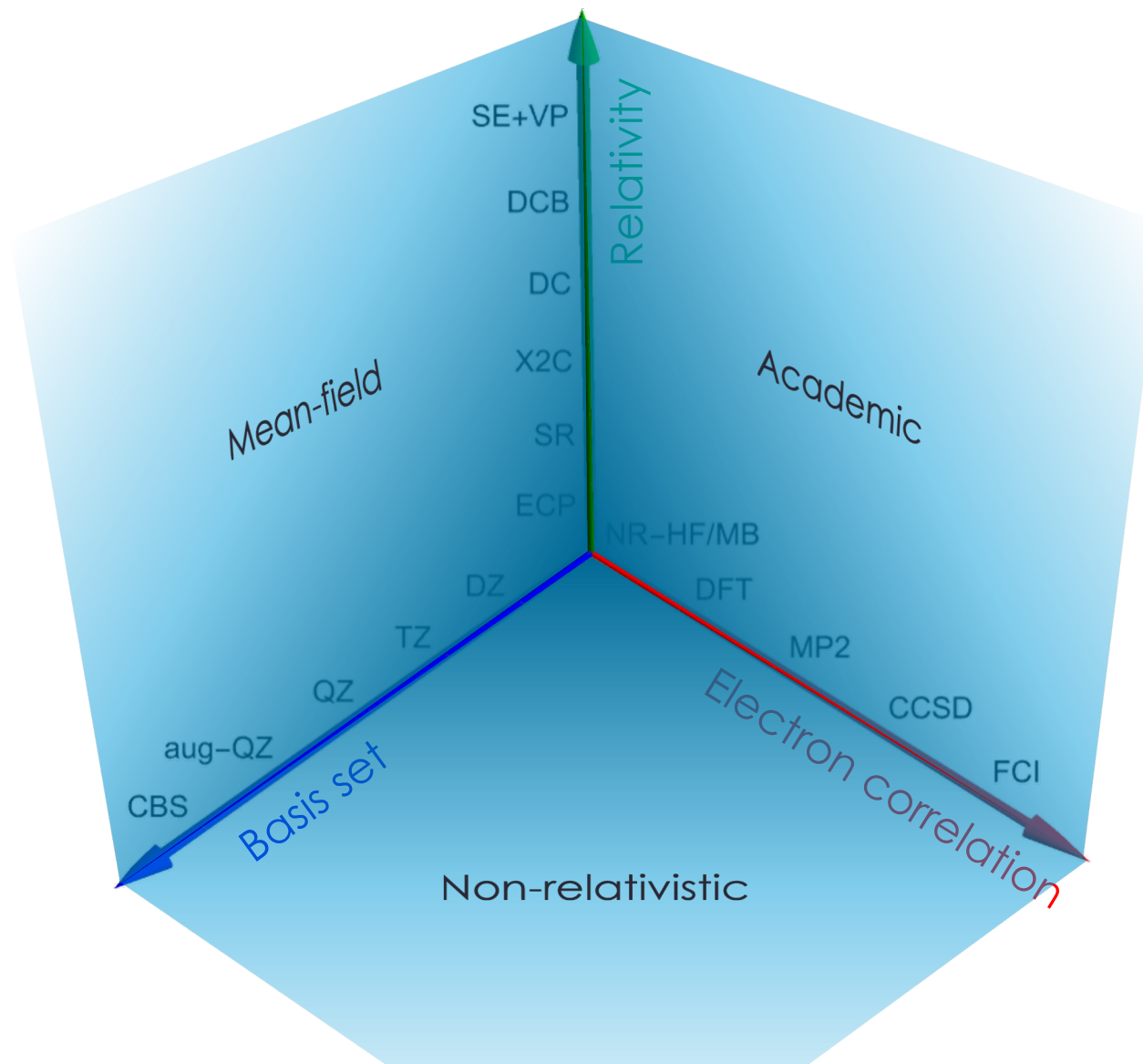
$$h_B = -\frac{1}{2r_{ij}} [\alpha_i \cdot \alpha_j + (\alpha_i \cdot \mathbf{r}_{ij})(\alpha_j \cdot \mathbf{r}_{ij})/r_{ij}^2]$$

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

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

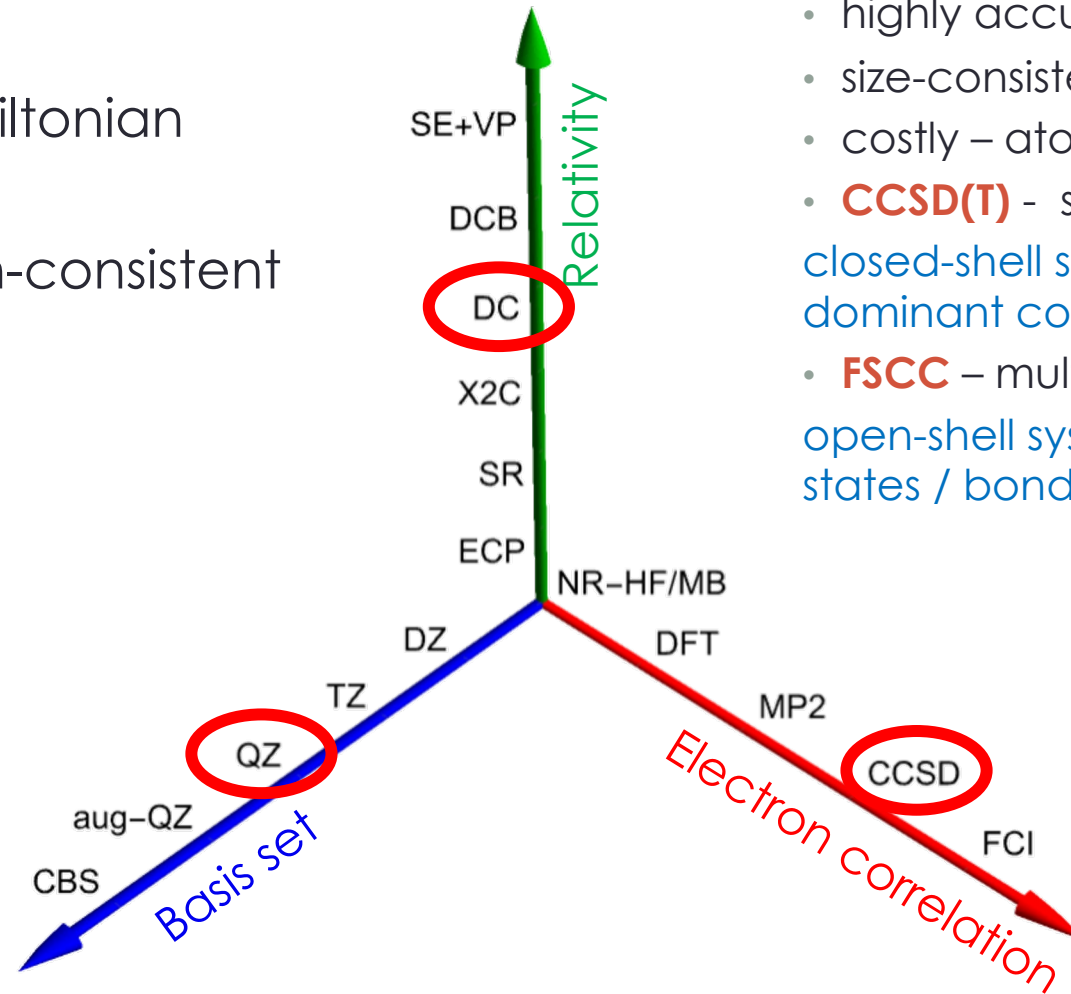
$$T = T_1 + T_2 + T_3 + \dots + T_N$$

Computational methods



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

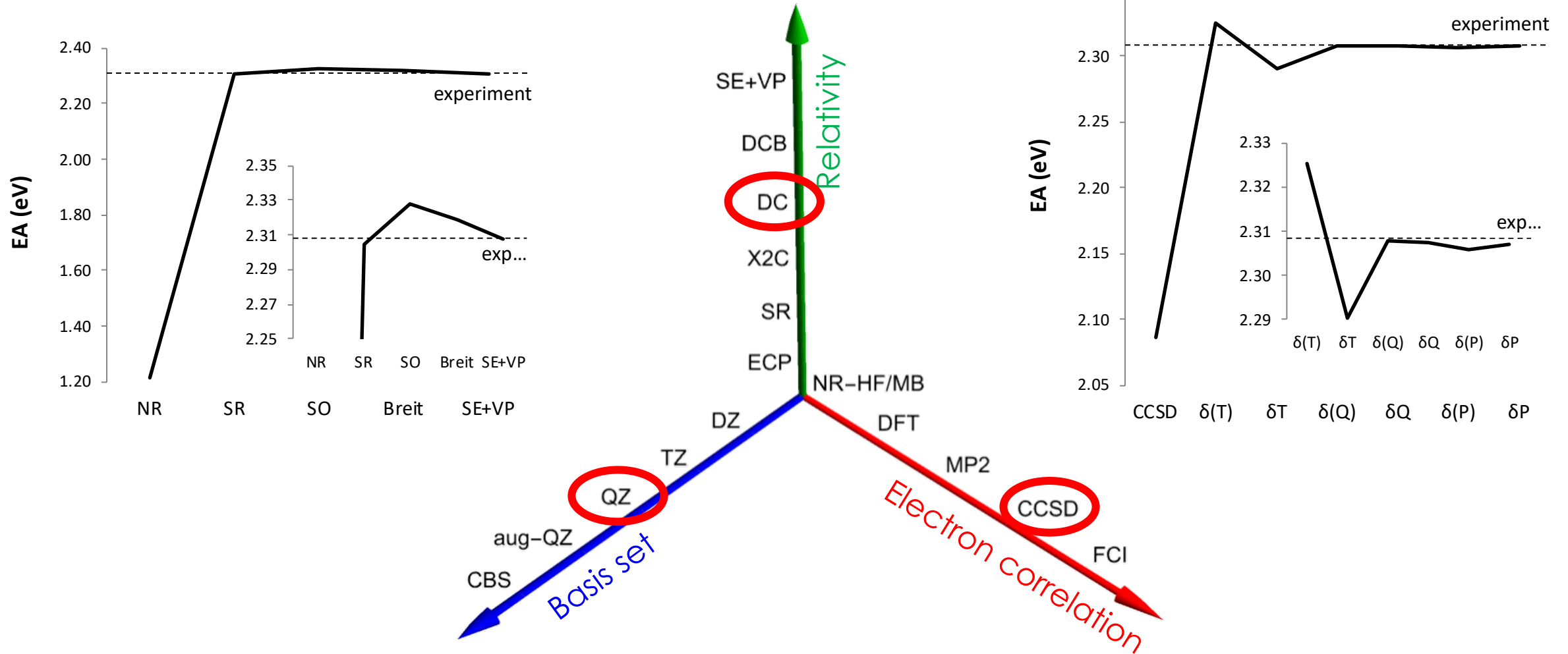
What can we calculate

- 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 , W_s (eEDM experiments)
 - W_A (NSD-PV, nuclear anapole moments)
 - W_M (NMQ moments)
 - E_{PV} (parity-violating energy shifts)
 - sensitivity to α -variation
- Expected accuracy
 - ~ 10 meV for energies, ~ 5 % for properties
 - can do better
- Systematic improvement and uncertainty evaluation

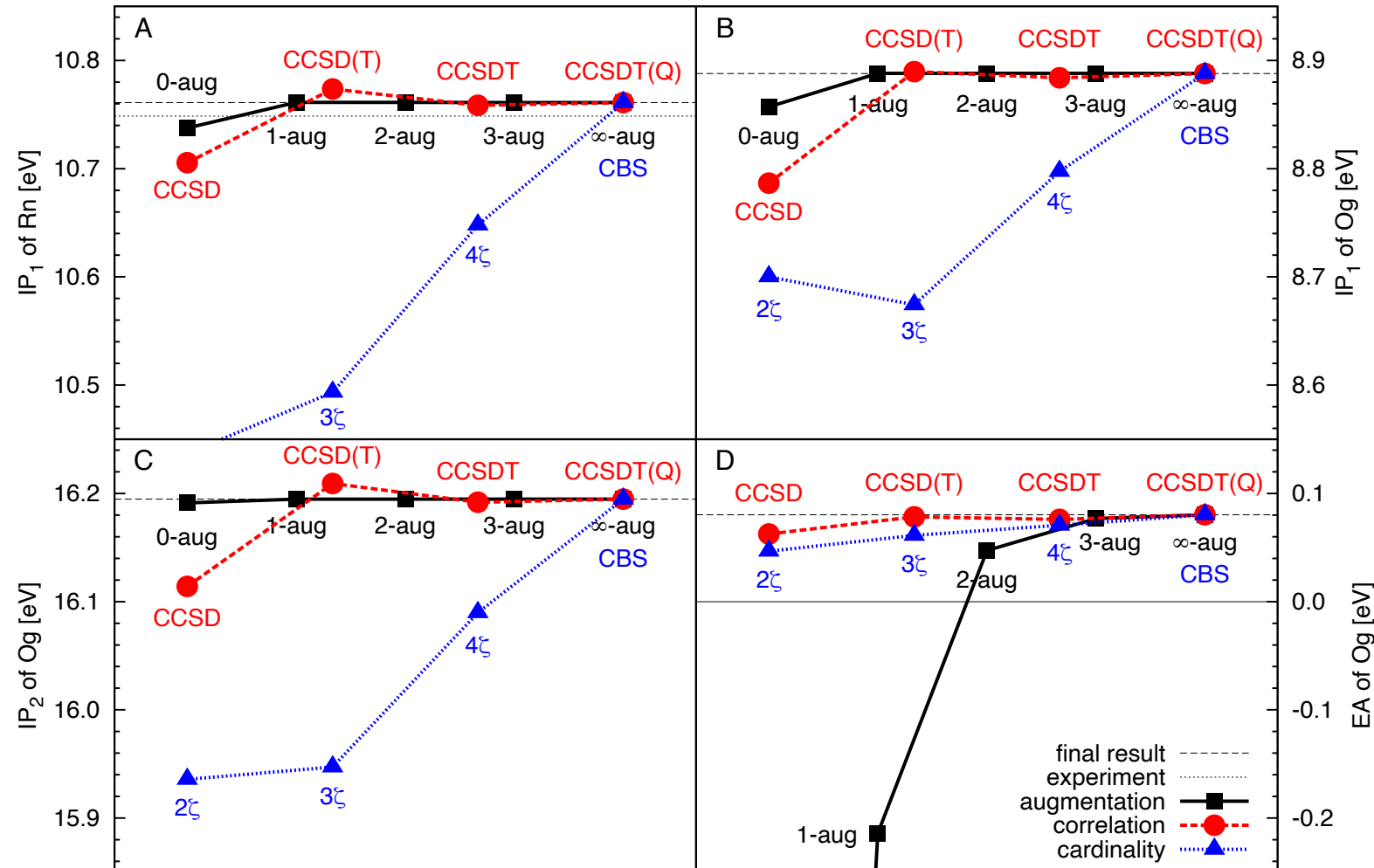
Uncertainty estimation

- same property in an experimentally known lighter homologue
- different experimentally known property in the same system
- use systematics trends due to method incompleteness

Uncertainty estimation



Uncertainty estimation – IP/EA of Rn/Og



In service to NL-eEDM

NL-eEDM collaboration

Scientific staff:

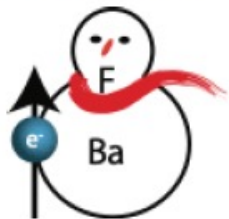
Anastasia Borschevsky
Rick Bethlem
Steven Hoekstra
Klaus Jungmann
Rob Timmermans
Wim Ubachs
Lorenz Willmann

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



university of
 groningen
 van swinderen institute for
 particle physics and gravity

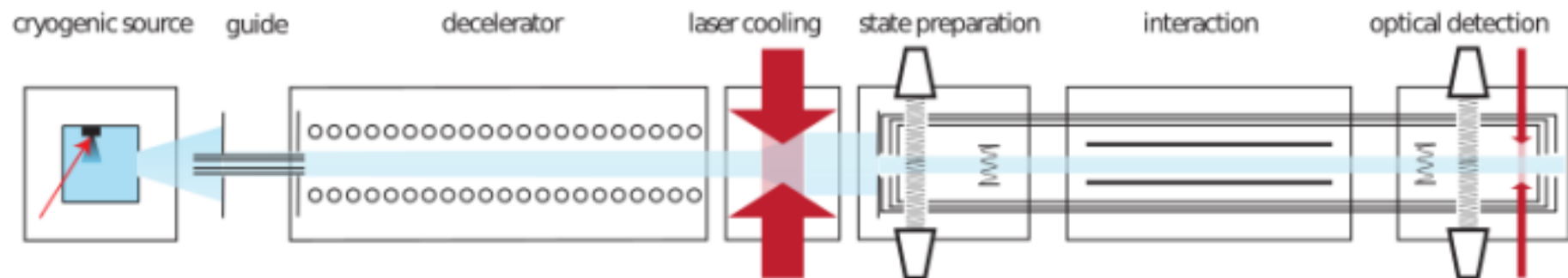
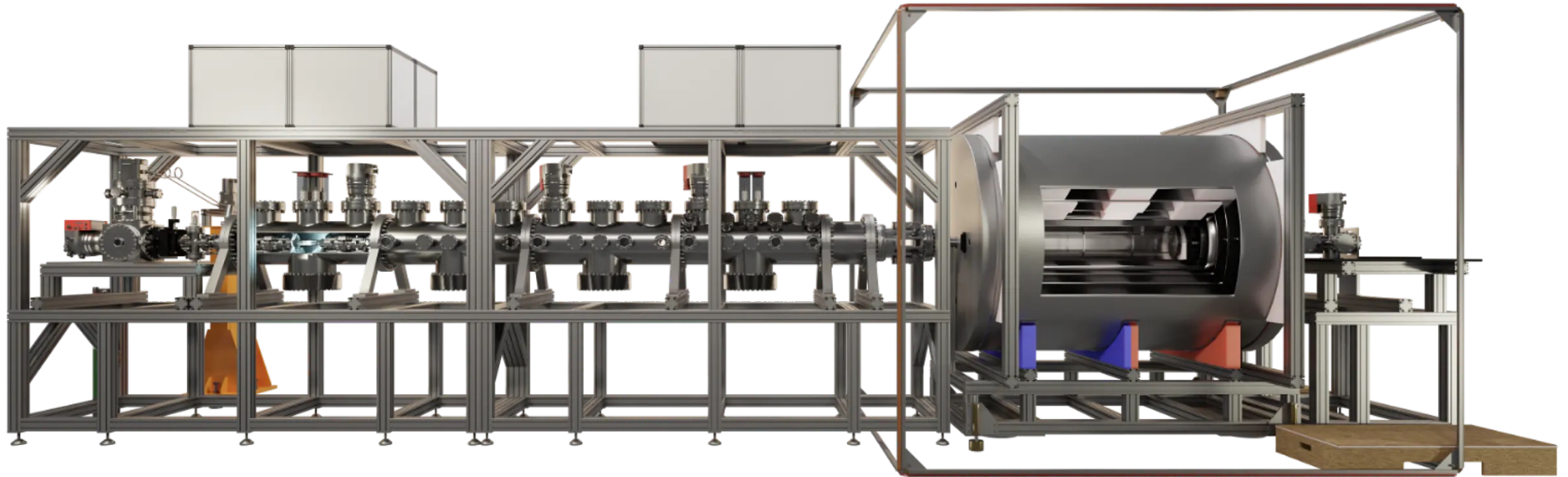
Nikhef

Dutch National Institute for (astro)Particle Physics



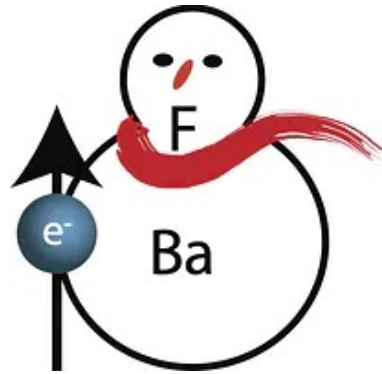
VRIJE
 UNIVERSITEIT
 AMSTERDAM

NL-eEDM experiment



Selected applications

- BaF (and friends)
 - coupling constants
 - laser cooling
 - IPs



- Polyatomic molecules
 - BaCH₃
 - YbCH₃
 - BaOH



Anastasia Borschevsky



Steven Hoekstra

W_d/W_s parameters

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

Electron electric dipole moment (eEDM)

$$H_{sr}^{\mathcal{P}, \mathcal{T}\text{-odd}} = (W_s k_s + W_d d_e) \Omega$$

$$W_s = \frac{1}{\Omega k_s} \langle \Psi^{(0)} | H^{\text{S-PS}} | \Psi^{(0)} \rangle$$

$$H^{\text{S-PS}} = \frac{iG_F k_s}{e\sqrt{2}} \sum_{i,k} \rho_k(\mathbf{r}_i) \gamma^0 \gamma^5$$

$$W_d = \frac{1}{\Omega d_e} \langle \Psi^{(0)} | H^{\text{eEDM}} | \Psi^{(0)} \rangle$$

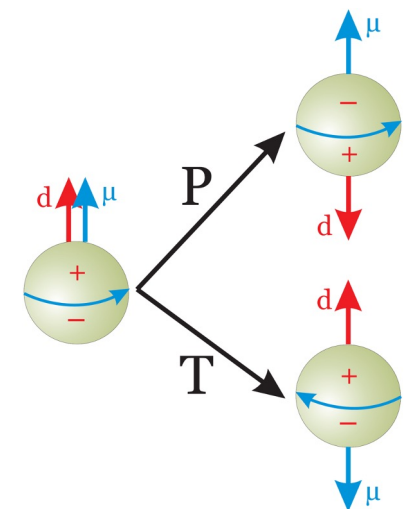
$$H^{\text{eEDM-II}} = \frac{2icd_e}{e\hbar} \sum_i \gamma^0 \gamma^5 \mathbf{p}_i^2$$

- 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

Kriplovich, Nauka (1981), EN trans. G&B (1991)

Kozlov, Zh. Eksp. Teor. Fiz. 89, 1933 (1985)

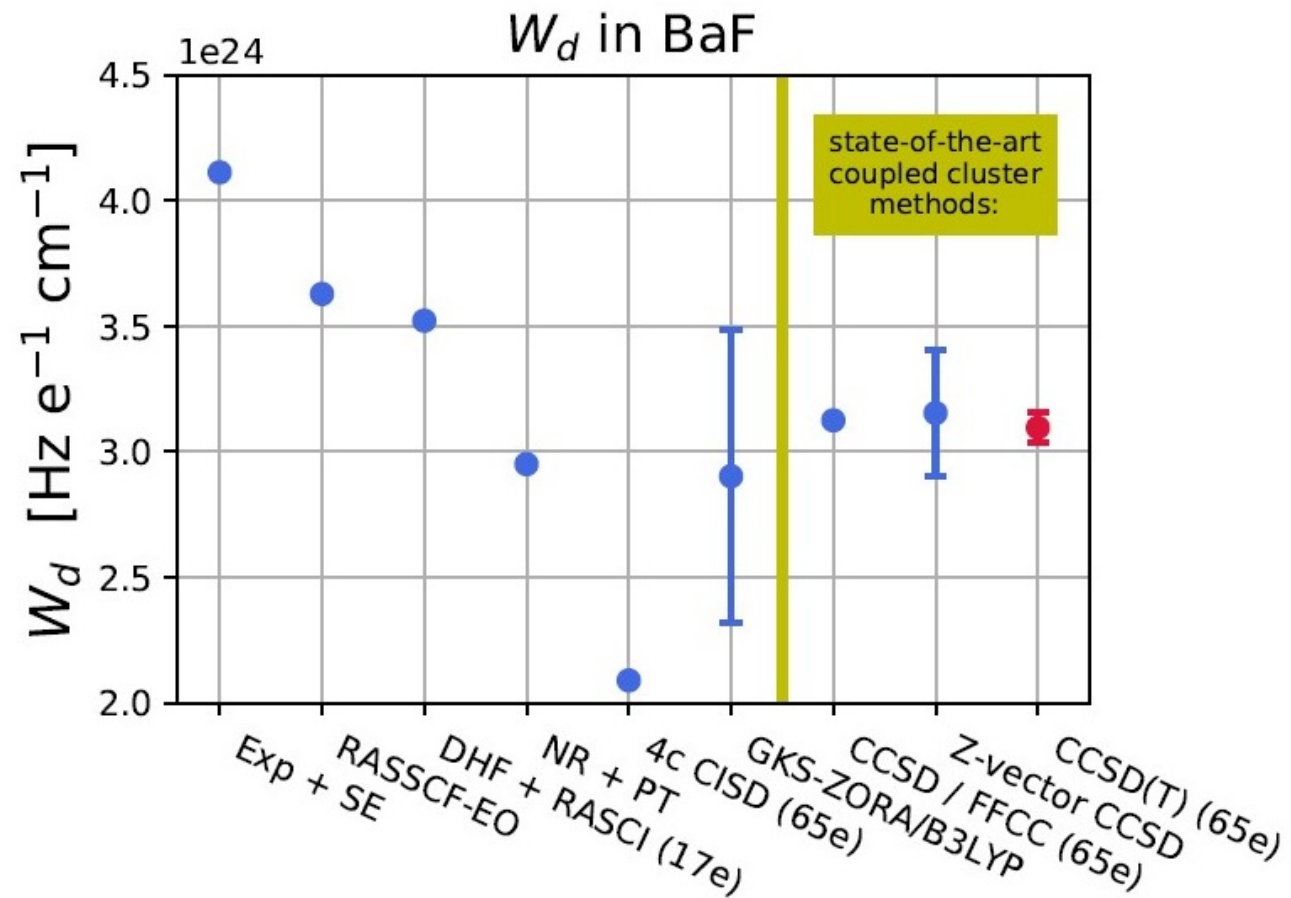
Dimitriev et al, Phys. Lett. A 167, 280 (1992)



BaF: W_d/W_s parameters

- Calculated values

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



BaF: W_d/W_s parameters

- Uncertainties

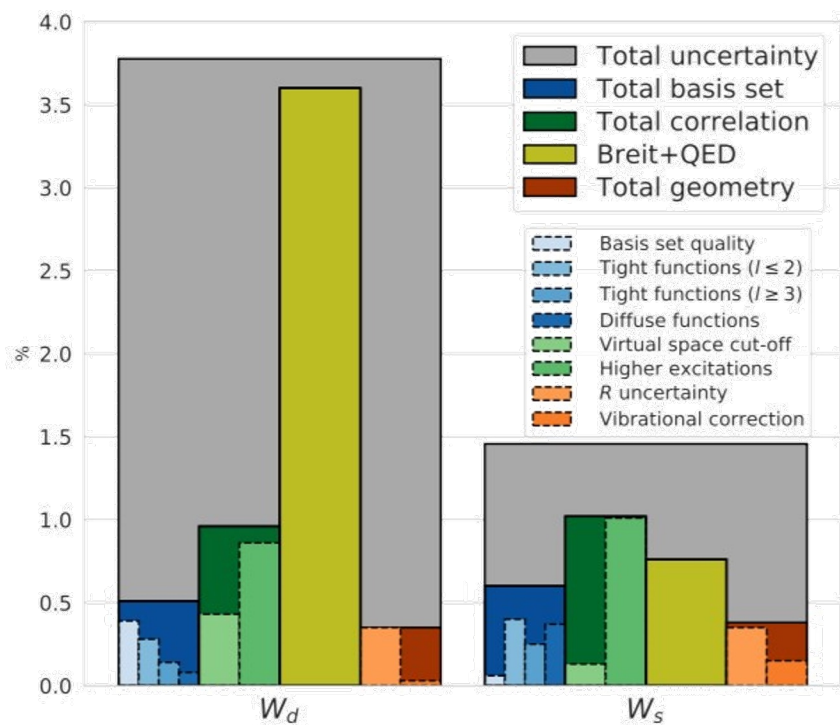
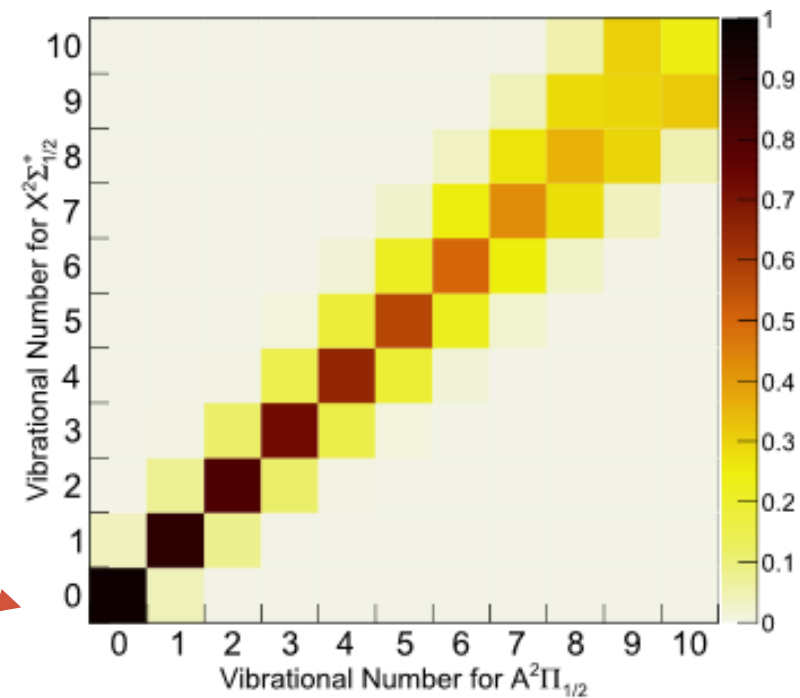
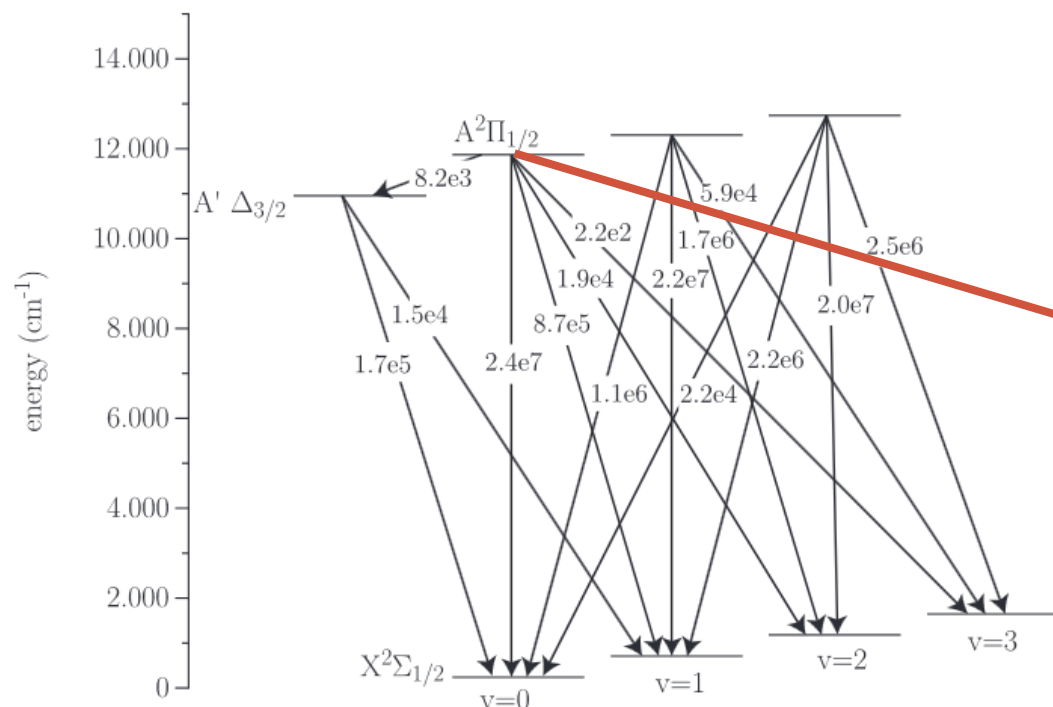


Table 8. A_{\parallel} and A_{\perp} of ^{137}Ba in BaF (MHz)

method	^{137}BaF			
	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)	

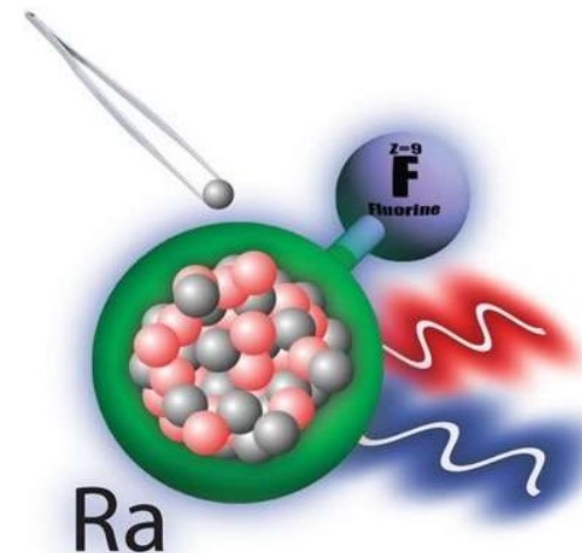
BaF: cooling scheme

- transition rates, FCFs, lifetimes



RaF

- promising candidate for precision measurements
- many (high-impact) experimental studies
- spectra, isotope shifts
- new measurements: IP
- theory before experiment



nature

Explore content ▾ About the journal ▾ Publish with us ▾

[nature](#) > [articles](#) > [article](#)

Article | [Open access](#) | Published: 27 May 2020

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](#)

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 al.

[Nature Physics \(2023\)](#).

Featured in Physics

Editors' Suggestion

Open Access

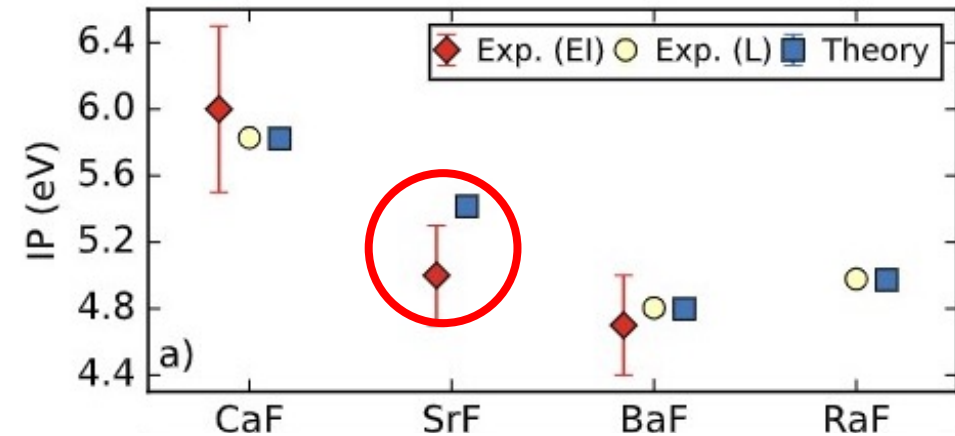
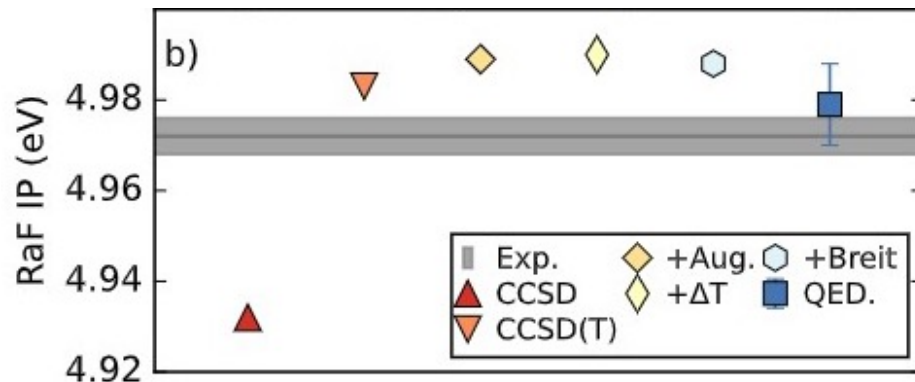
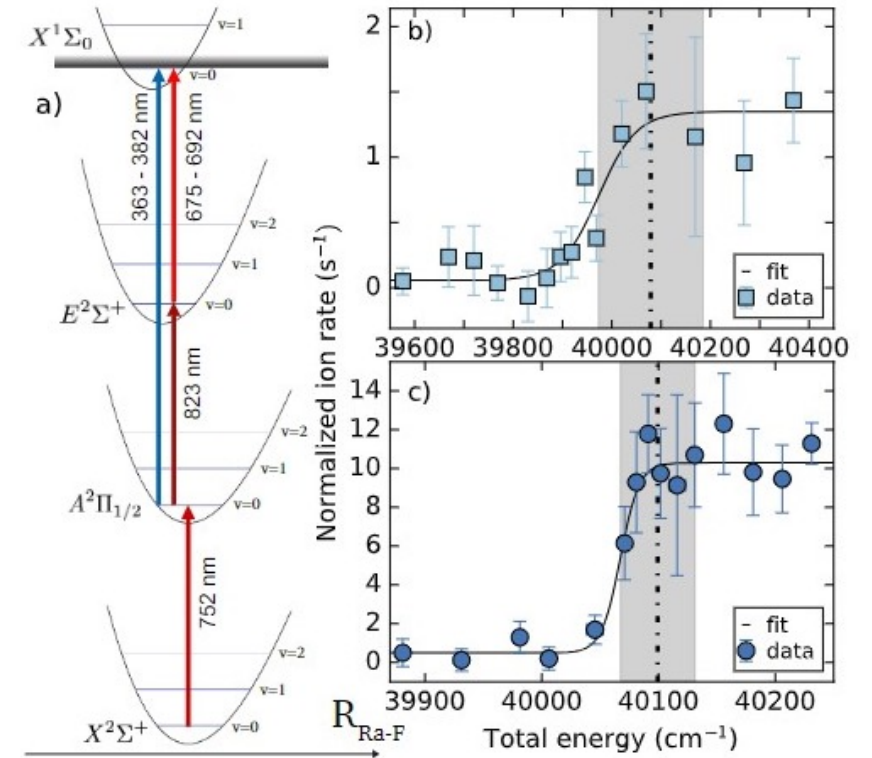
Isotope Shifts of Radium Monofluoride Molecules

S. M. Udrescu *et al.*

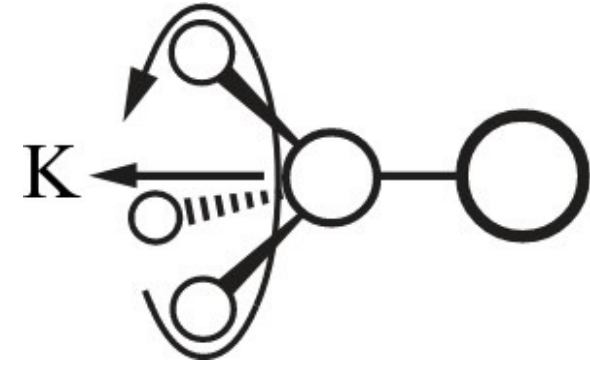
Phys. Rev. Lett. **127**, 033001 – Published 14 July 2021

RaF: ionization potential

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



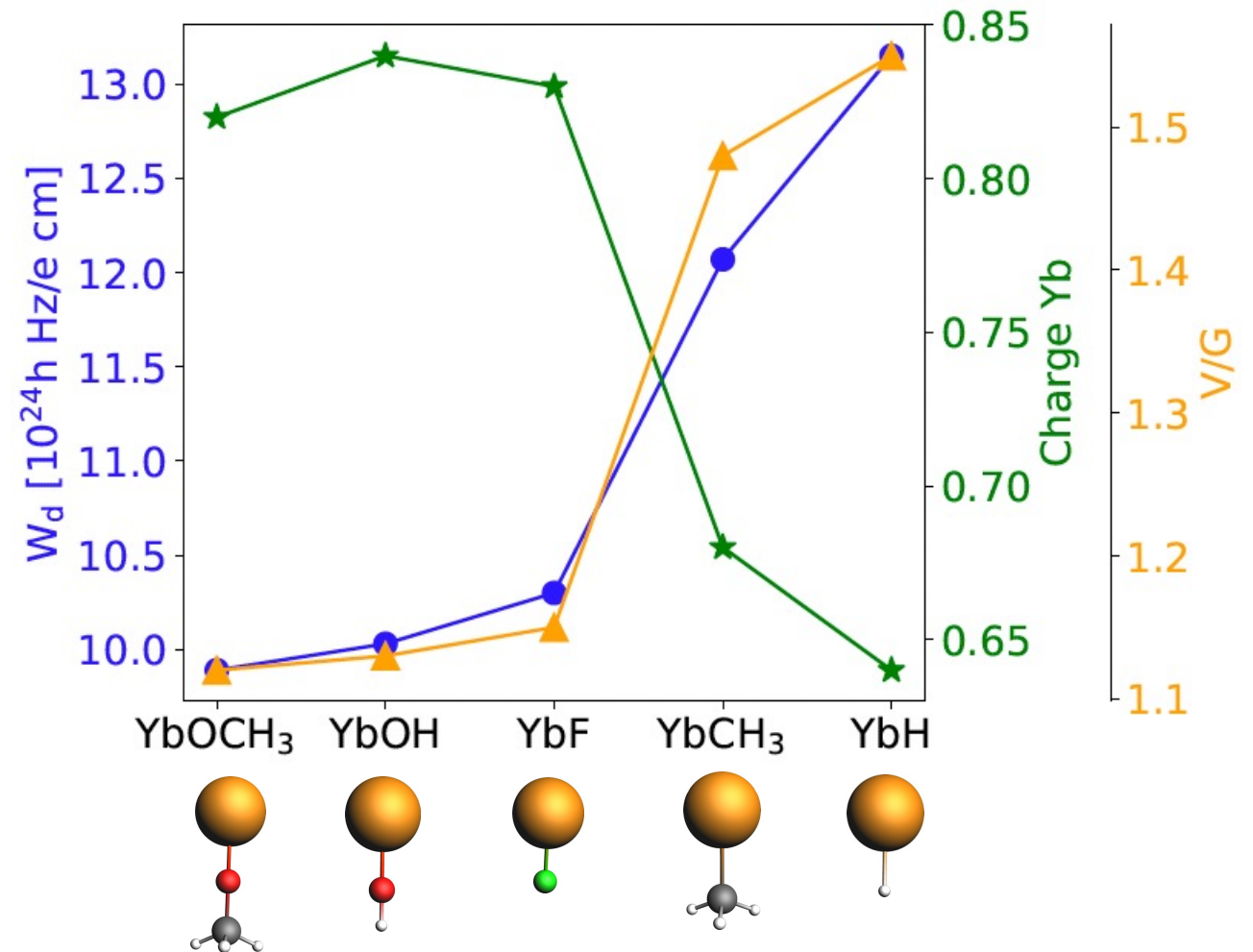
Symmetric top molecules



- 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

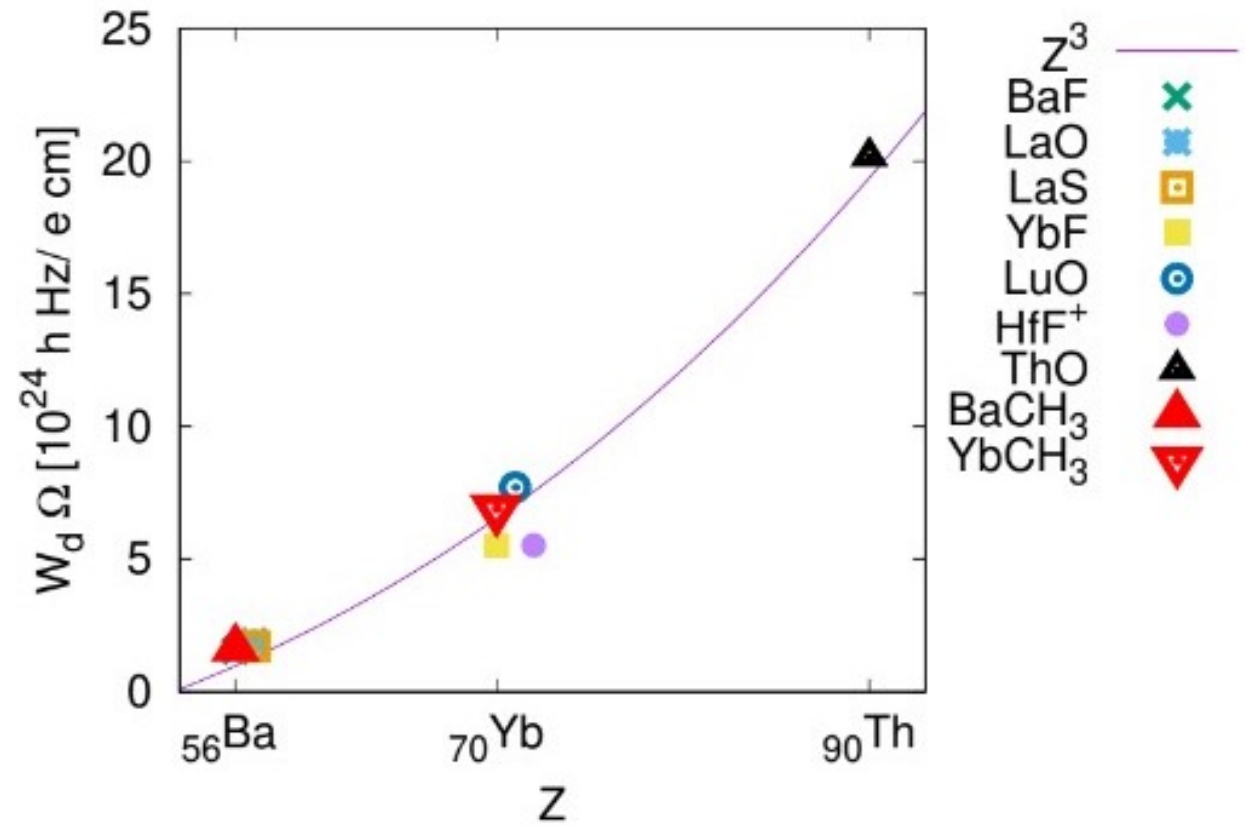
Bonding effects

- 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



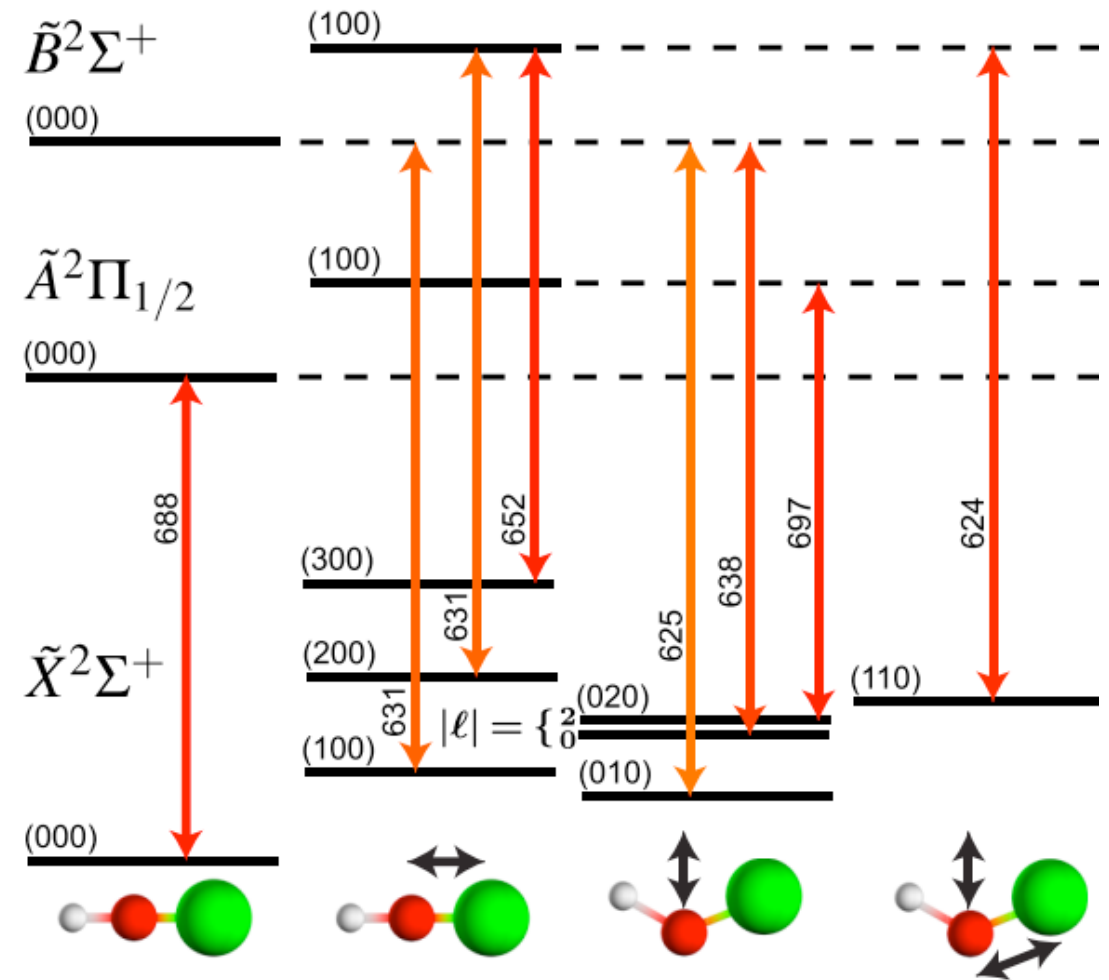
Z-scaling

- W_d scales as Z^3



BaOH: work in progress

- bending mode lifetime
- cooling scheme
- polarizability and scattering tensors



(this is fake news – actually SrOH)

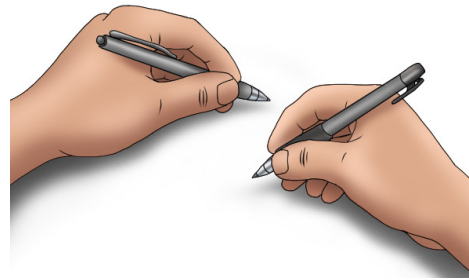
Parity violation in chiral molecules

Is universe right or left handed?



Symmetry breaking in nature

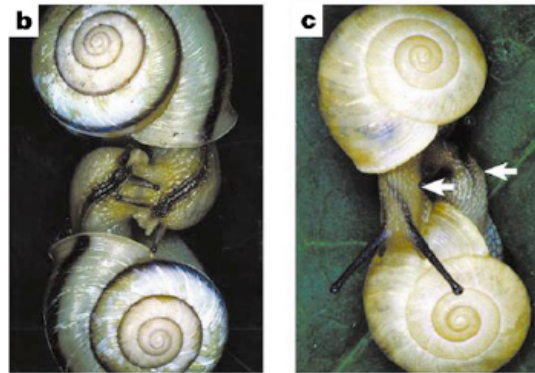
- left-/right-handedness (1:10)



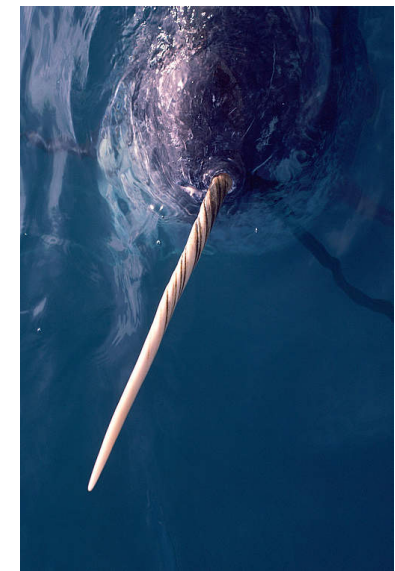
- dextro-/levo-cardia (1:12 000)



- left/right snail shells (1:20 000)

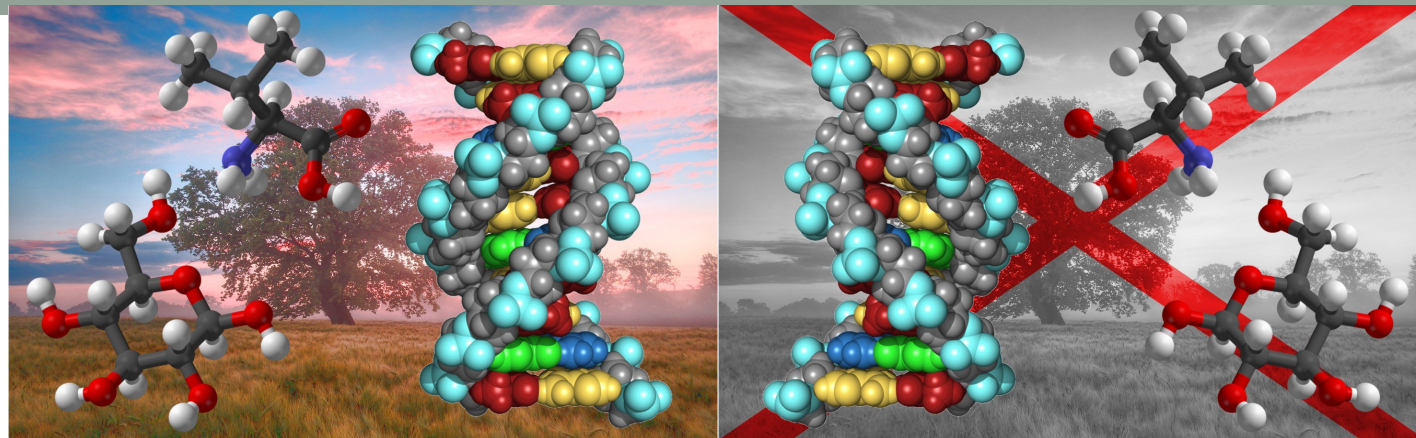


- right/left-twisting narwhal tusks (1:?)



Biohomochirality

- Only one enantiomer appears in live organisms
- D-sugars, L-proteins, D-DNA, ...
- Arthur C. Clarke – Technical Error
- Condition for life?
- Origin
 - parity violation
 - circularly polarized light
 - chiral surfaces
 - panspermia
- Amplification mechanisms
 - asymmetric autocatalysis



Planet	Earth	Saturn	Arion	Hypatia	Pirx
Homochiral life?	✓	?	?	?	?
Racemic life?	✗	?	?	?	?

Biohomochirality

- Racemic drug

Cetirizine (Zyrtec)

Ibuprofen (Advil)

- Enantiopure drug

Levocetirizine (Xyzal)

Dexibuprofen (Seractil)

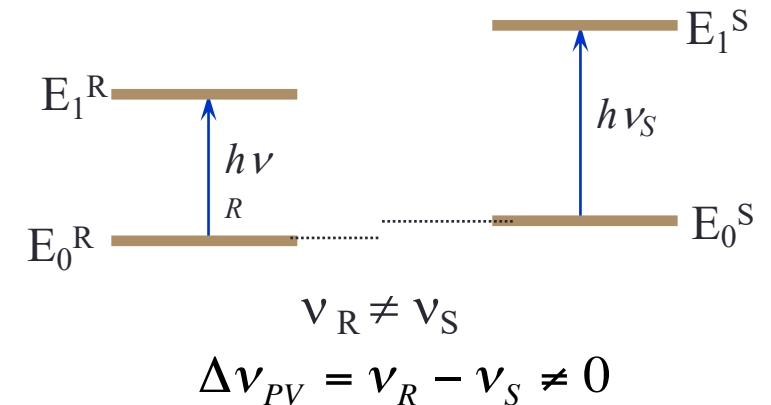
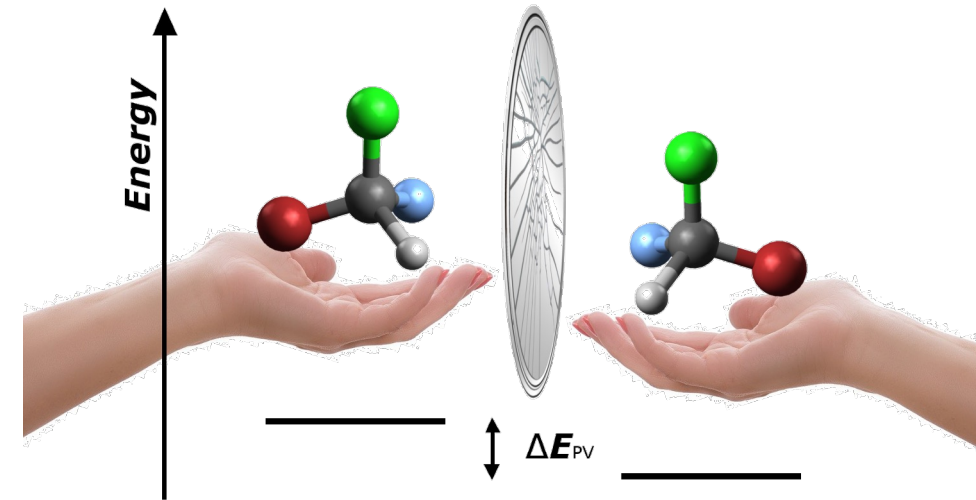
- Thalidomide cautionary tale

- (S) is sedative (morning sickness)
- (R) is teratogenic (birth defects)
- *in vivo* conversion



PV in molecules

- chiral molecules
 - inherent parity violation effects
 - unseen experimentally
- attempts
 - camphor $|\Delta\nu/\nu| < 10^{-8}$ theory: $|\Delta\nu/\nu| \sim 10^{-19}$
 - CHFClBr $|\Delta\nu/\nu| < 10^{-13}$ theory: $|\Delta\nu/\nu| \sim 10^{-17}$
- sensitive molecules and predictions needed



Letokhov, Phys. Lett. 53A, 275 (1975)

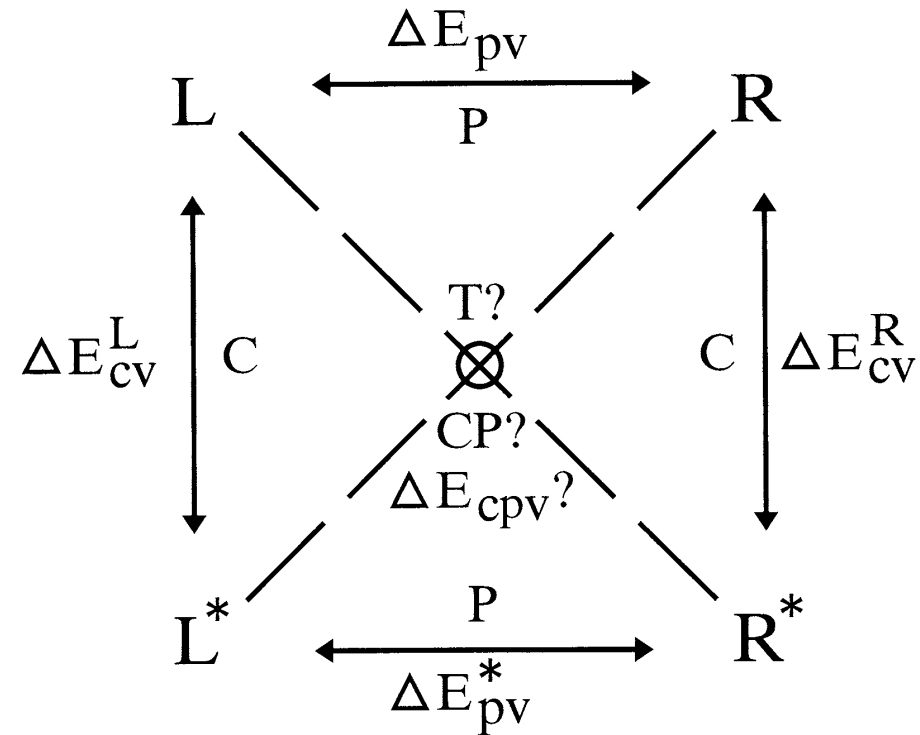
Glorieux, Oka, Opt. Commun. 23, 369 (1977); .Schwerdtfeger, et al., Chem. Phys. Lett. 383, 496 (2004)

Daussy et al., PRL 83, 1554 (1999); Ziskind et al., Euro. Phys. J. D 20, 219 (2002)

Quack, Stohner, J. Chem. Phys. 119, 11228–11240 (2003); Rauhut, Schwerdtfeger, PRA 103, 042819 (2021)

PV in molecules

- CP violation test
- $E_{PV}^* \stackrel{?}{=} E_{PV}$



PV from EW theory

- Interaction Lagrangian between fermions and EW bosons

$$\mathcal{L}_{\text{int}} = \sum_{k=1}^3 \left\{ -e \left((-1) \bar{e}_k \gamma^\mu e_k + (2/3) \bar{u}_k \gamma^\mu u_k + (-1/3) \bar{d}_k \gamma^\mu d_k \right) A_\mu \right.$$

γ boson (photon)

$$- \frac{e}{2\sqrt{2} \sin \theta_w} \left[(\bar{\nu}_{ek} \gamma^\mu (1 - \gamma^5) e_k + \bar{u}_k \gamma^\mu (1 - \gamma^5) d'_k) W_\mu^+ \right.$$

W^+ boson

$$\left. + (\bar{e}_k \gamma^\mu (1 - \gamma^5) \nu_{ek} + \bar{d}'_k \gamma^\mu (1 - \gamma^5) u_k) W_\mu^- \right]$$

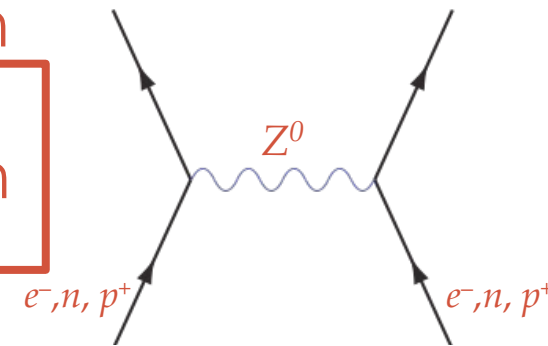
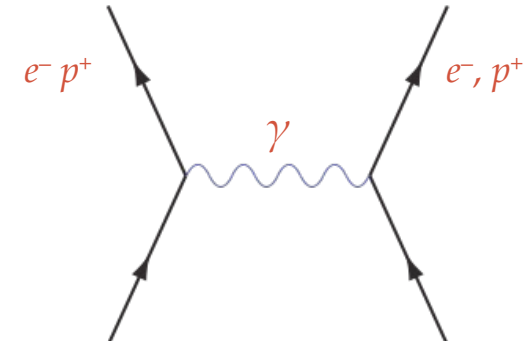
W^- boson

$$- \frac{e}{2 \sin \theta_w \cos \theta_w} \left(\sum_{f=1}^4 \bar{f}_k \gamma^\mu (g_V^f - g_A^f \gamma^5) f_k \right) Z_\mu \left. \right\}$$

Z^0 boson

- Weinberg mixing angle θ_w $\begin{pmatrix} \gamma \\ Z^0 \end{pmatrix} = \begin{pmatrix} \cos \theta_w & \sin \theta_w \\ -\sin \theta_w & \cos \theta_w \end{pmatrix} \begin{pmatrix} B \\ W_3 \end{pmatrix}$

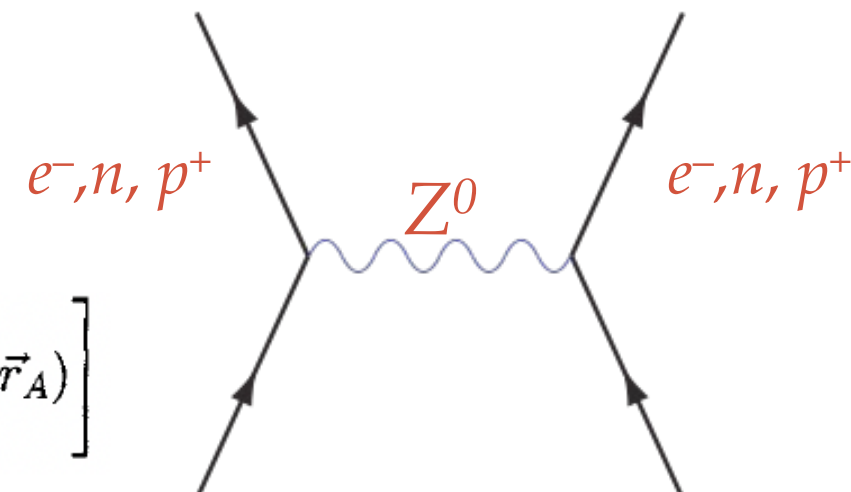
$$\cos \theta_w = \frac{m_W}{m_Z}$$



PV from EW theory

- Effective PV Hamiltonian

$$\begin{aligned}
 \hat{H}_{\text{pv}}^{(\text{e-nucl})} &= \hat{H}_{\text{pv}}^{(\text{e-nucl},1)} + \hat{H}_{\text{pv}}^{(\text{e-nucl},2)} \\
 &= \sum_{i=1}^n \left[\hat{h}_{\text{pv}}^{(1)}(i) + \hat{h}_{\text{pv}}^{(2)}(i) \right] \\
 &= \frac{G_F}{2\sqrt{2}} \sum_{i=1}^n \left[\sum_{A=1}^N Q_w(A) \gamma_i^5 \rho(\vec{r}_i - \vec{r}_A) + \sum_{A=1}^N \kappa_A \vec{\alpha}_i \cdot \hat{I} \rho(\vec{r}_i - \vec{r}_A) \right]
 \end{aligned}$$



spin-independent (SI, $V_n A_e$) \gg spin-dependent (SD, $V_e A_n$)

$$Q_w = -N + Z (1 - 4 \sin^2 \theta_W) \approx -N$$

$$\kappa_A = \lambda_A (1 - 4 \sin^2 \theta_W) / 2 \approx 0.038 \lambda_A$$

$$\sin^2 \theta_W \approx 0.231$$

Properties of H_{PV}

- Effective Hamiltonian H_{PV} – perturbation to H_{DC}

$$H_{PV} = \sum_A H_{PV}^A \quad H_{PV}^A = \frac{G_F}{2\sqrt{2}} Q_w^A \sum_i \gamma_5(i) \rho^A(\mathbf{r}_i)$$

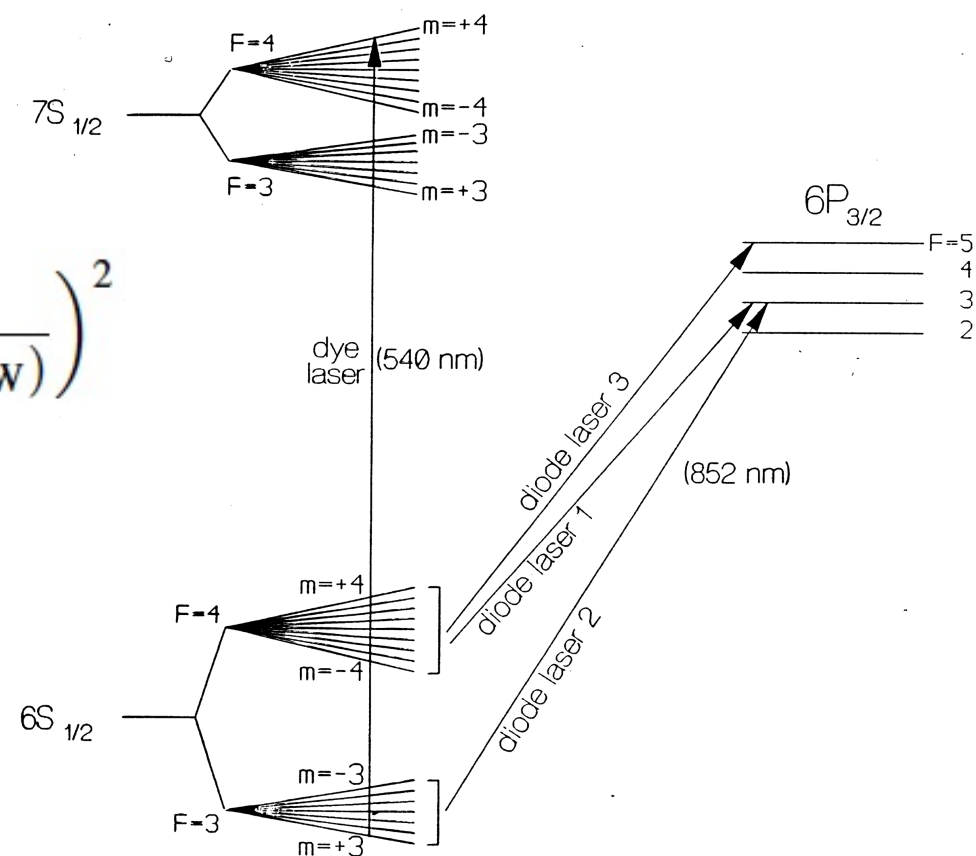
- Small prefactor

$$G_F = 2.22255 \times 10^{-14} E_h a_0^3 \approx 2\sqrt{2} \left(\frac{4\pi\hbar^2}{4\pi\epsilon_0 M_Z^2 c^4} \right) \left(\frac{ec}{2 \sin(2\theta_w)} \right)^2$$

- $H_{DC} + H_{PV}$ commutes with J
 - mixing of orbitals with same J , but different L
 - notably s-p mixing
 - Laporte rule violation (e.g. Cs $6s$ - $7s$ E1 transition)

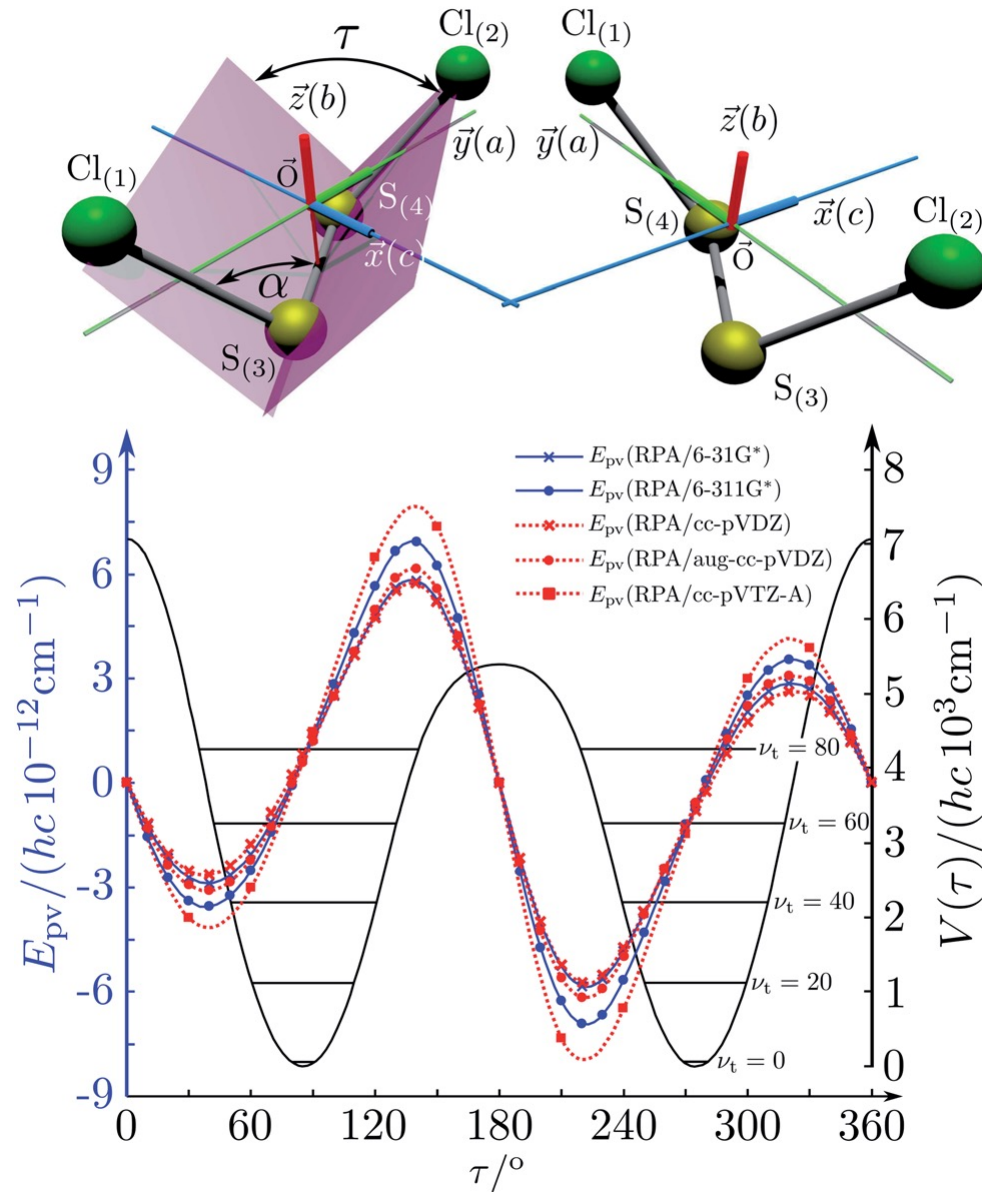
$$\Psi_{s_{1/2}}^{PV} = \Psi_{s_{1/2}} + \epsilon_{PV} \Psi_{p_{1/2}}$$

$$\epsilon = \frac{i \langle \Psi_{2s_{1/2}} | H_{PV} | \Psi_{2p_{1/2}} \rangle}{E_{2s_{1/2}} - E_{2p_{1/2}}}$$



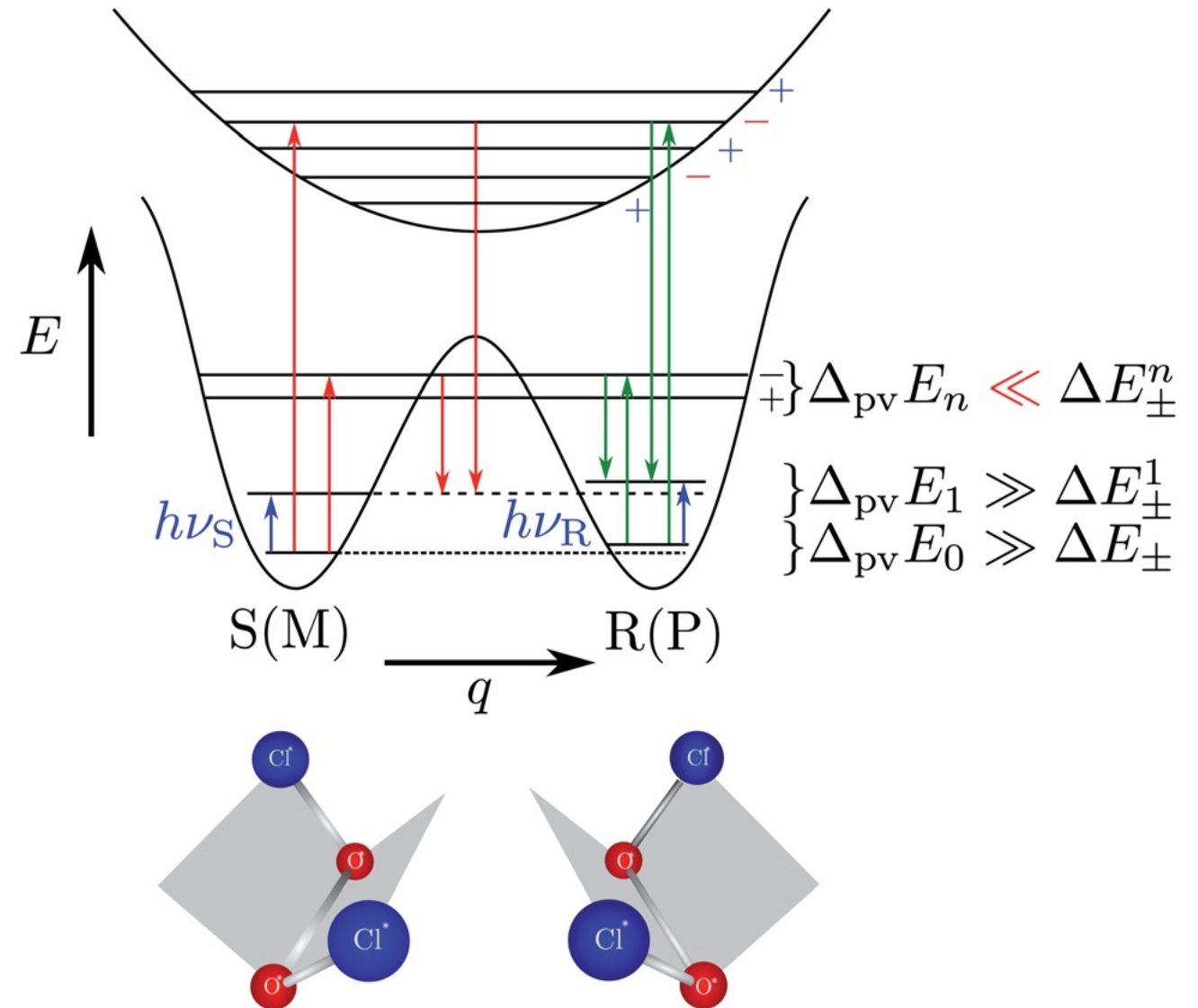
PV in molecules

- Torsion of X_2Y_2 (here S_2Cl_2)
- E_{pot} even
- E_{PV} odd



PV in molecules

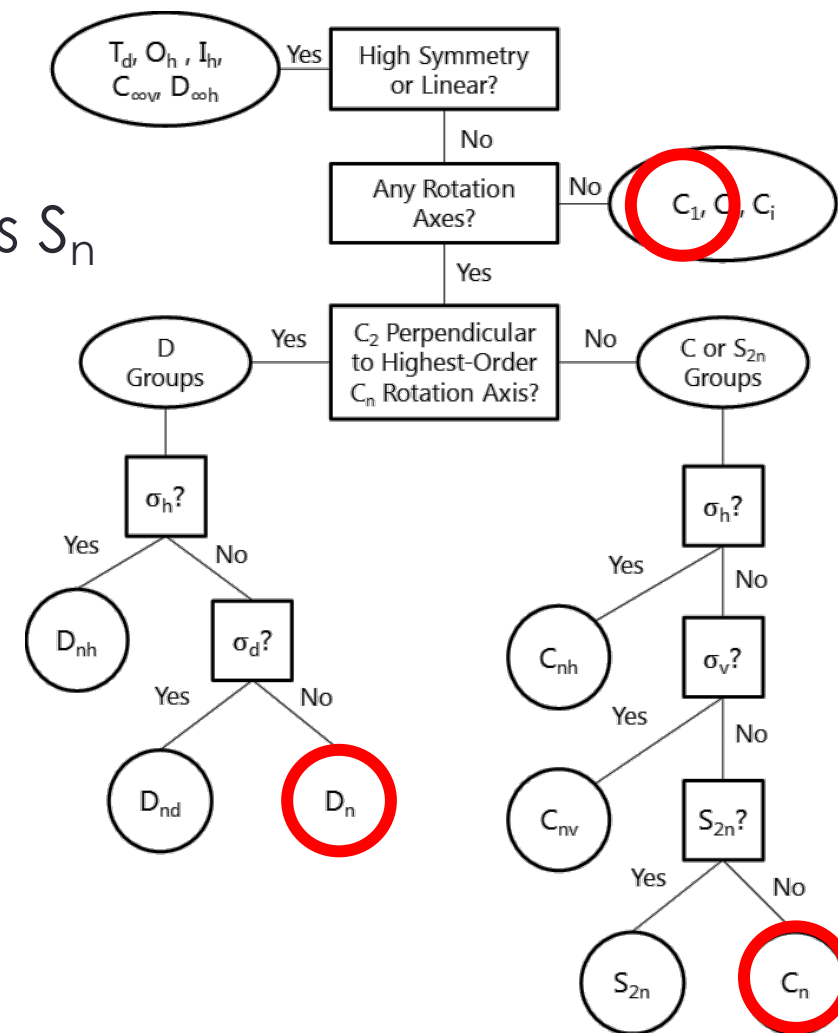
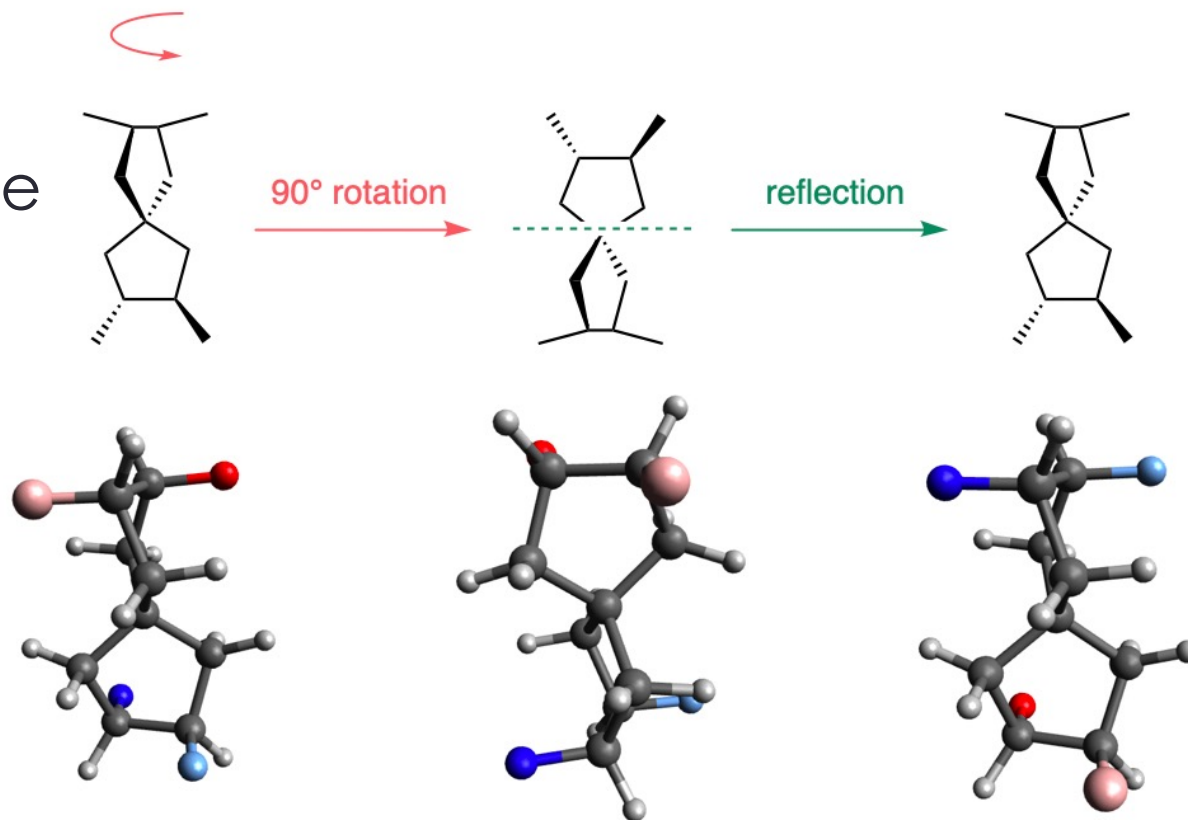
- PV measurement schemes
 - direct vibrational
 - via electronically excited state



Molecular chirality

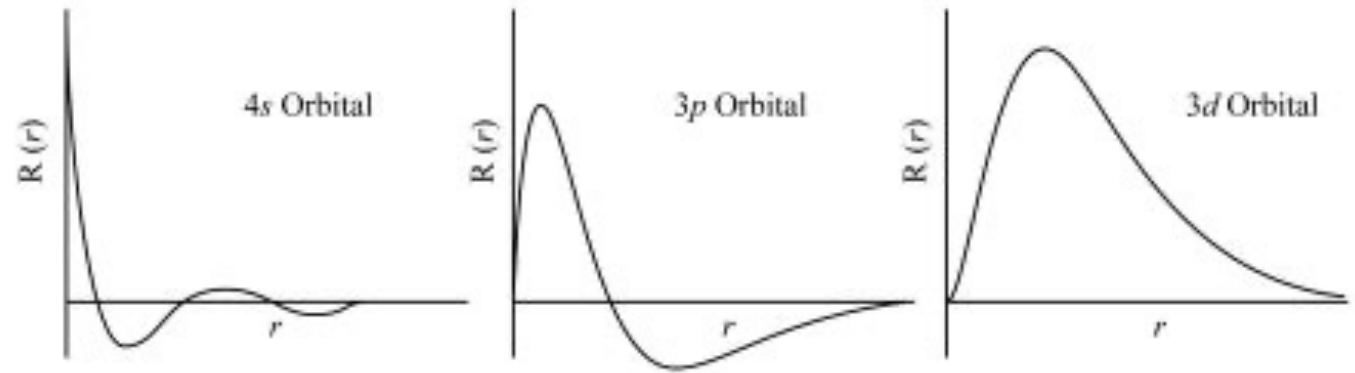
- General definition – lack of improper rotation axis S_n
- $S_1 = i$, $S_2 = \sigma$

- S_4 example



Some trends

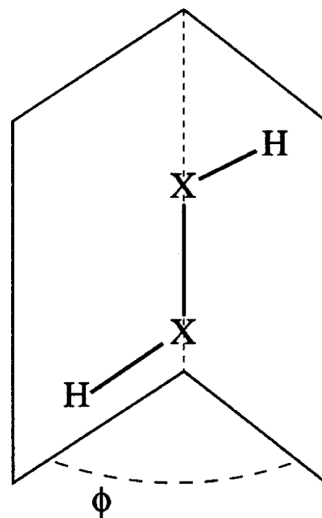
- H_2Po_2 PV matrix elements
 - PN vs FN model
 - core vs valence contributions
 - $s_{1/2} | p_{1/2}$ vs $p_{3/2} | d_{3/2}$



	$2p_{1/2}$	$3p_{1/2}$	$4p_{1/2}$	$5p_{1/2}$	$6p_{1/2}$
$1s_{1/2}$	1.385[+5] (1.551[+5])	-7.082[+4] (-7.942[+4])	3.583[+4] (4.018[+4])	1.573[+4] (1.764[+4])	-4.904[+3] (-5.499[+3])
$2s_{1/2}$	5.486[+4] (6.148[+4])	-2.806[+4] (-3.148[+4])	1.419[+4] (1.593[+4])	6.233[+3] (6.992[+3])	-1.943[+3] (-2.180[+3])
$3s_{1/2}$	-2.646[+4] (-2.966[+4])	1.354[+4] (1.519[+4])	-6.847[+3] (-7.683[+3])	-3.007[+3] (-3.373[+3])	9.372[+2] (1.051[+3])
$4s_{1/2}$	1.345[+4] (1.508[+4])	-6.881[+3] (-7.720[+3])	3.481[+3] (3.906[+3])	1.529[+3] (1.715[+3])	-4.765[+2] (-5.346[+2])
$5s_{1/2}$	-6.182[+3] (-6.929[+3])	3.162[+3] (3.548[+3])	-1.600[+3] (-1.795[+3])	-7.024[+2] (-7.881[+2])	2.190[+2] (2.457[+2])
$6s_{1/2}$	2.260[+3] (2.534[+3])	-1.156[+3] (-1.297[+3])	5.849[+2] (6.562[+2])	2.568[+2] (2.881[+2])	-8.006[+1] (-8.982[+1])

Some trends

- H_2Po_2 at 45°

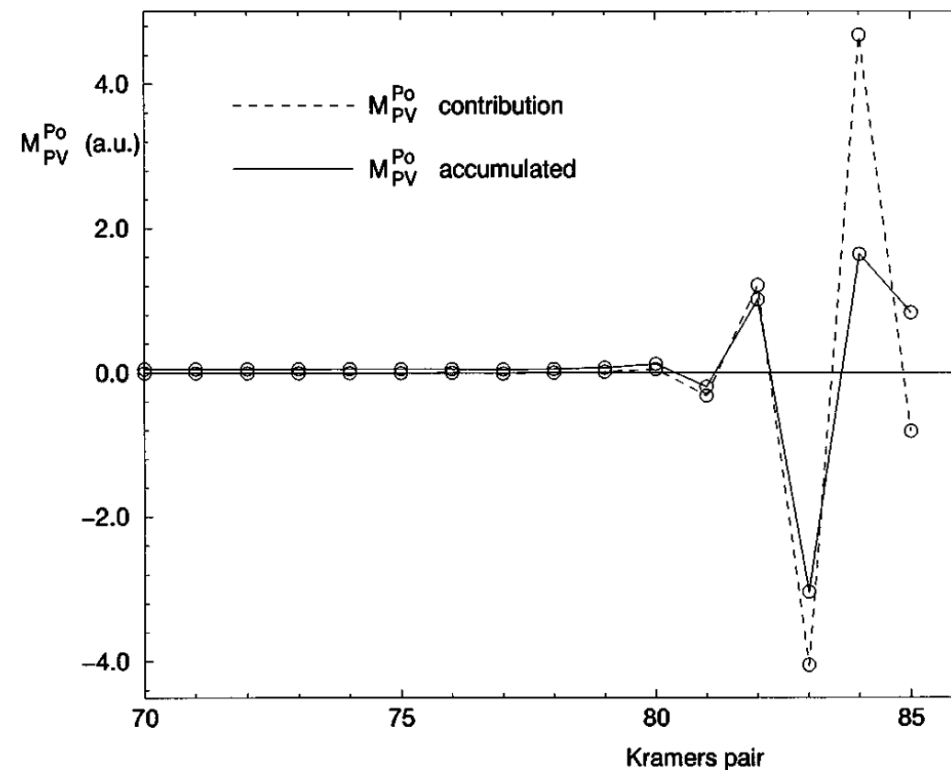


- s/p mixing

$$\begin{bmatrix} \psi_+ \\ \psi_- \end{bmatrix} = \begin{bmatrix} \cos \theta & e^{i\phi} \sin \theta \\ -e^{-i\phi} \sin \theta & \cos \theta \end{bmatrix} \begin{bmatrix} s_{1/2}^X \\ p_{1/2}^X \end{bmatrix}; \quad \theta \in \left[-\frac{\pi}{2}, \frac{\pi}{2}\right]$$

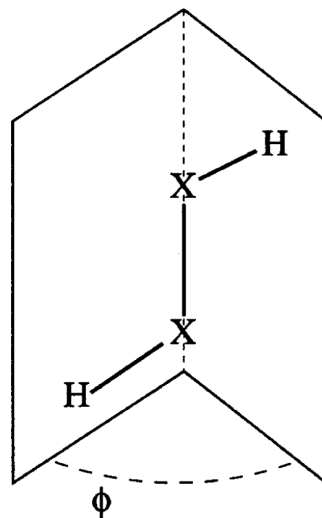
$$\langle \psi_+ | \gamma_5 \rho^X | \psi_+ \rangle = 2 \cos \theta \cos \phi \sin \theta \langle s_{1/2}^X | \gamma_5 \rho^X | p_{1/2}^X \rangle = -\langle \psi_- | \gamma_5 \rho^X | \psi_- \rangle$$

- spherically symmetric core MOs $\Rightarrow \psi_-$ and ψ_+ contribute equally \Rightarrow core cancellation



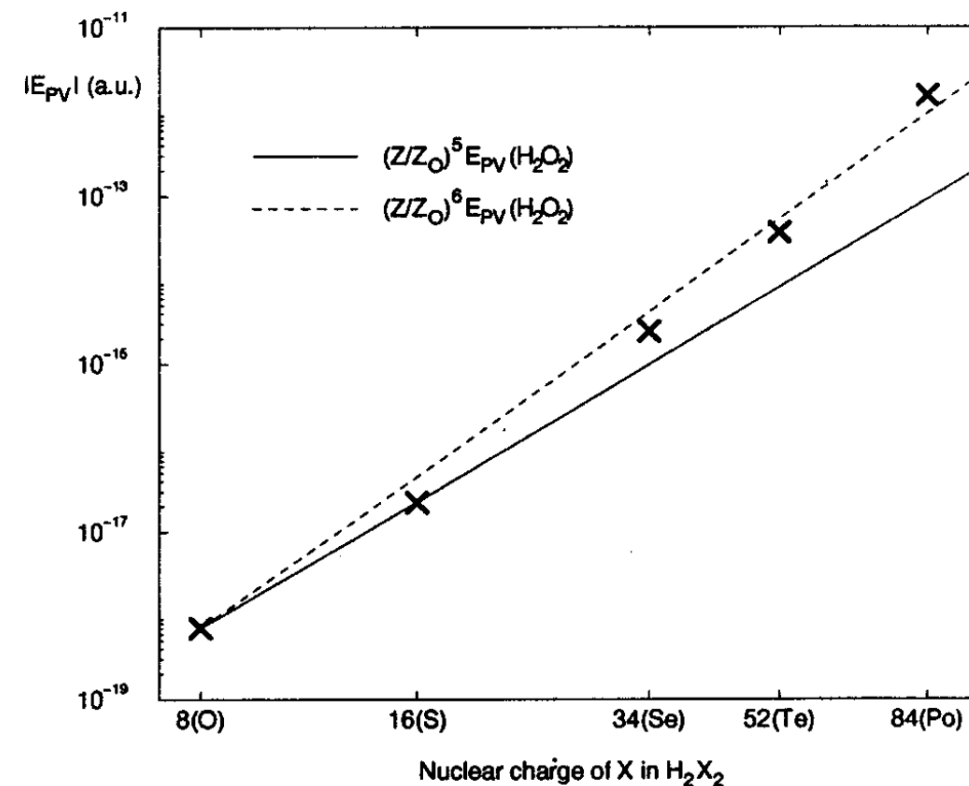
Some trends

- H_2X_2
- Z^5 scaling
- 1c-RSPT2



$$E_{pv} = 2 \operatorname{Re} \left\{ \sum_j \frac{\langle 0 | \hat{H}_{pv} | \Psi_j \rangle \langle \Psi_j | \hat{H}_{so} | 0 \rangle}{E_0 - E_j} \right\}$$

$\sim Z^2 \alpha N$
 $\sim Z^2 \alpha Q_w$ $\sim (Z\alpha)^2$



H_2X_2	M_{PV}^X (a.u.)	M_{PV}^H (a.u.)	N	$Q_{w,X}$	E_{PV} (a.u.)
H_2O_2	6.057×10^{-6}	9.5×10^{-9}	8	-7.421	-7.06×10^{-19}
H_2S_2	9.581×10^{-5}	9.1×10^{-8}	16	-14.84	-2.24×10^{-17}
H_2Se_2	3.586×10^{-3}	2.1×10^{-7}	46	-43.54	-2.45×10^{-15}
H_2Te_2	3.149×10^{-2}	3.7×10^{-7}	78	-74.24	-3.67×10^{-14}
H_2Po_2	8.279×10^{-1}	3.2×10^{-7}	125	-118.9	-1.55×10^{-12}




Bouchiat², PRB 48, 111 (1974)

Harris, Stodolsky, PRB 78, 313 (1978)

Hegstrom, Rein, Sandars, JCP 73, 2329 (1980)

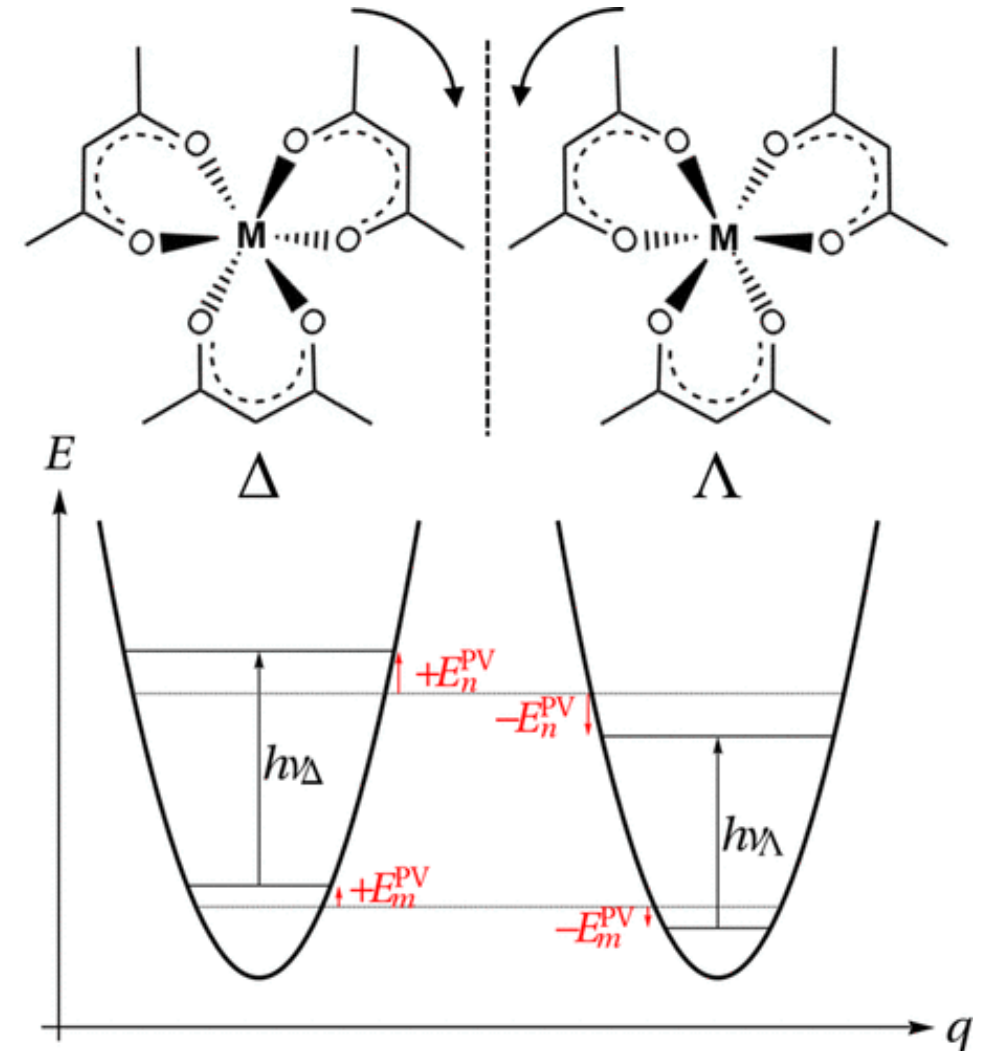
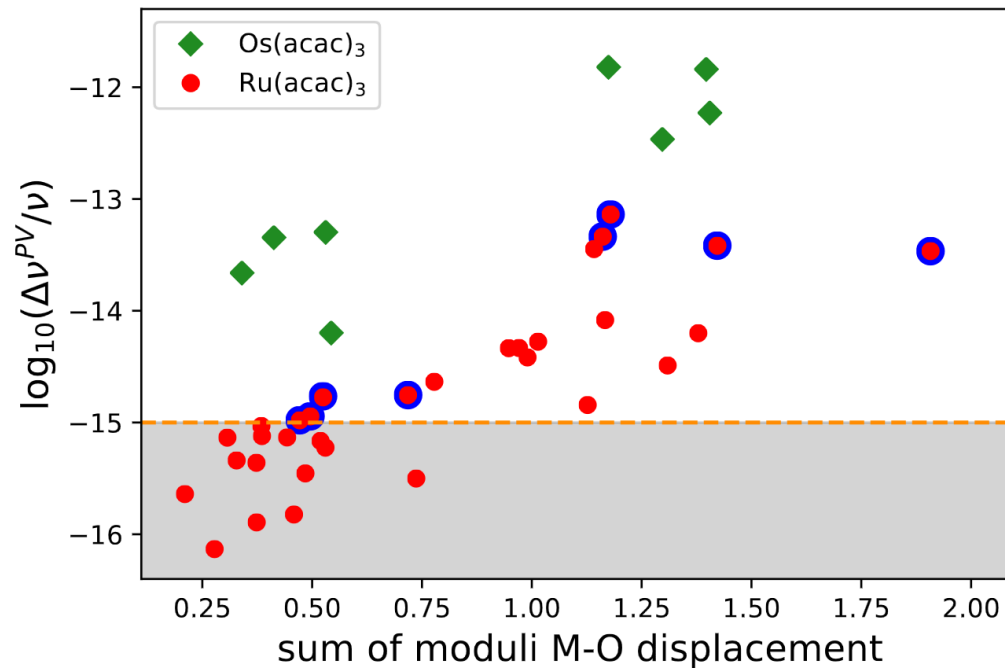
Laerdahl, Schwerdtfeger, PRA 60, 4439 (1999)

Experiments under construction

	PI	Type	Target species	Projected accuracy
	Benoît Darquié, LPL Paris	beam	neutral	0.1 Hz
	David Leibbrandt, UCLA	trap	cation	1 Hz
	Yuval Shagam, Technion, Israel	trap	cation	1 Hz

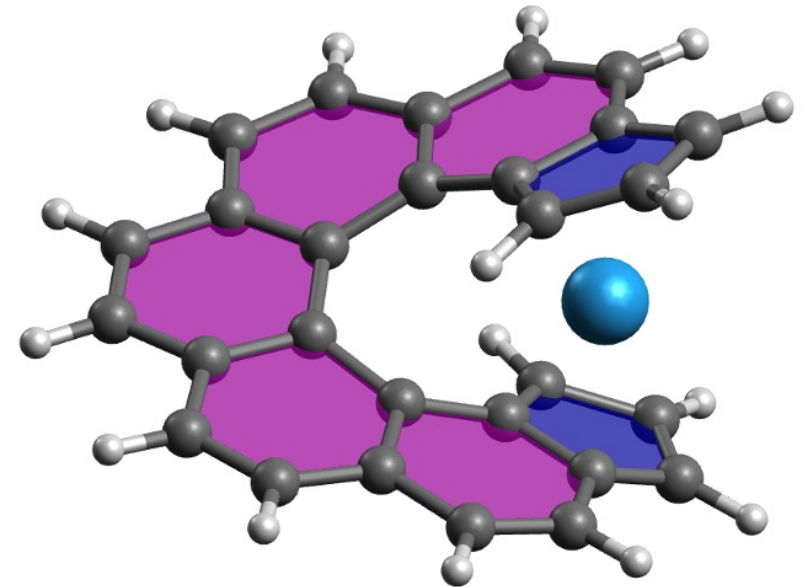
M(acac)₃ propellers

- M = Ru, Os, Ir
- methodology tests
- beyond Z⁵



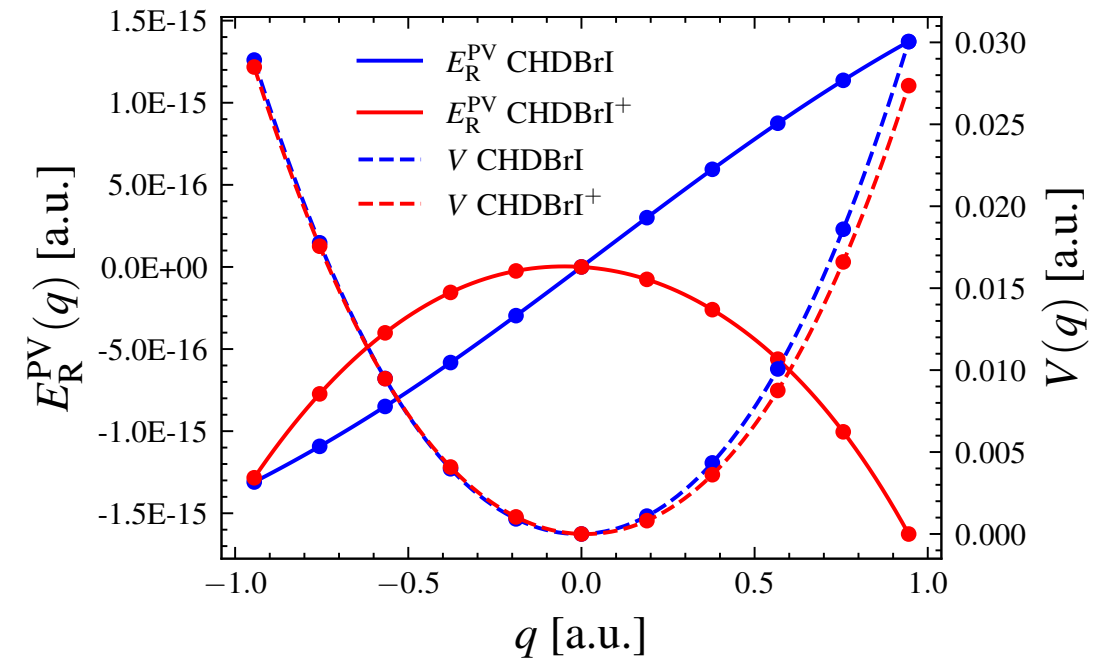
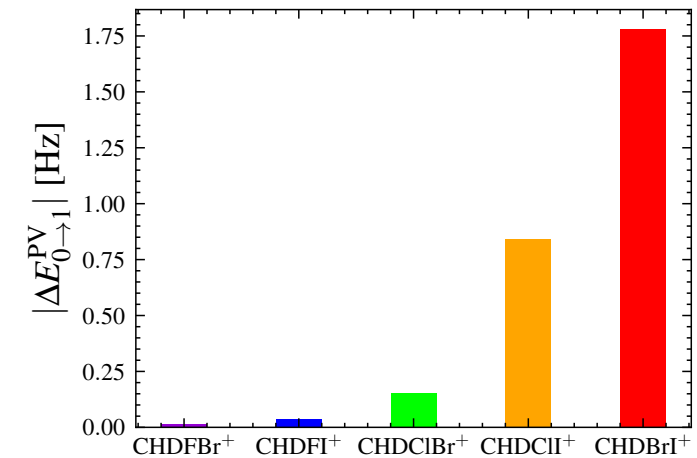
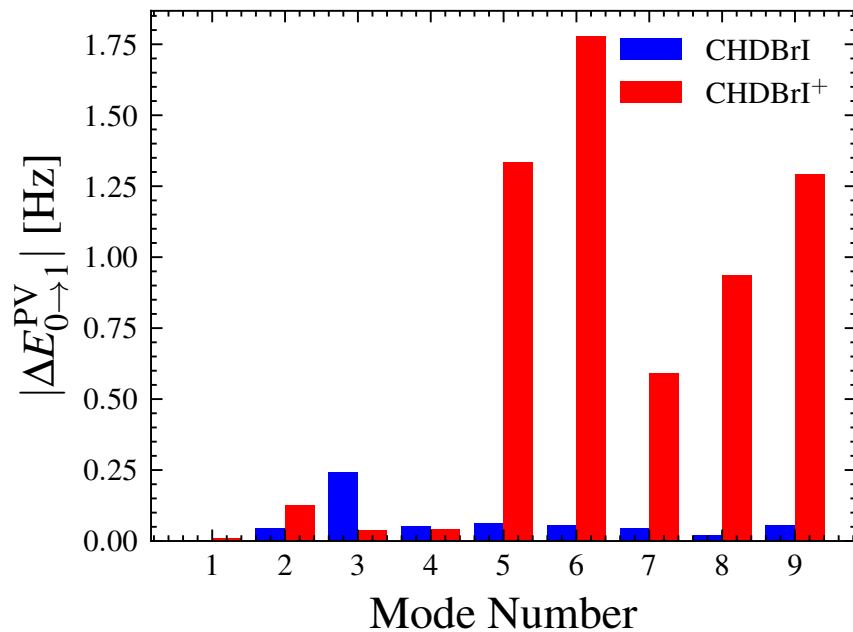
Metalohelicenes

- organometallic complexes
- helical ferrocene known
- Ru/Os analogues need to be synthesised
- shifts up to 3Hz



Isotopically chiral ions

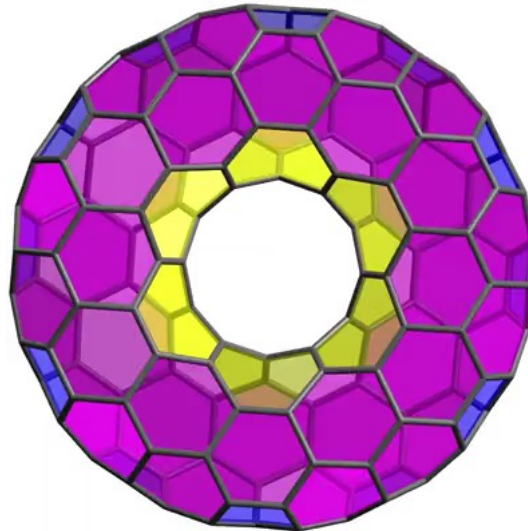
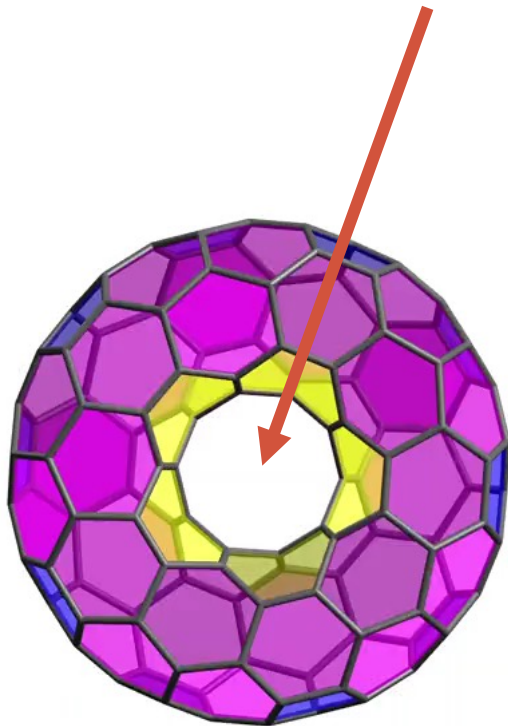
- CHDBrI⁺
- amplification

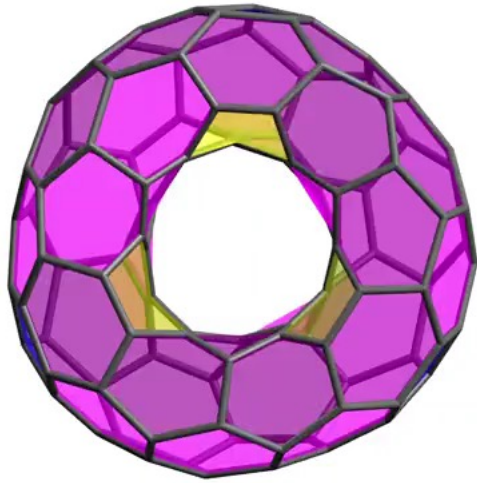
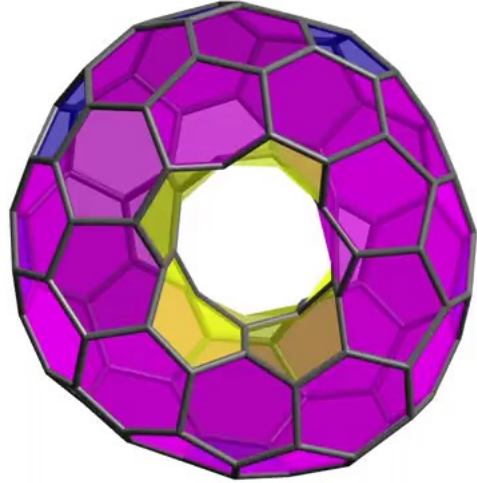
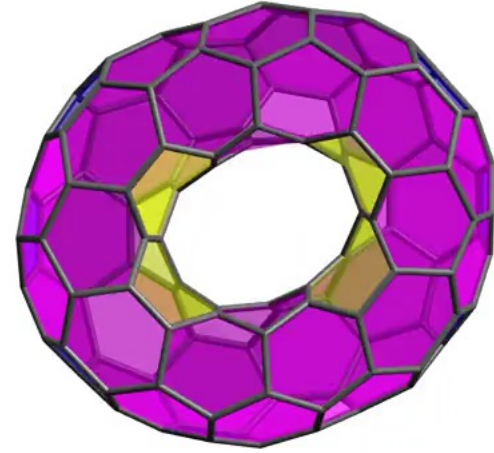
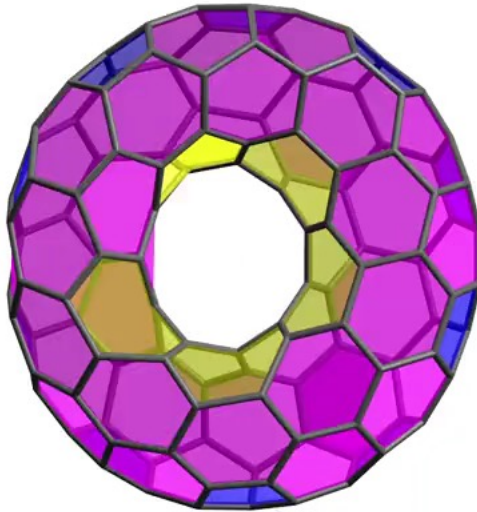
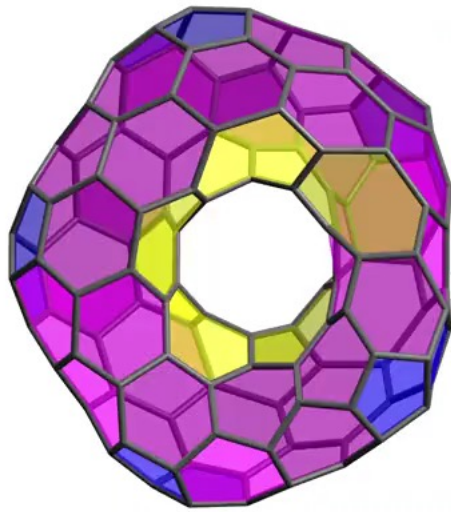
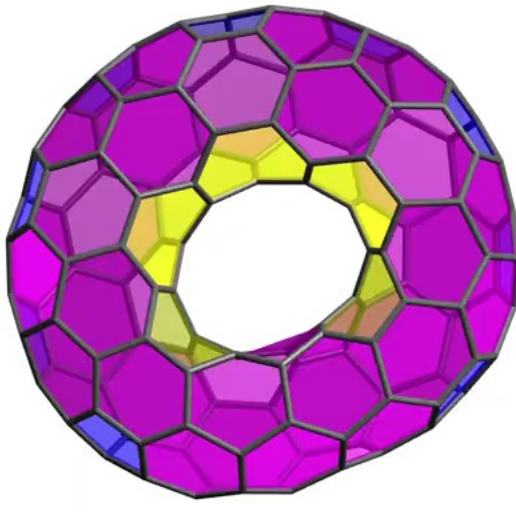


$$\Delta P_{0 \rightarrow 1} = 2(P_1 - P_0) \approx \frac{\hbar}{\mu\omega_e} \left[P^{[2]} - \frac{1}{\mu\omega_e^2} P^{[1]} V^{[3]} \right]$$

Carbon nanotoroids

- carbon allotropes - fullerenes, nanotubes, nanotoroids
- complex with metals



 D_3  C_2  D_2  C_2  C_2  C_2 

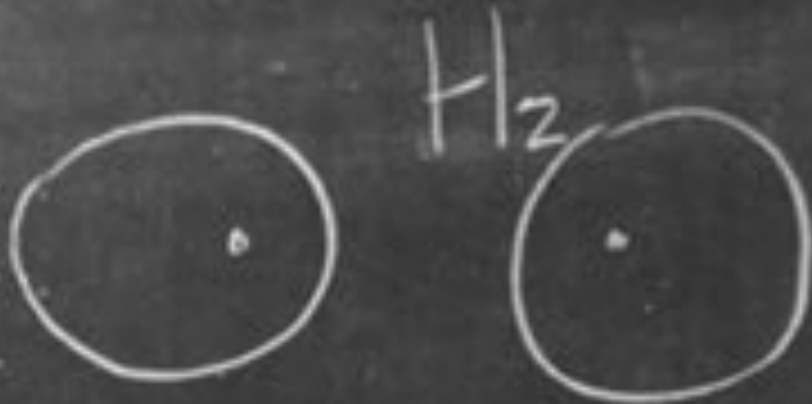
Searching for variation of fundamental constants

(with molecules and solids)

Dirac's large numbers hypothesis

$$V = \sum P^a V_{P^a}$$

$$V = V_0 - \sum V_{\gamma_A} \left\{ 1 - \left(\frac{\sigma_A}{\omega_A} \right) \right\}$$



Very large (or small) dimensionless universal constants cannot be pure mathematical numbers and must not occur in the basic laws of physics. These numbers are related by equations in which the coefficients are close to unity.

(P.A.M. Dirac, 1937, 1938, 1974, 1979)

antisym

sym

Dirac's large number hypothesis

- ratio of EM and gravitational force (in H):

$$F_{\text{em}}/F_{\text{g}} = e^2/4\pi\epsilon_0 G m_e m_p = 2.27 \times 10^{39}$$

- age of the universe in units of fundamental constants:

$$t_{\text{universe}} \approx 13.7 \times 10^9 \text{ years} = 5.12 \times 10^{39} e^2/4\pi\epsilon_0 m_e c^3$$

- Coincidence or $F_{\text{em}}/F_{\text{g}} \sim t_{\text{universe}}?$

$$G = 6.67384 \times 10^{-11} \text{ m}^3 \text{ kg}^{-1} \text{ s}^{-2}$$

$$m_e = 9.10938291 \times 10^{-31} \text{ kg}$$

$$c = 2.99792458 \times 10^8 \text{ m/s}$$

$$e = 1.602176634 \times 10^{-19} \text{ C}$$

$$m_p = 1.67262178 \times 10^{-27} \text{ kg}$$

$$k_e = 1/4\pi\epsilon_0 = 8.98755179 \times 10^9 \text{ N m}^2 \text{ C}^{-2}$$

Dirac's large number hypothesis

Physical Constants Involved	Large Numbers
1. Electrostatic force F_E and gravitational force F_G between a proton and an electron	$F_E/F_G \simeq 10^{40}$
2. Radius of the universe R and the radius of an electron r	$R/r \simeq 10^{40}$
3. Intensity of electromagnetic and gravitational interaction of elementary particles	$\frac{e^2/\hbar c}{Gm_e^2/\hbar c} \simeq 10^{40}$
4. Mass of a typical star M_\star and electron mass m_e	$M_\star/m_e \simeq 10^{60} = (10^{40})^{3/2}$
5. Mass of the universe M_U and proton mass m_p	$M_U/m_p \simeq 10^{80} = (10^{40})^2$
6. Mass of the universe M_U and Planck mass m_P	$M_U/m_P \simeq 10^{61}$
7. Hubble radius R_H and Planck length l_P	$R_H/l_P \simeq 10^{60}$
8. Planck mass density ρ_P and the observed matter density of the universe ρ	$\rho_P/\rho \simeq 10^{120} = N_1^{1/3}$
9. Planck energy E_P and CMBR temperature T_γ	$(E_P/T_\gamma)^2 \simeq 10^{60}$

Shortest article ever

The Ratio of Proton and Electron Masses

FRIEDRICH LENZ

Düsseldorf, Germany

(Received April 5, 1951)

THE most exact value at present¹ for the ratio of proton to electron mass is 1836.12 ± 0.05 . It may be of interest to note that this number coincides with $6\pi^5 = 1836.12$.

¹ Sommer, Thomas, and Hipple, *Phys. Rev.* **80**, 487 (1950).

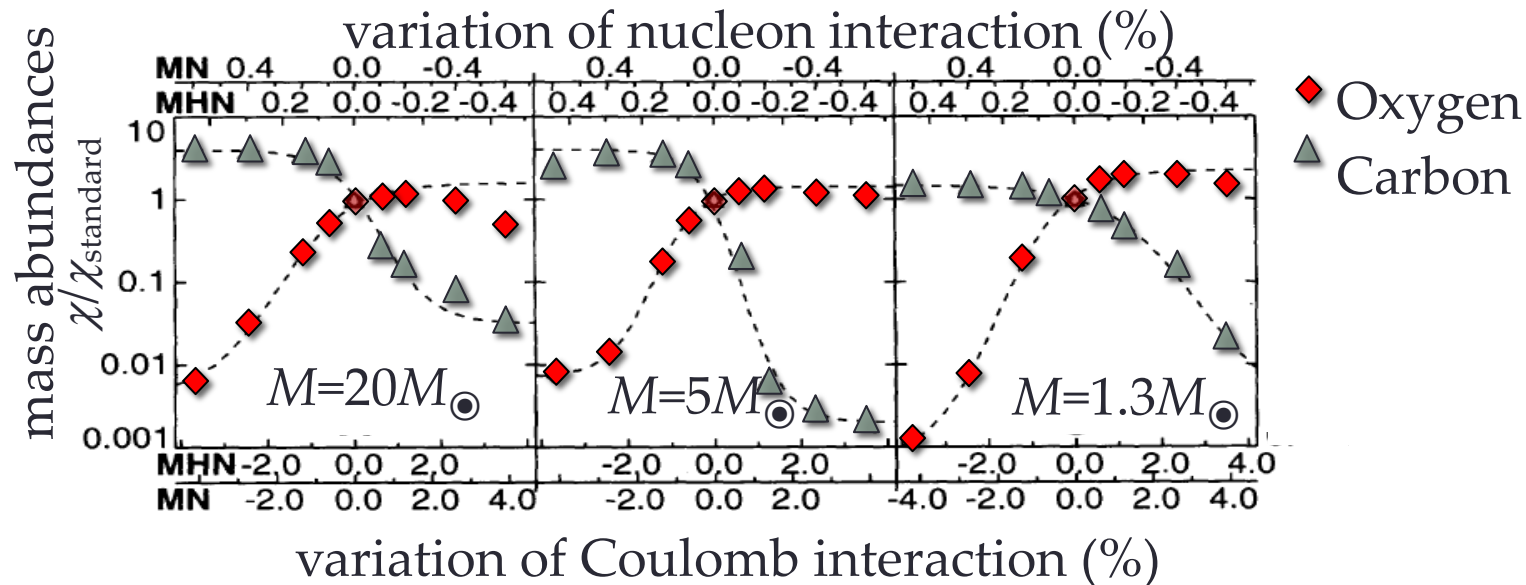
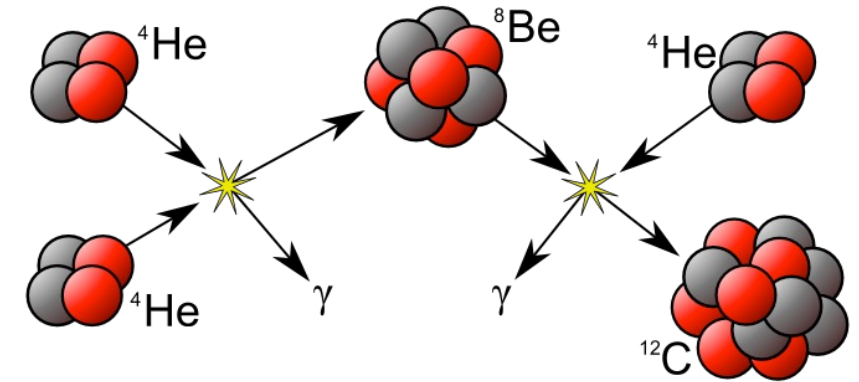
Fine tuning and anthropic principle

- fine-tuning of the fundamental constants is required for life to exist
- observation selection effect/bias



Carbon production

- If α_s varies by 0.5% and α_{EM} by 4%, the stellar production of carbon or oxygen will be reduced by a factor 30–1000



p^+/n mass difference

- $m_n = 939.565378 \text{ MeV}/c^2$, $m_p = 938.272046 \text{ MeV}/c^2$
- neutron-proton mass difference $\Delta m = 1.2933 \text{ MeV}/c^2$
- (Λ -QCD $2.52 \text{ MeV}/c^2$ and QED $-1.00 \text{ MeV}/c^2$)

- $0.5 < \Delta m < 1.0 \text{ MeV}/c^2 \rightarrow$ BBN would produce much more ^4He and far less H

- $\Delta m < 0.45 \text{ MeV}/c^2 \rightarrow$ protons would undergo inverse β -decay (electron capture) resulting in predominantly neutrons

- $\Delta m > 1.3 \text{ MeV}/c^2 \rightarrow$ much faster β -decay for neutrons \rightarrow far fewer neutrons \rightarrow difficult synthesis of the heavy elements

Variation of fundamental constants

- new physics beyond the Standard Model

- unitless constants

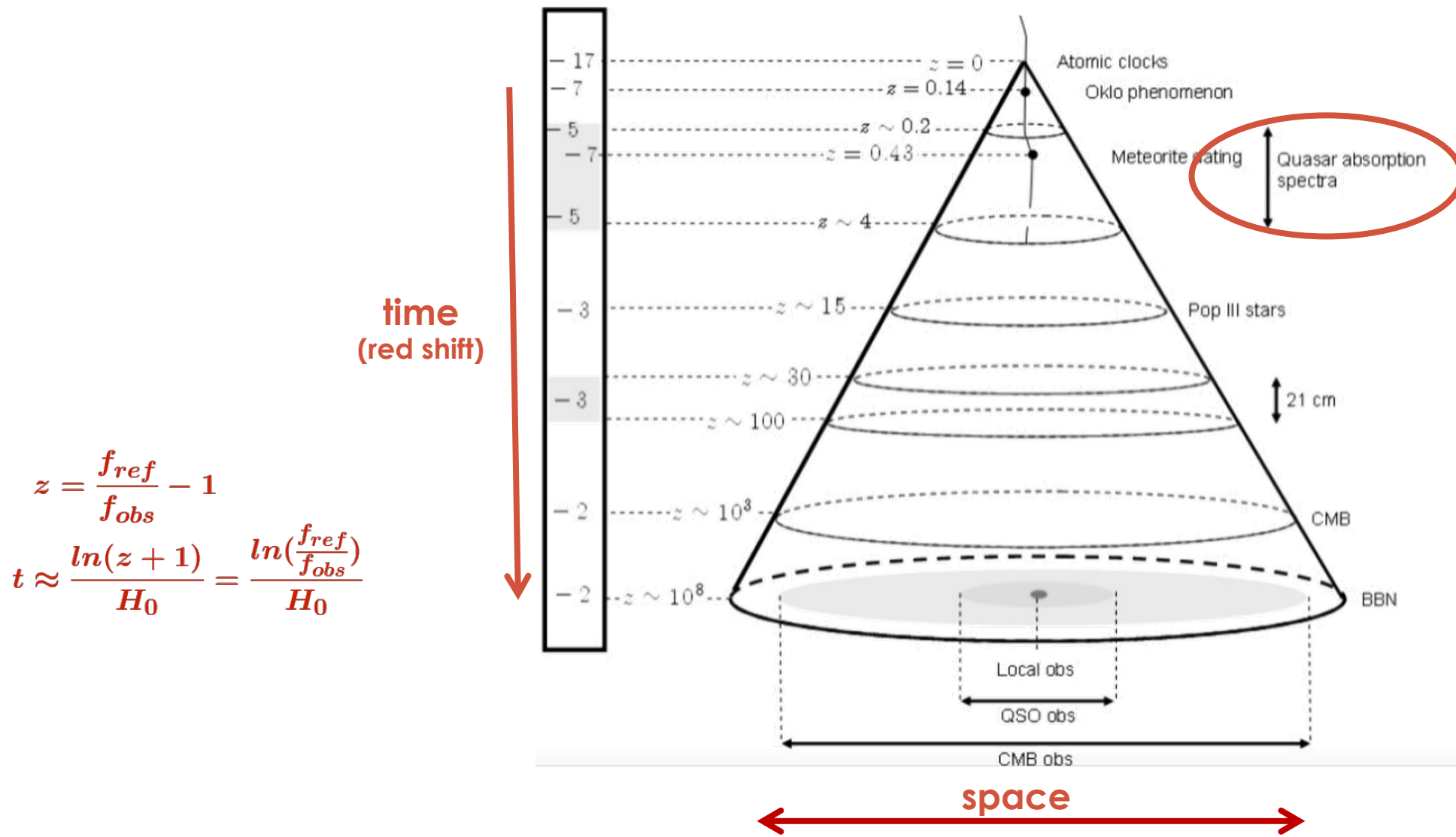
- fine-structure constant $\alpha = \frac{e^2}{4\pi\epsilon_0\hbar c}$

- proton-to-electron mass ratio $\mu = \frac{m_p}{m_e}$

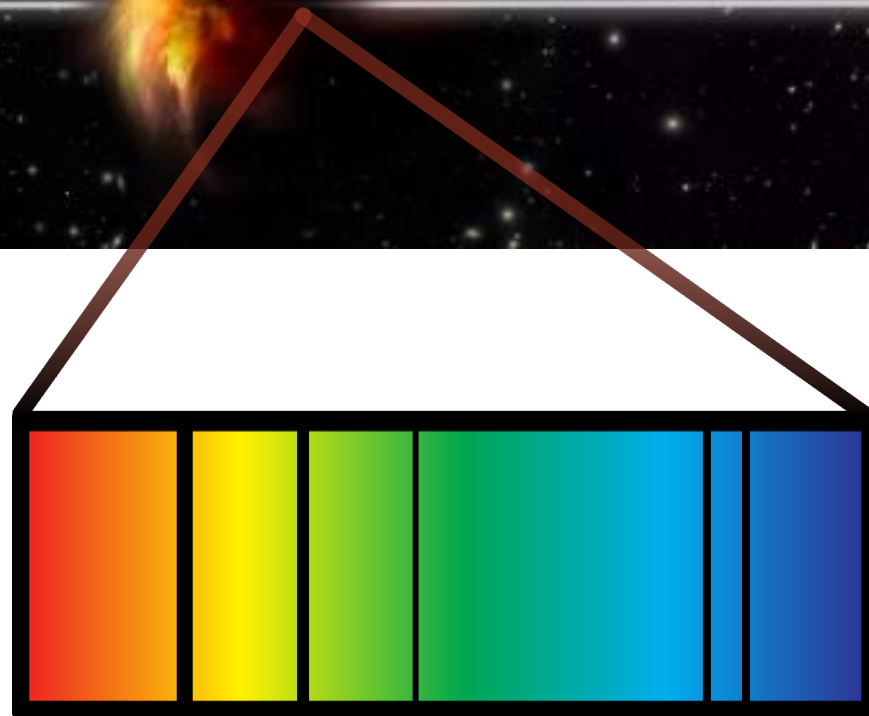
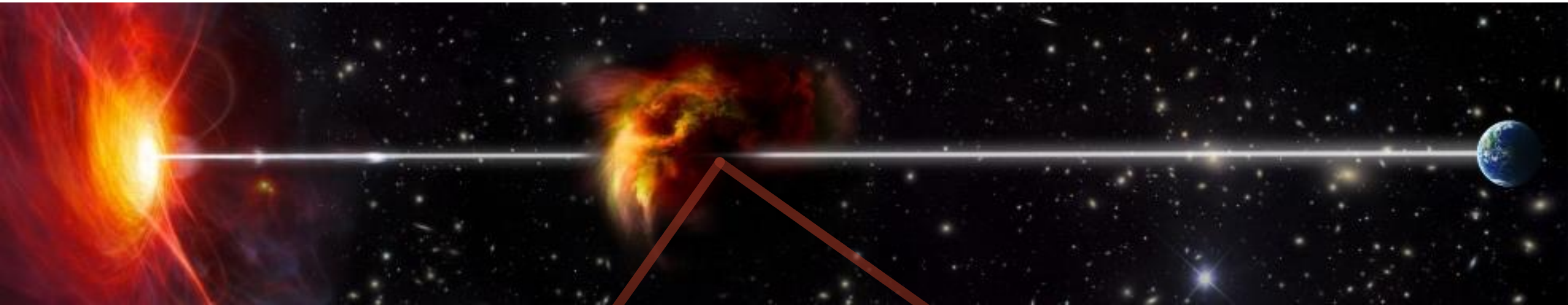
Why α and μ ?

- α is the EM coupling constant directly
- μ related to strong coupling constant α_s indirectly
- $\mu \sim m_p \sim \Lambda_{\text{QCD}}$ (energy scale)
- α_s running constant (not the same as VFC)
- $$\alpha_s = -\frac{2\pi}{\beta_0 \ln(E/\Lambda_{\text{QCD}})}$$

Searching for VFC



Quasar spectra



Quasar spectra

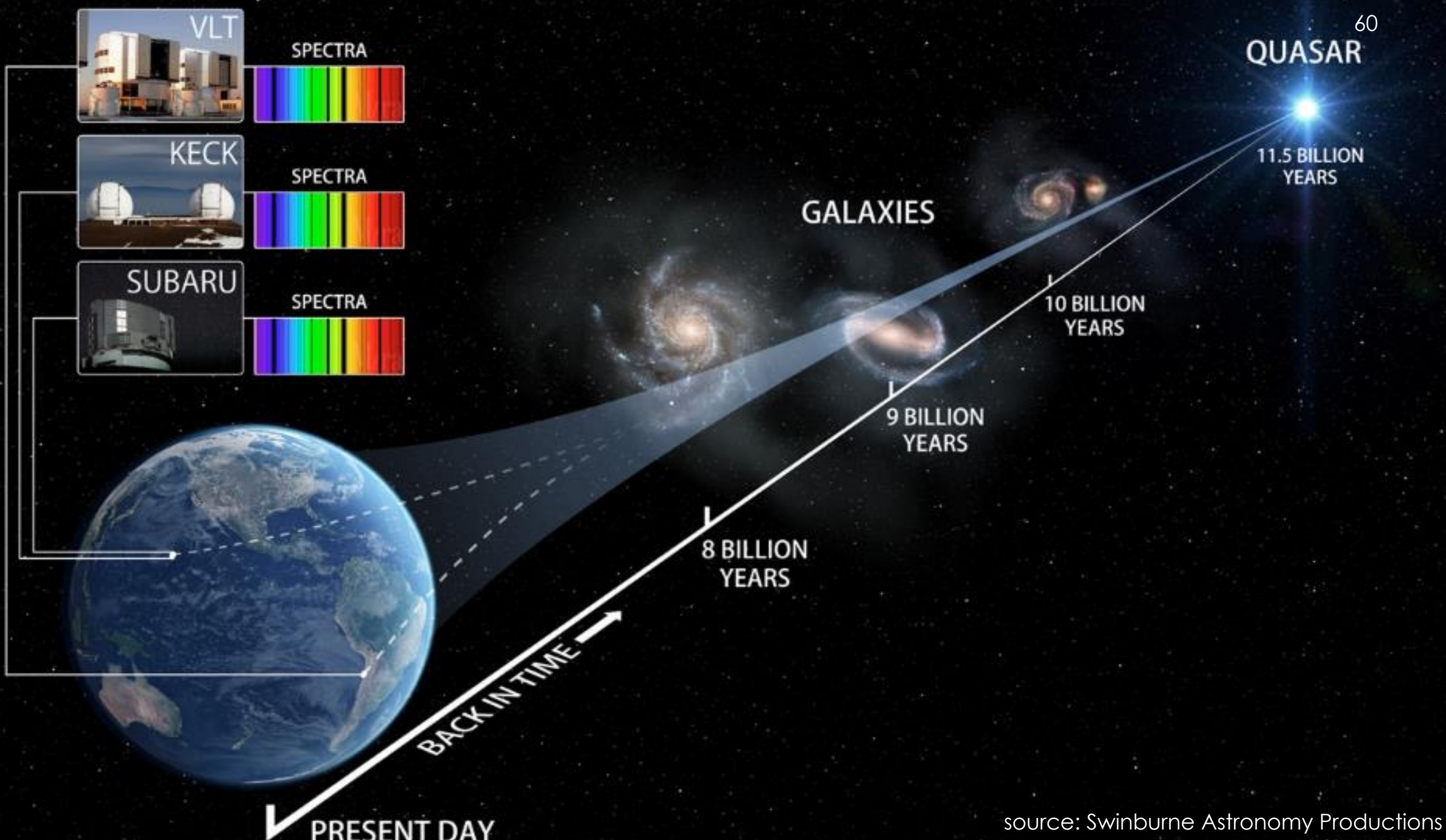
quasar



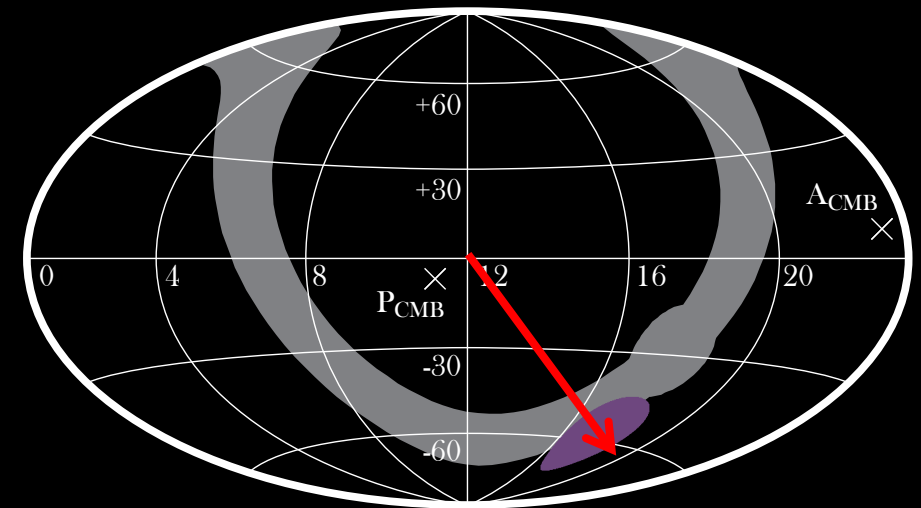
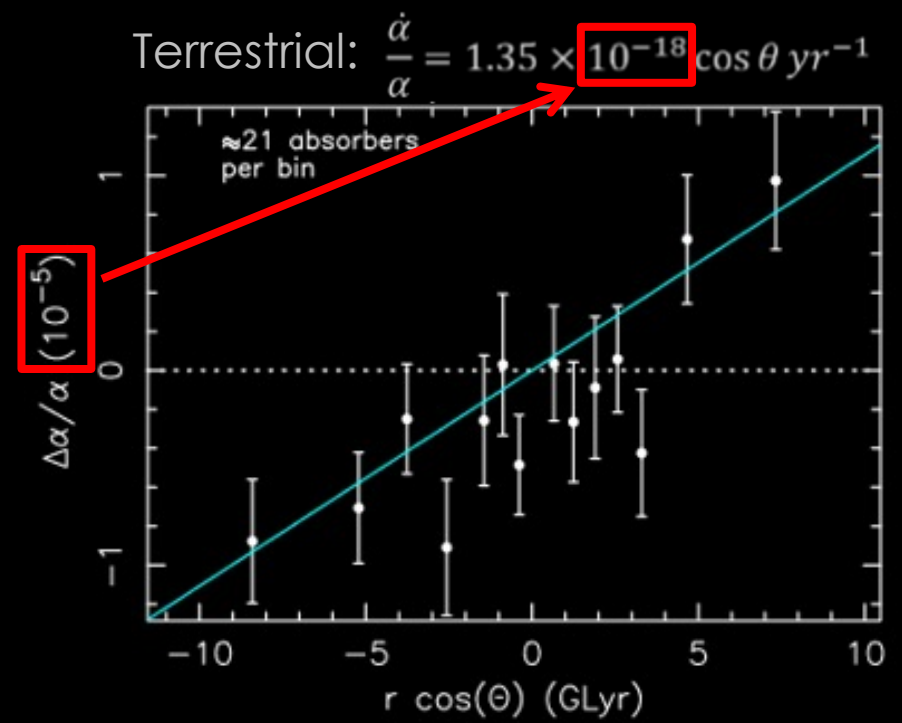
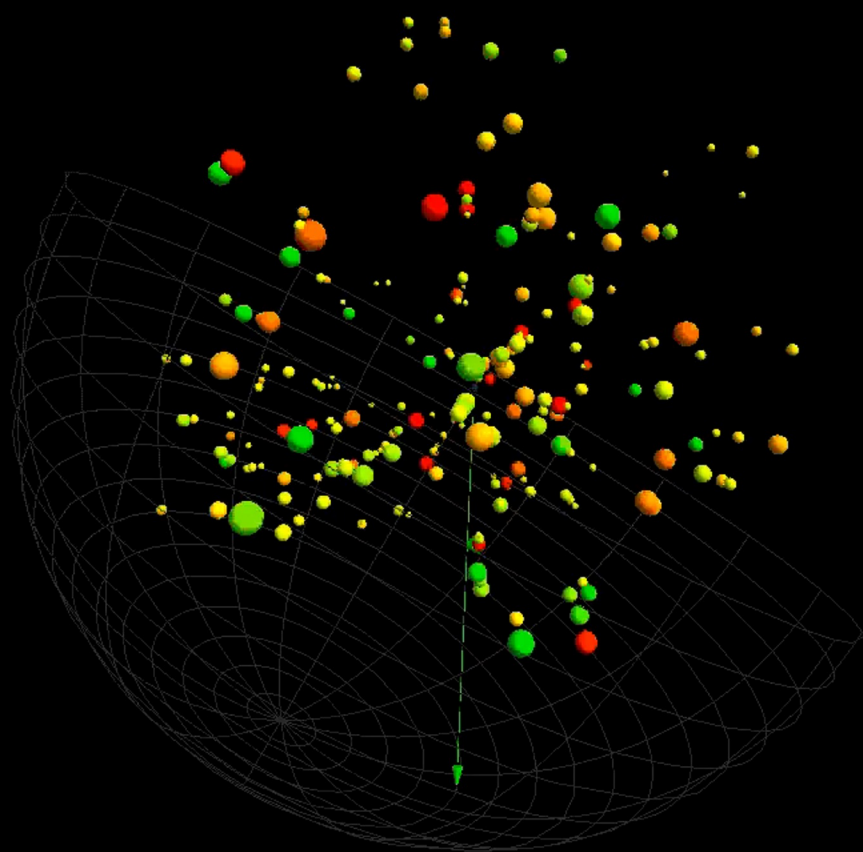
computer



α -meter



α -variation

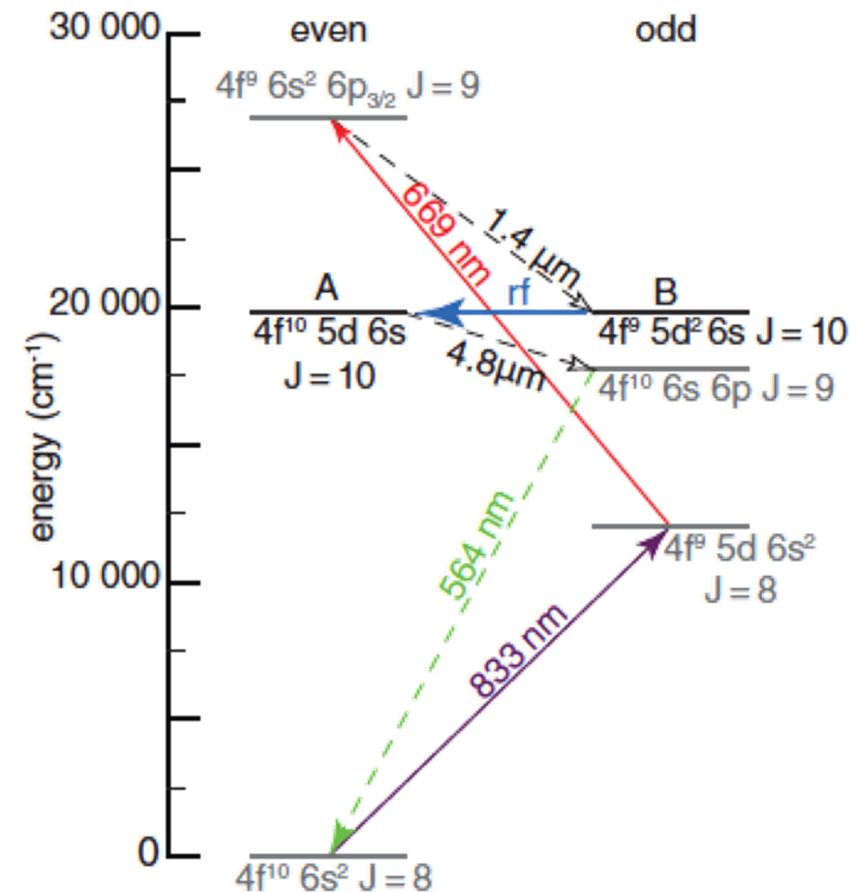


Lab vs astro

- astronomical experiments
 - large scales
 - low error control
- laboratory (terrestrial) experiments
 - local
 - high accuracy and error control
 - requires
 - very sensitive systems
 - extremely precise measurements

Search for VFC in atomic spectra

- $^{162/164}\text{Dy}$ transitions
- 2 year-long experiment
- temporal variation
 - $|\alpha/\alpha| = (-5.8 \pm 6.9) \times 10^{-17} \text{ yr}^{-1}$
- serves as a **constraint** only

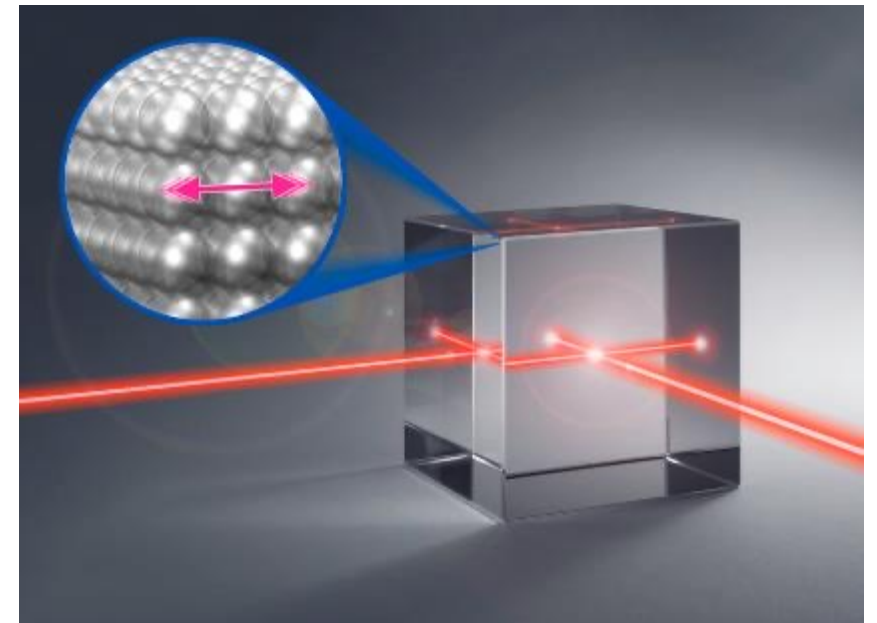
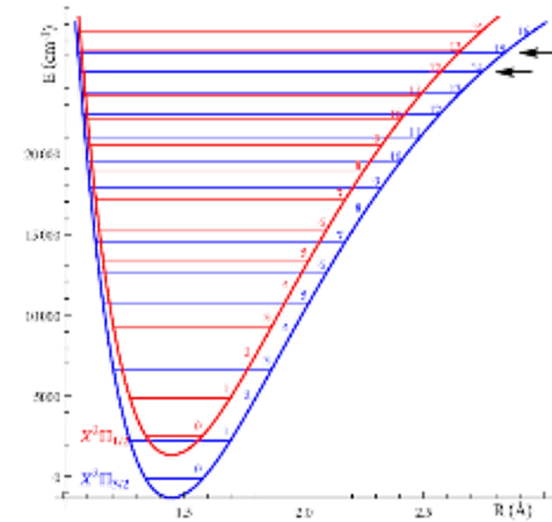
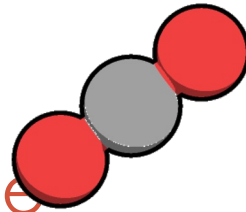


Search for VFC in atomic spectra

Clock 1	Clock 2	Constraint (yr^{-1})
	$\frac{d}{dt} \ln \left(\frac{\nu_{\text{clock 1}}}{\nu_{\text{clock 2}}} \right)$	
^{87}Rb	^{133}Cs	$(0.2 \pm 7.0) \times 10^{-16}$
^{87}Rb	^{133}Cs	$(-0.5 \pm 5.3) \times 10^{-16}$
^1H	^{133}Cs	$(-32 \pm 63) \times 10^{-16}$
$^{199}\text{Hg}^+$	^{133}Cs	$(0.2 \pm 7) \times 10^{-15}$
$^{199}\text{Hg}^+$	^{133}Cs	$(3.7 \pm 3.9) \times 10^{-16}$
$^{171}\text{Yb}^+$	^{133}Cs	$(-1.2 \pm 4.4) \times 10^{-15}$
$^{171}\text{Yb}^+$	^{133}Cs	$(-0.78 \pm 1.40) \times 10^{-15}$
^{87}Sr	^{133}Cs	$(-1.0 \pm 1.8) \times 10^{-15}$
^{87}Dy	^{87}Dy	$(-2.7 \pm 2.6) \times 10^{-15}$
$^{27}\text{Al}^+$	$^{199}\text{Hg}^+$	$(-5.3 \pm 7.9) \times 10^{-17}$

A way out?

- higher sensitivity
 - highly charged or muonic atoms
 - molecular spectroscopy
 - up to 5 orders more sensitive
- higher precision
 - laser interferometry
 - up to 5 orders more precise

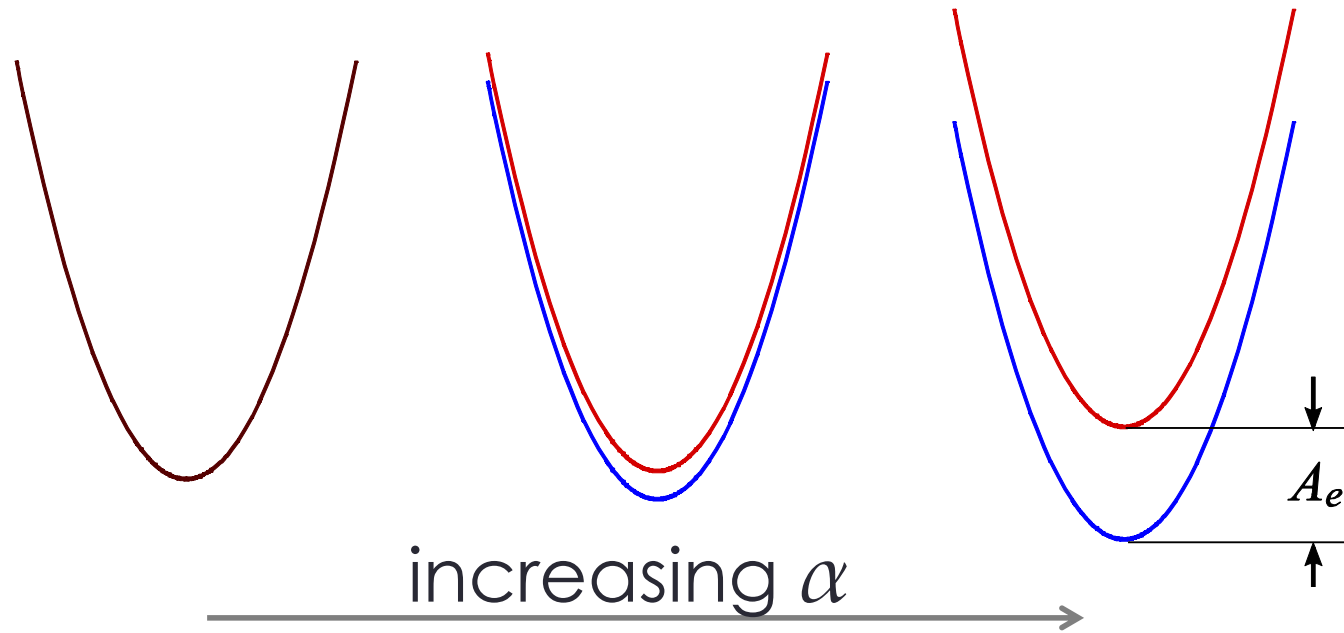


Searching for variation of fundamental constants

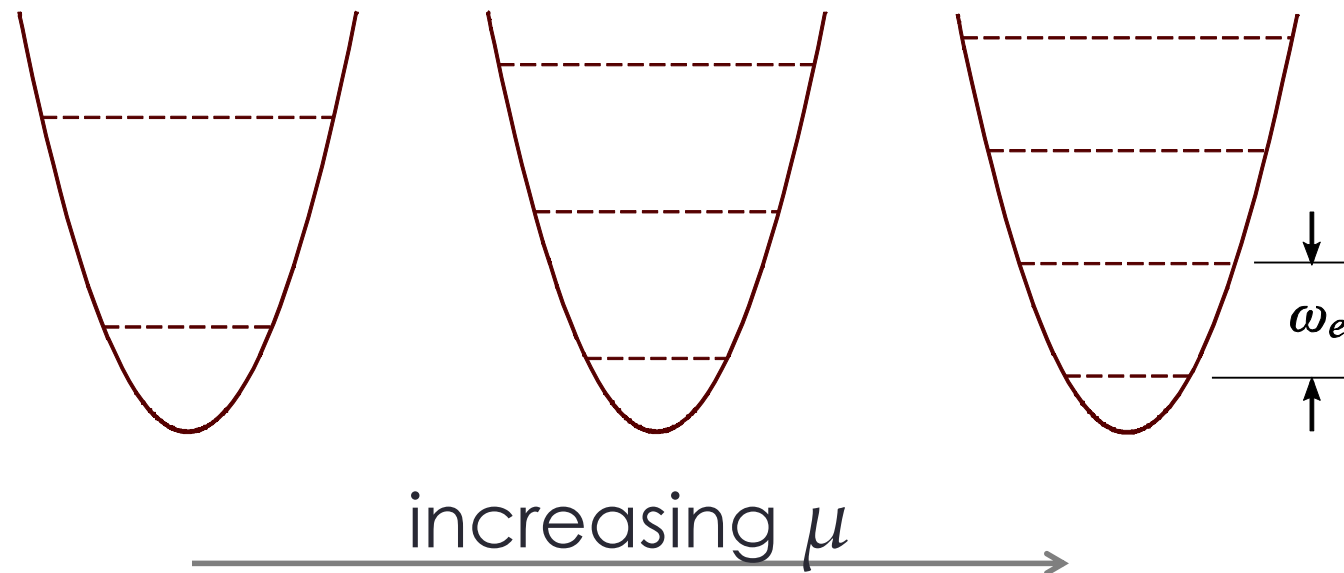
(with diatomic molecules)

$^2\Pi$ cations

- X $^2\Pi$ cations of dihalogens and hydrogen halides
- cations – trappable
- $^2\Pi$ states split into SO substates $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$
 - strong α -dependence
 - forbidden electronic transitions ($\Delta\Sigma \neq 0$, Laporte) – narrow linewidths
- easily available

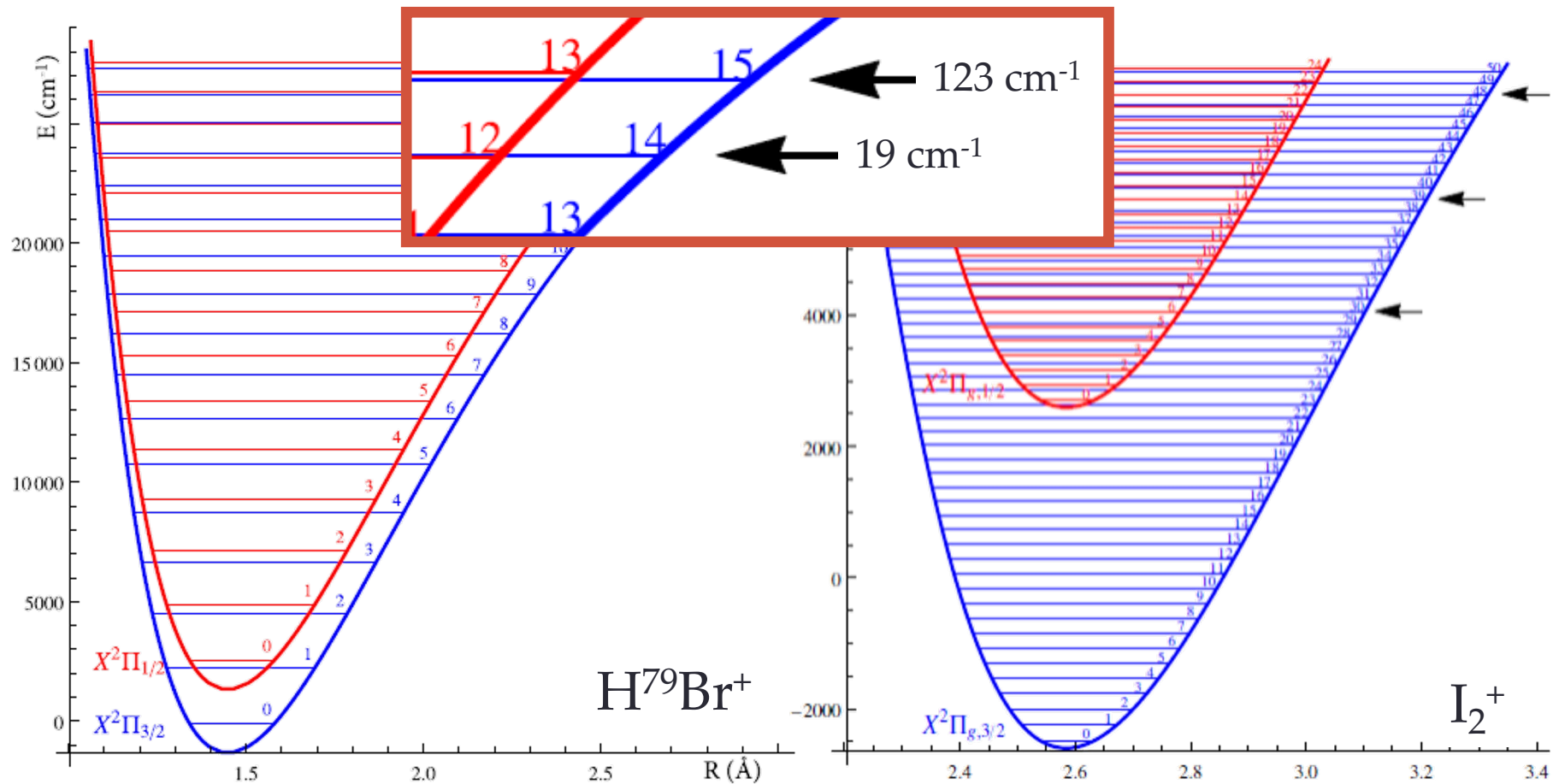


$A_e \sim \alpha^2$
 but not
 sensitive to μ

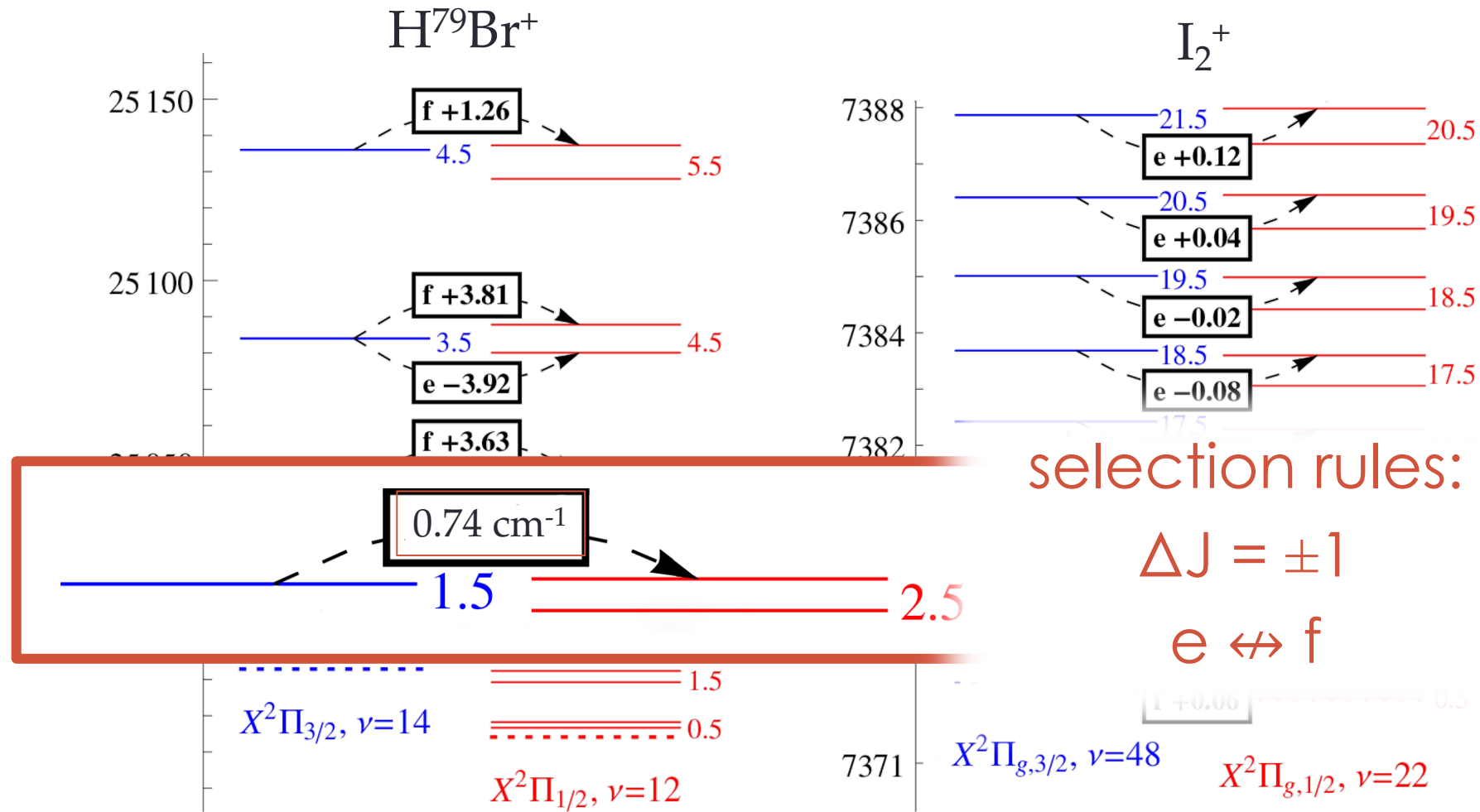


$\omega_e \sim \mu^{-1/2}$
 but not
 sensitive to α

2Π cations



2Π cations

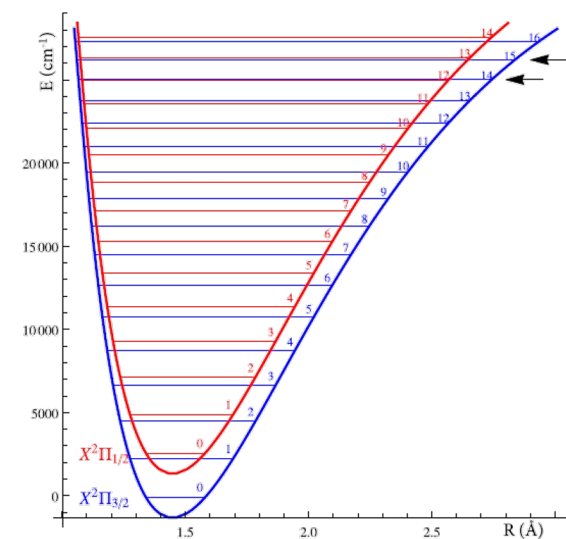


Enhancement factors

$$\frac{\delta\omega}{\omega} = K_\alpha \frac{\delta\alpha}{\alpha} + K_\mu \frac{\delta\mu}{\mu}$$

$$K_\mu = \left[\frac{1}{2}\omega_e(\nu'' - \nu') - \omega_e x_e(\nu'' - \nu')(\nu'' + \nu' + 1) \right. \\ \left. + B_e(J'' - J')(J'' + J' + 1) \right. \\ \left. + \frac{1}{4}A^{(1)}(\nu'' + \nu' + 1) \right] \omega^{-1} = \bar{K}_\mu \omega^{-1}$$

$$K_\alpha = \left[-2A_e - A^{(1)}(\nu'' + \nu' + 1) \right] \omega^{-1} = \bar{K}_\alpha \omega^{-1}$$



cation	ν''	ν'	J''	J'	s	ω	\bar{K}_μ	K_μ	\bar{K}_α	K_α
H^{79}Br^+	14	12	1.5	2.5	<i>f</i>	0.74	-80.8	-110	5250	7120
	15	13	11.5	12.5	<i>f</i>	0.14	-426	-3030	5250	37200
H^{81}Br^+	14	12	5.5	6.5	<i>f</i>	-0.27	-145	543		-19700
	15	13	6.5	5.5	<i>f</i>	0.52	-119	-228		10100
D^{79}Br^+	9	7	7.5	8.5	<i>f</i>	2.20	881	400	5270	2390
	10	8	1.5	0.5	<i>e</i>	1.99	871	437	5270	2650

	ν''	ν'	J''	J'	ω	\bar{K}_μ	K_μ	\bar{K}_α	K_α
I_2^+	30	6	30.5	31.5	-0.00	2270	-682000	9990	-3010000
I^{81}Br^+	36	19	5.5	4.5	0.01	1170	216000	9320	1720000
DI^+	7	3	1.5	2.5	0.27	2230	8220	10700	39300
$^{79,81}\text{Br}_2^+$	30	21	3.5	4.5	-0.09	1160	-12900	5450	-60400

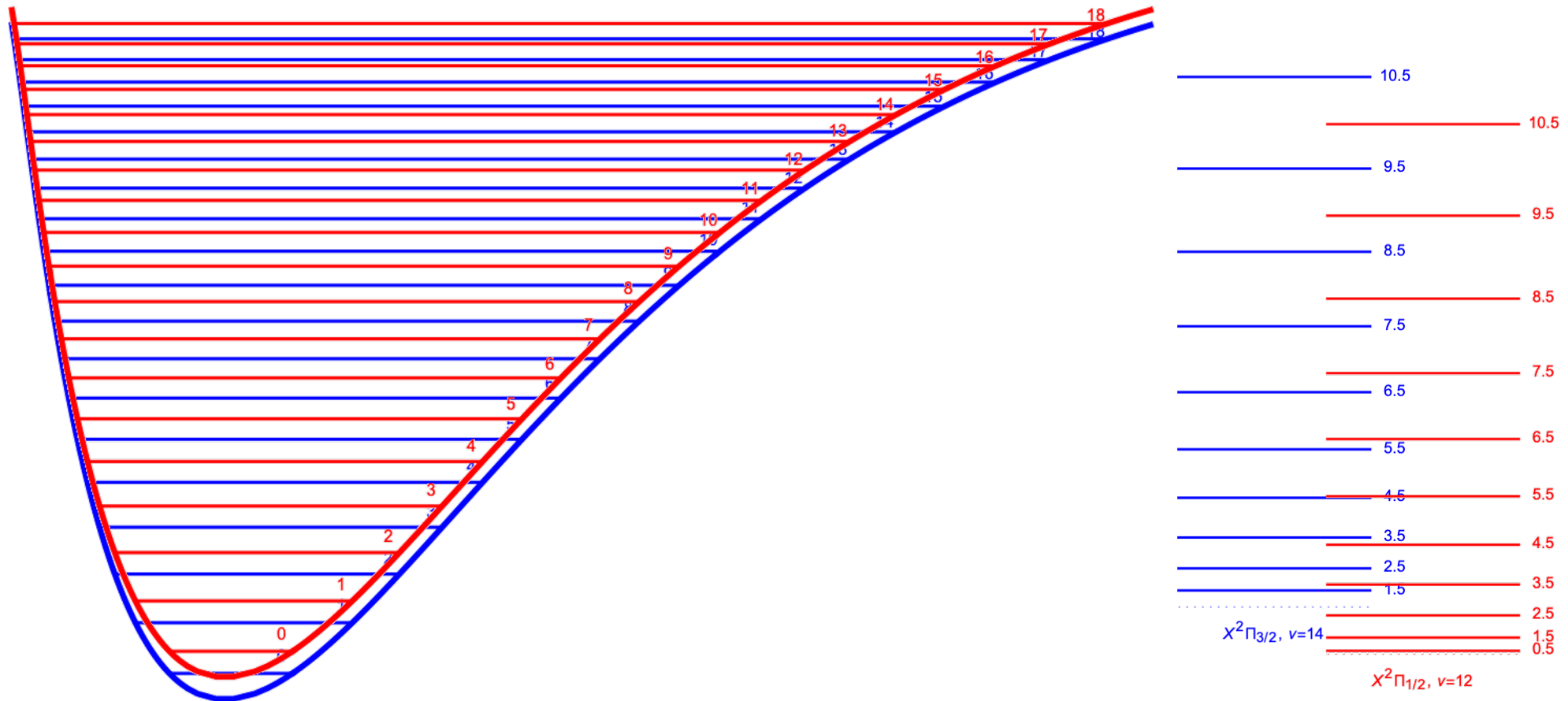
$^{79}\text{Br}_2^+$	48	22	19.5	18.5	<i>e</i>	-0.02	1900	-79100		-401000
	11	3	24.5	25.5	<i>f</i>	-0.10	1350	-13700		-56600
$^{79,81}\text{Br}_2^+$	31	22	21.5	22.5	<i>f</i>	0.04	1190	33200		150000
	9	1	20.5	21.5	<i>e</i>	0.09	1360	14500	5600	59700

Promising systems; dedicated measurements are needed

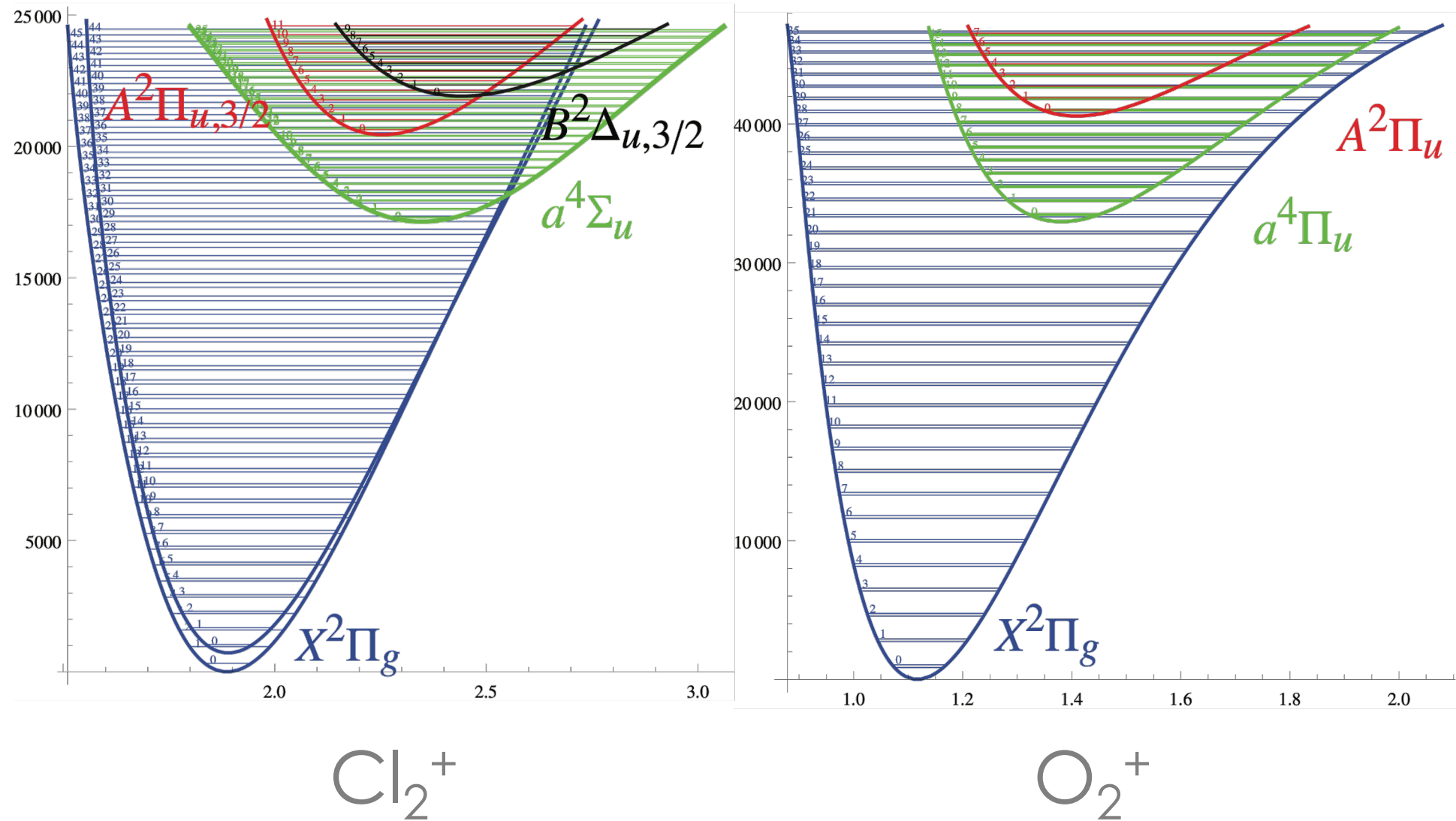
I^{79}Br^+	28	19	36.5	37.5	<i>e</i>	0.05	1190	25700	5450	118000
	25	8	33.5	34.5	<i>f</i>	0.11	1720	16300		87700
I^{81}Br^+	39	22	33.5	34.5	<i>f</i>	-0.04	1020	-27900		-249000
	24	7	37.5	38.5	<i>f</i>	0.04	1760	45200		240000
	36	19	5.5	4.5	<i>f</i>	0.01	1170	216000	9320	1720000
	37	20	40.5	41.5	<i>e</i>	0.07	1120	15600	9320	131000

Precision

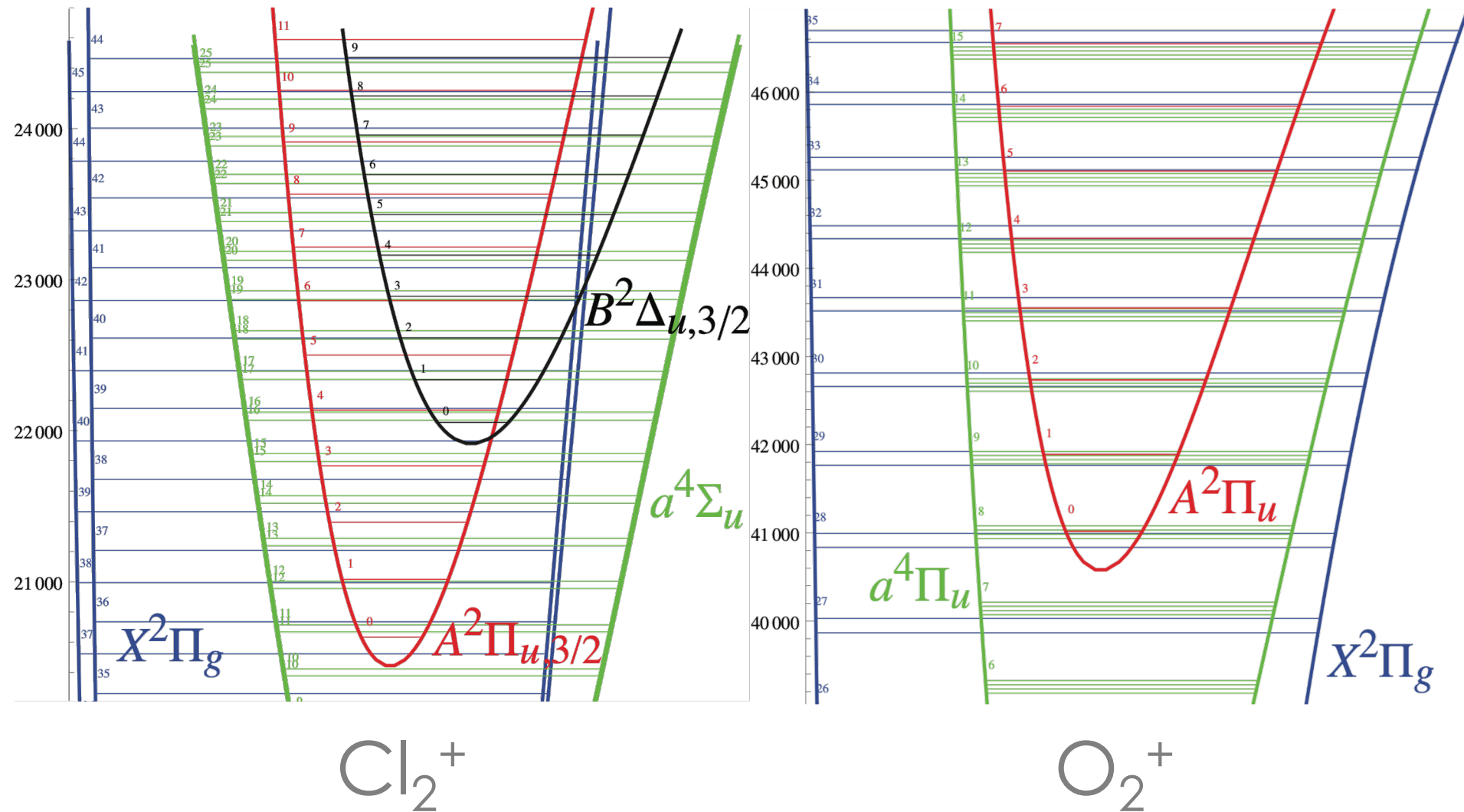
- Are we good enough?



Excited electronic states



Excited electronic states



Quasidegeneracies

Near cancellation between

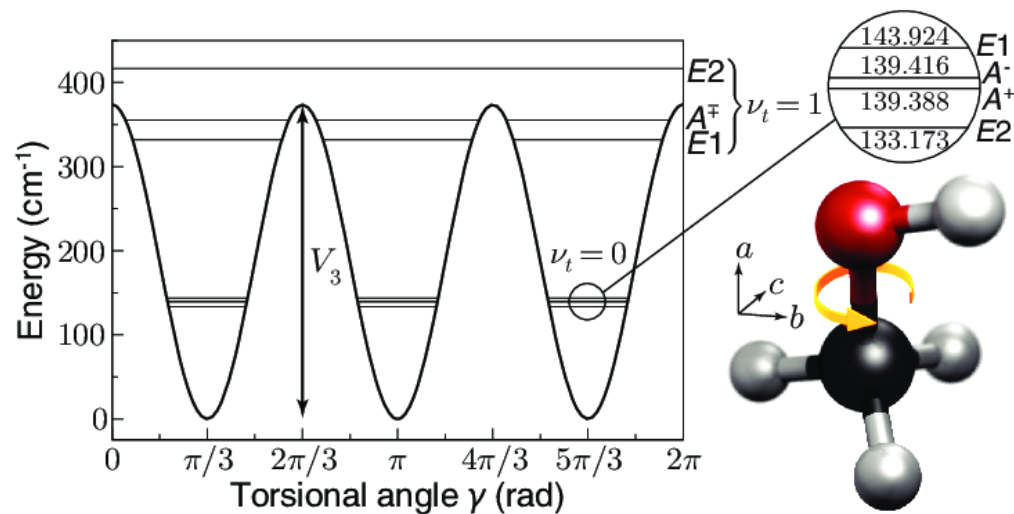
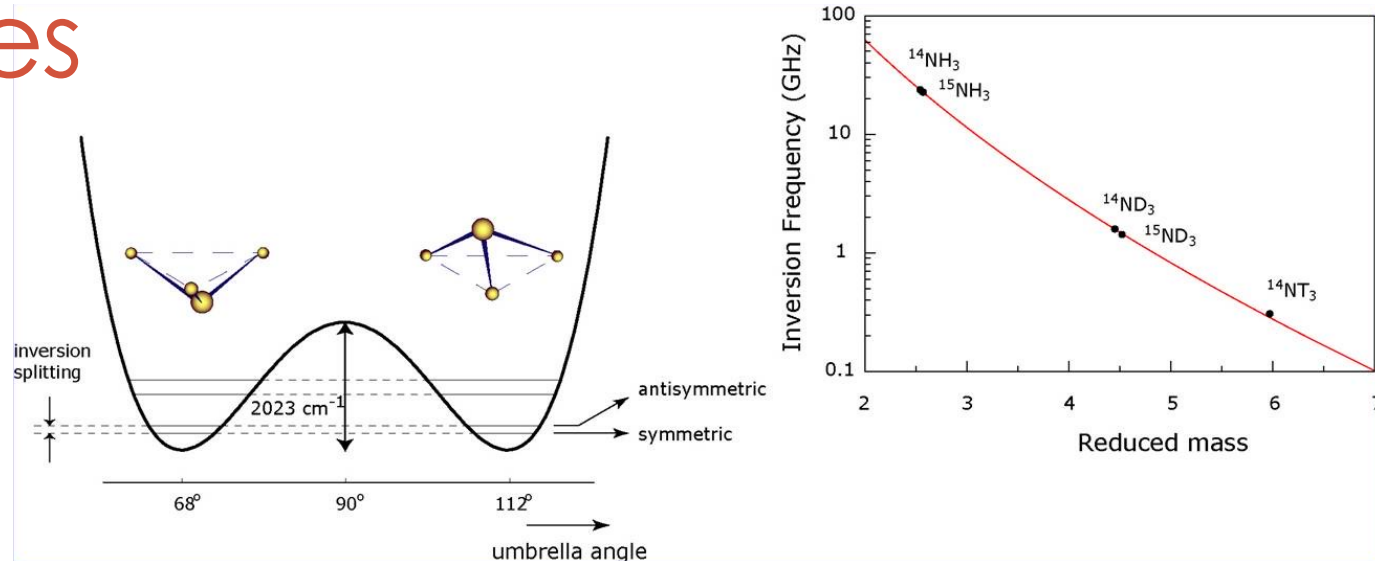
- vibrational and SO splitting
- hyper-fine and rotational splitting
- hyper-fine and Λ -doubling

$$E_{\text{HFS}} \sim \alpha^2 g_p \mu^{-1}$$

$$\frac{\delta(\omega_1/\omega_2)}{(\omega_1/\omega_2)} = (K_\mu^1 - K_\mu^2) \frac{\delta\mu}{\mu} + (K_\alpha^1 - K_\alpha^2) \frac{\delta\alpha}{\alpha}$$

Polyatomic molecules

- Inversion tunneling in NH_3
 - lab and astro $\frac{\delta\mu}{\mu} = (-0.6 \pm 1.9) \times 10^{-6}$
- Hindered rotation of methanol
 - $K = 40$



Flambaum, Kozlov, PRL 98, 240801 (2007); Murphy et al. Science 320, 1611 (2008)
 Jansen et al., PRL 106, 100801 (2011)

Searching for variation of fundamental constants

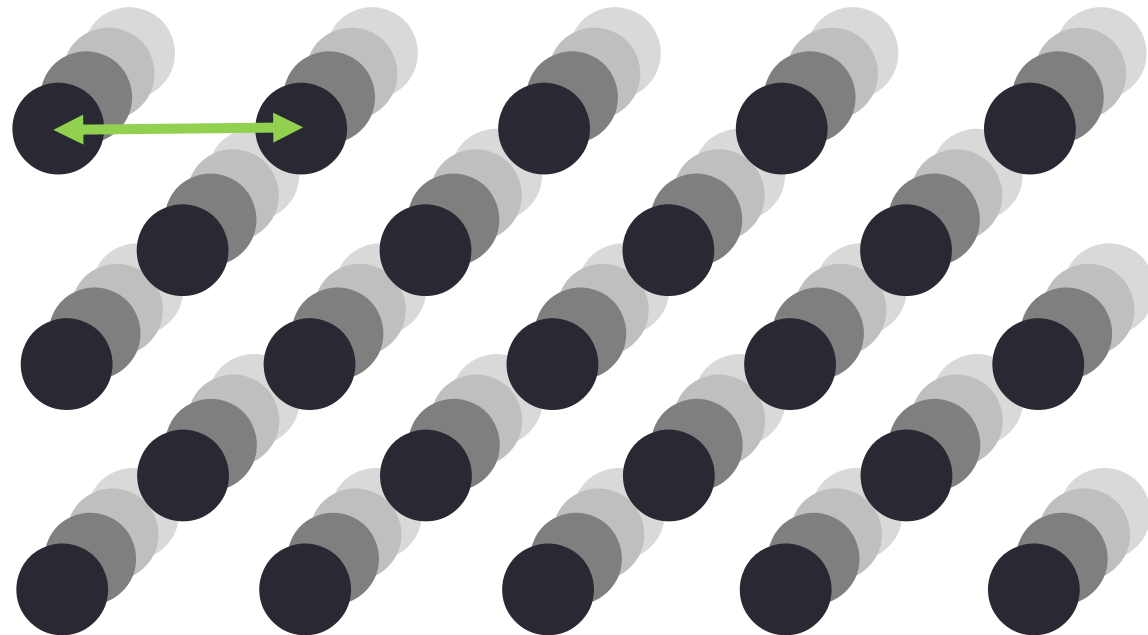
(with solids)

Laser interferometry

- highest instrumental precision
- matter structure may depend on fundamental constants

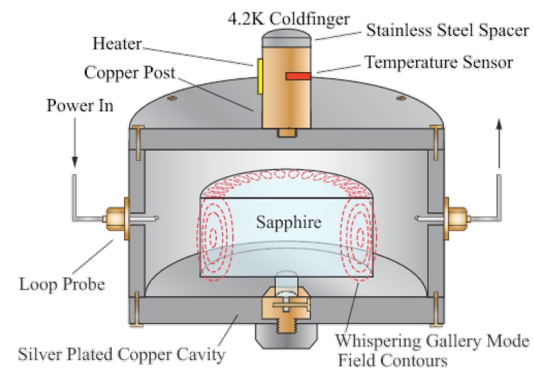
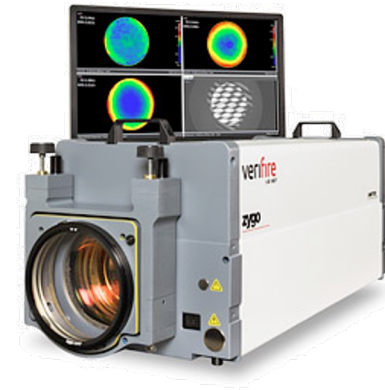
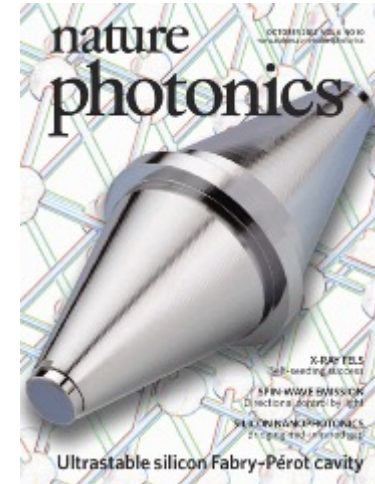


α -meter



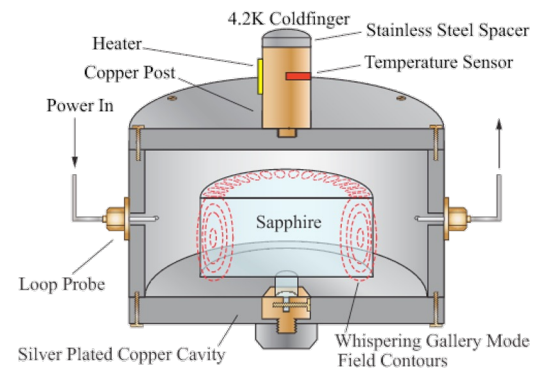
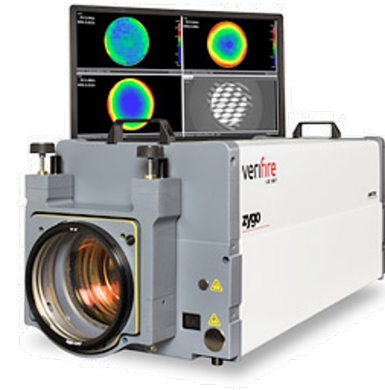
Matter structure

- tabletop optical cavity laser interferometers
- resonant-mass detectors (Al, Cu, Nb)
- cryogenic sapphire/silicon oscillators



Matter structure

- Cu, Ag, Au
- Al
- Nb
- WC
- ~~C~~, Si, Ge, Sn, Pb
- Al_2O_3
- SiC
- Ti



Overview

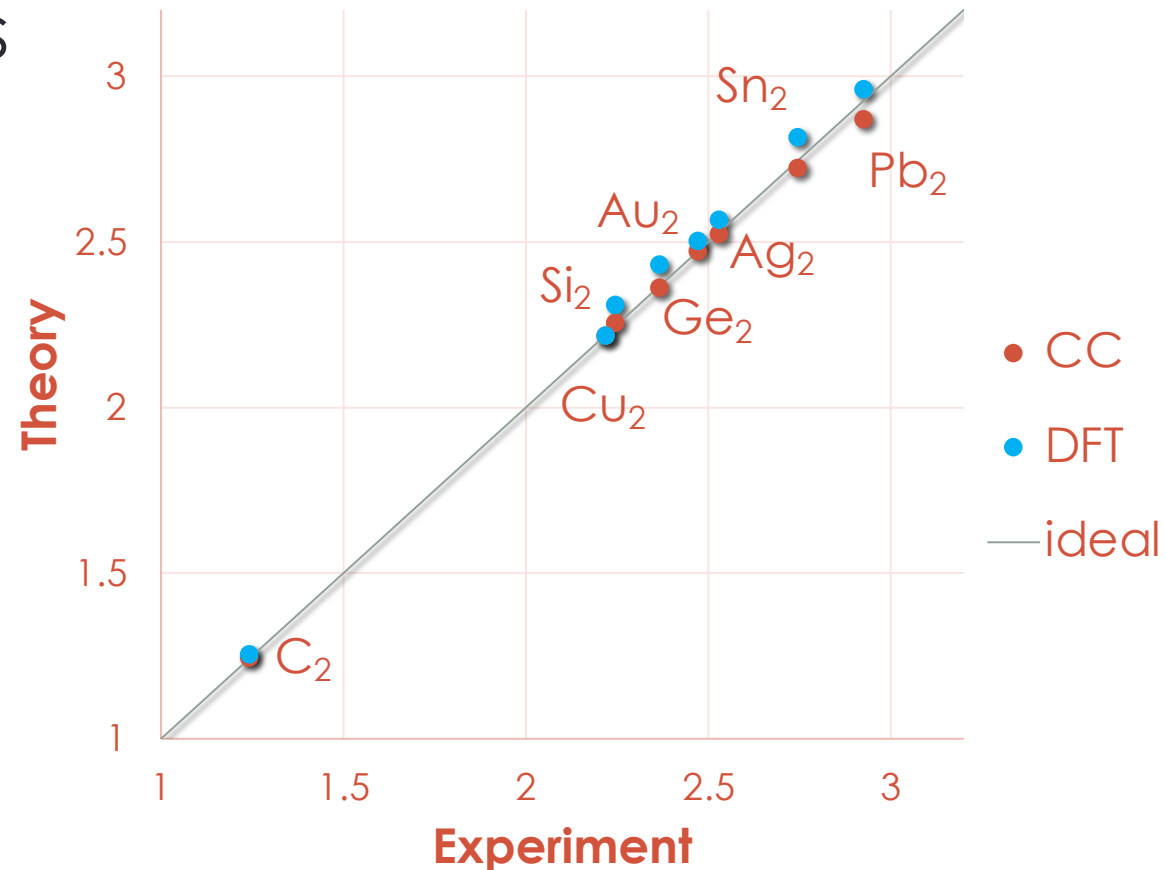
- Diatomics – bond lengths
- Solids – lattice constants
- α -dependence
- μ -dependence

Diatomics

(the test case)

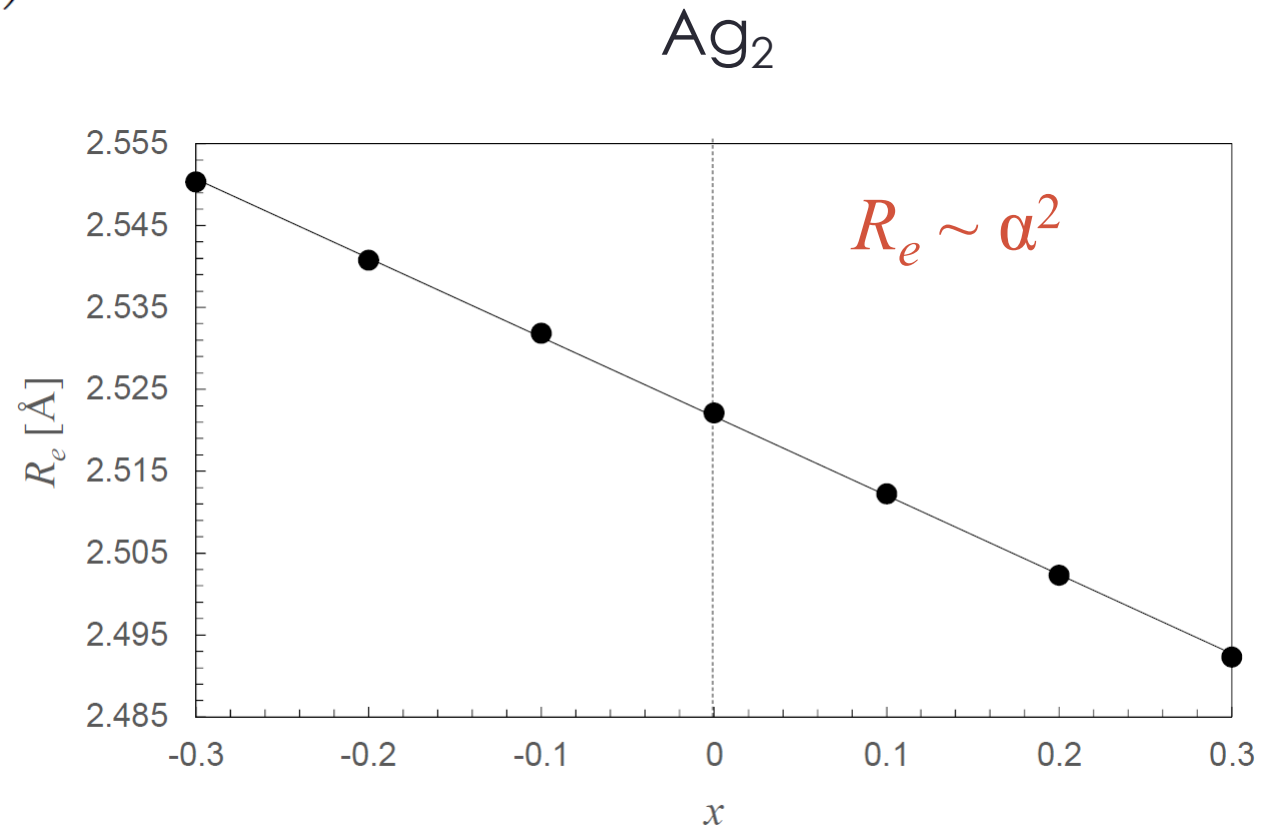
Diatomics: Bond lengths

- Average errors
 - CC: 0.5%
 - DFT: 1.6%



Diatomics: α -dependence

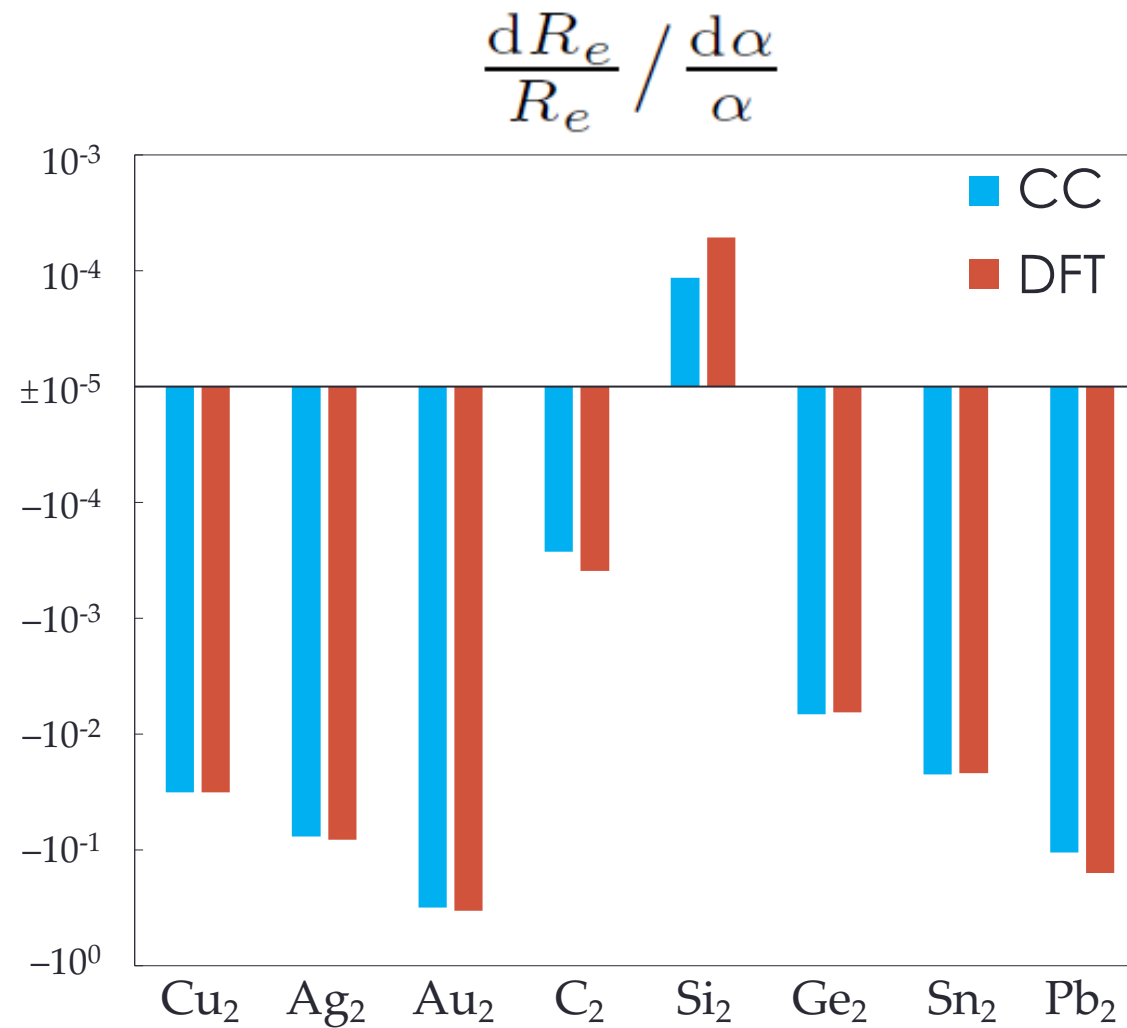
- varying $\alpha =$ varying c (because a.u.)
- optimizing R_e w.r.t. $x = \left(\frac{\alpha}{\alpha_0}\right)^2 - 1$



Diatomics: α -dependence

mol.	state	$\frac{dR_e}{R_e} / \frac{d\alpha}{\alpha}$	
		CC	DFT
Cu ₂	$1\Sigma_g^+$	-3.19×10^{-2}	-3.18×10^{-2}
Ag ₂	$1\Sigma_g^+$	-7.66×10^{-2}	-8.21×10^{-2}
Au ₂	$1\Sigma_g^+$	-3.15×10^{-1}	-3.37×10^{-1}
C ₂	$1\Sigma_g^+$	-2.65×10^{-4}	-3.88×10^{-4}
Si ₂	$3\Sigma_g^-$	8.66×10^{-5}	1.94×10^{-4}
Ge ₂	$3\Sigma_g^-$	-6.74×10^{-3}	-6.48×10^{-3}
Sn ₂	0_g^+	-2.24×10^{-2}	-2.17×10^{-2}
Pb ₂	0_g^+	-1.05×10^{-1}	-1.58×10^{-1}

Diatomics: α -dependence



Diatomics: μ -dependence

• vibrational $B_0 = B_e - \frac{\alpha_e}{2} \quad B \sim \frac{1}{R^2} \quad B_e \sim \mu^{-1} \quad \alpha_e \sim \mu^{-\frac{3}{2}}$

$$\frac{dR_0}{R_0} / \frac{d\mu}{\mu} = -\frac{\alpha_e}{4(2B_e - \alpha_e)}$$

• non-BO effects

• within BOA

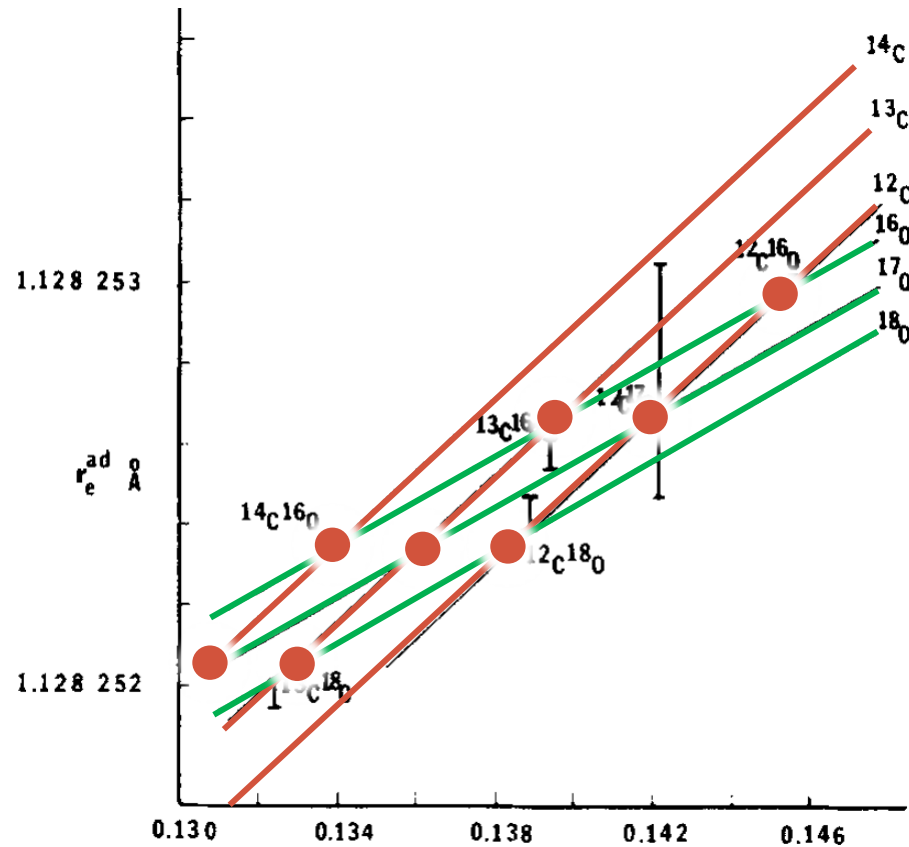
R_e is isotope mass-invariant (independent on μ)

• outside BOA

nuclear kinetic terms contribute to weak μ -dependence

$$R_e \sim \mu^{-1}$$

Diatomics: μ -dependence



Isotope	Γ_{01}/MHz^b	$r_e/\text{\AA}^{b,c}$
$^{12}\text{C}^{16}\text{O}$	57 898.3675 (± 25)	1.128 336 346 (± 25)
$^{12}\text{C}^{17}\text{O}$	56 432.4817 (± 300)	1.128 333 997 (± 300)
$^{13}\text{C}^{16}\text{O}$	55 346.2594 (± 40)	1.128 332 196 (± 40)
$^{12}\text{C}^{18}\text{O}$	55 135.2616 (± 40)	1.128 331 825 (± 40)
$^{11}\text{C}^{16}\text{O}$	53 166.7589 (± 20)	1.128 328 817 (± 22)
$^{13}\text{C}^{18}\text{O}$	52 583.1129 (± 40)	1.128 327 673 (± 40)

$$R_e \sim \mu^{-1}$$

Diatomics: μ -dependence

- non-BOA effects are negligible

mol.	state	vibrational	non-BOA
		$\frac{dR_0}{R_0} / \frac{d\mu}{\mu}$	$\frac{dR_e}{R_e} / \frac{d\mu}{\mu}$
Cu ₂	$1\Sigma_g^+$	-7.15×10^{-4}	-7.31×10^{-6}
Ag ₂	$1\Sigma_g^+$	-4.98×10^{-4}	-3.38×10^{-6}
Au ₂	$1\Sigma_g^+$	-2.95×10^{-4}	9.16×10^{-7}
C ₂	$1\Sigma_g^+$	-1.17×10^{-3}	-6.94×10^{-6}
Si ₂	$3\Sigma_g^-$	-7.08×10^{-4}	-6.63×10^{-6}
Ge ₂	$3\Sigma_g^-$	-2.34×10^{-3}	-4.46×10^{-6}
Sn ₂	0_g^+	-3.25×10^{-4}	-3.82×10^{-6}
Pb ₂	0_g^+	-3.76×10^{-4}	3.32×10^{-7}

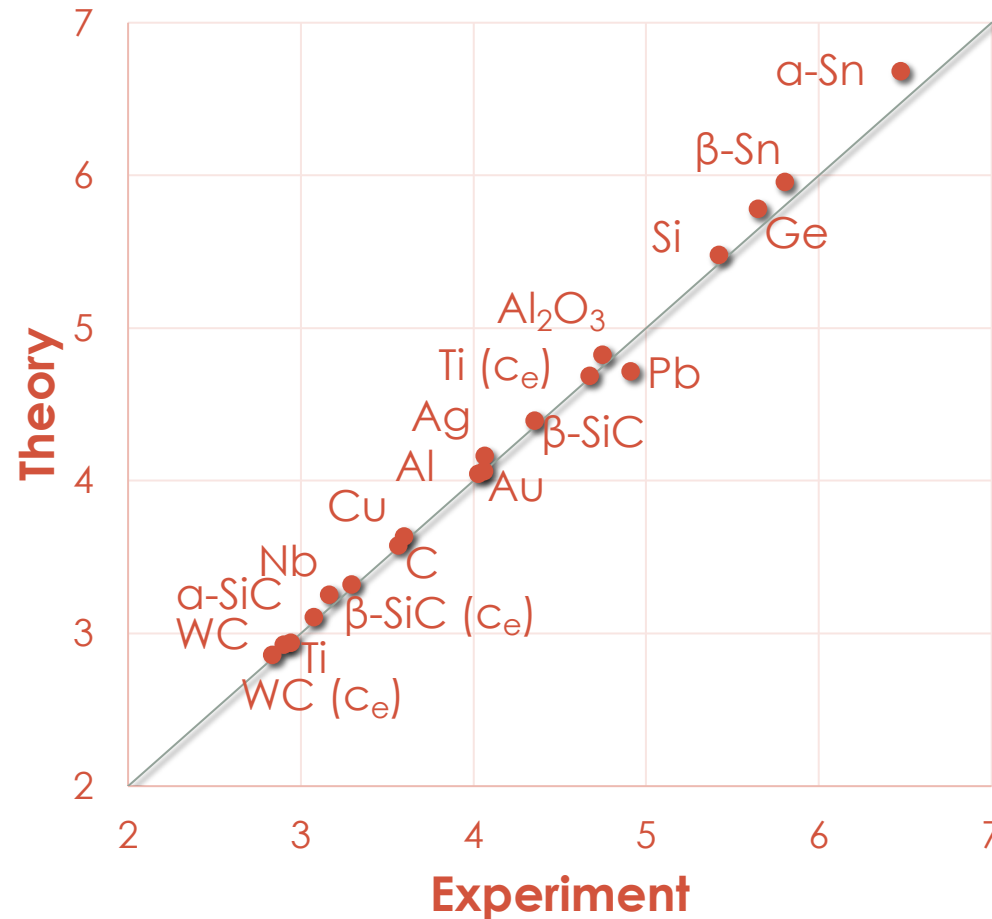


Solids

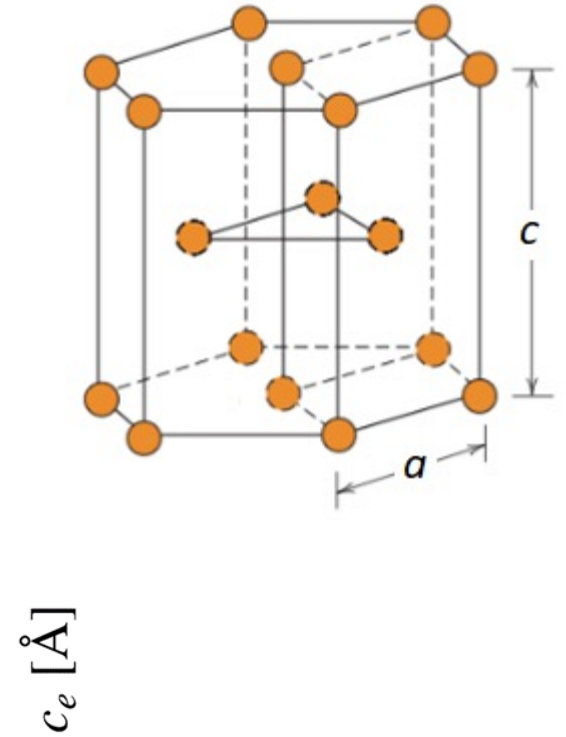
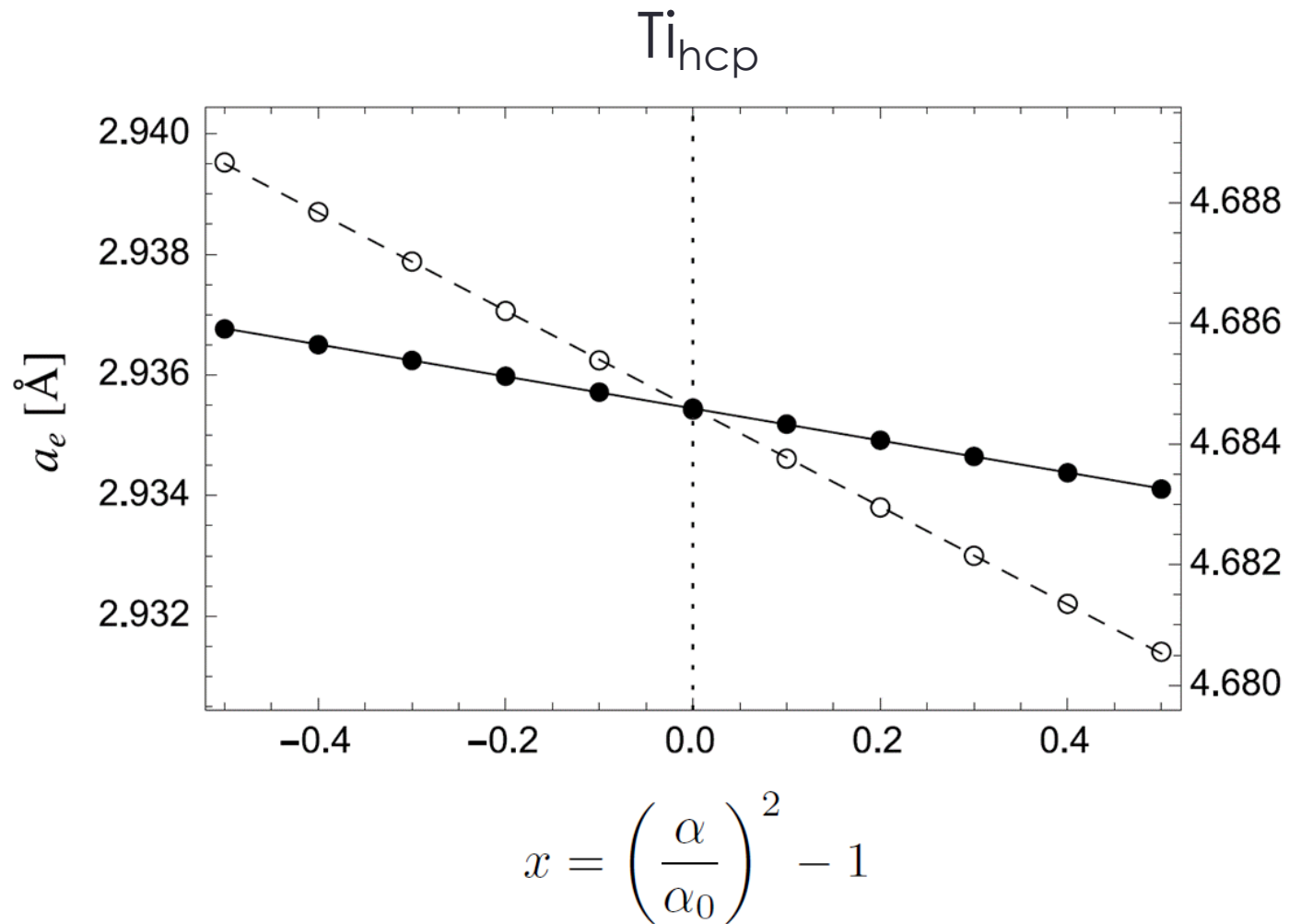
(the real deal)

Solids: Lattice parameters

- Average error
 - 1.3%

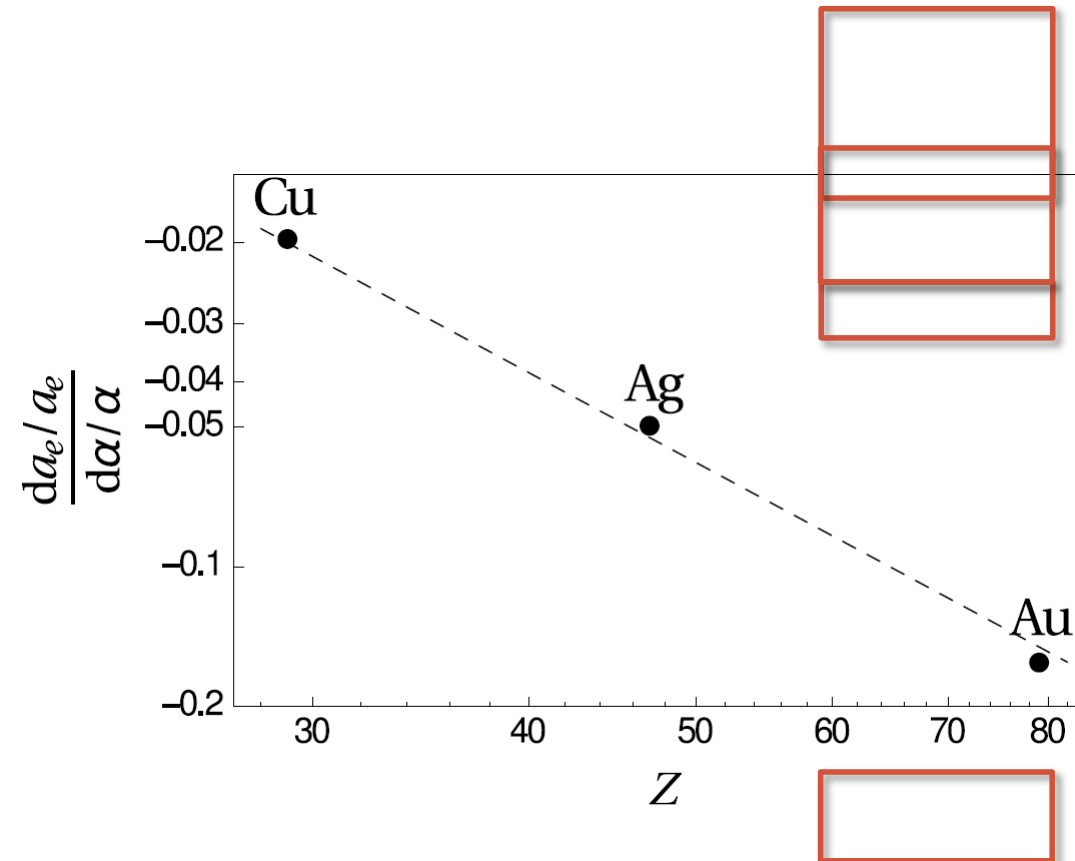


Solids: α -dependence



Solids: α -dependence

solid	structure	spc. group	$\frac{da_e}{a_e} / \frac{d\alpha}{\alpha}$
Cu	fcc	$Fm\bar{3}m$	-1.97×10^{-2}
Ag	fcc	$Fm\bar{3}m$	-4.97×10^{-2}
Au	fcc	$Fm\bar{3}m$	-1.61×10^{-1}

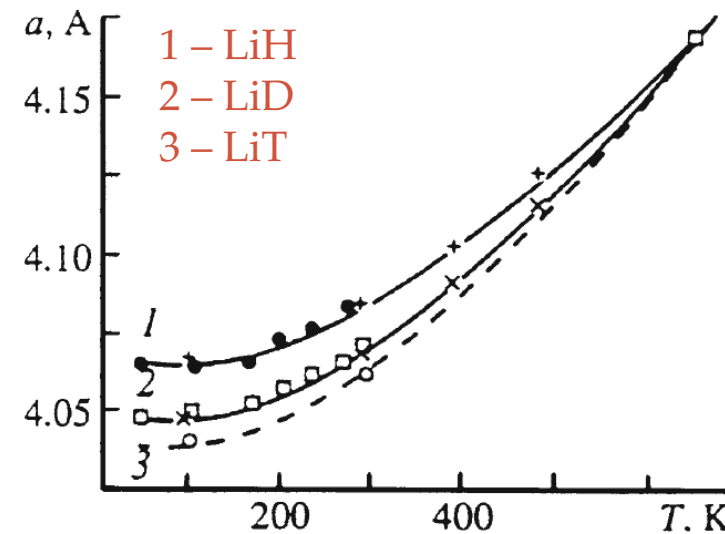


Solids: μ -dependence

- lattice parameter is mass-dependent
- vibrational effect
- isotope substitution studies

$$\frac{MdV}{VdM} = -\frac{9}{16} \frac{\gamma\kappa}{V} R\Theta_D$$

$$\frac{da_0}{a_0} / \frac{d\mu}{\mu} = -\frac{3}{16} \frac{\gamma}{BV} k_B \Theta_D$$



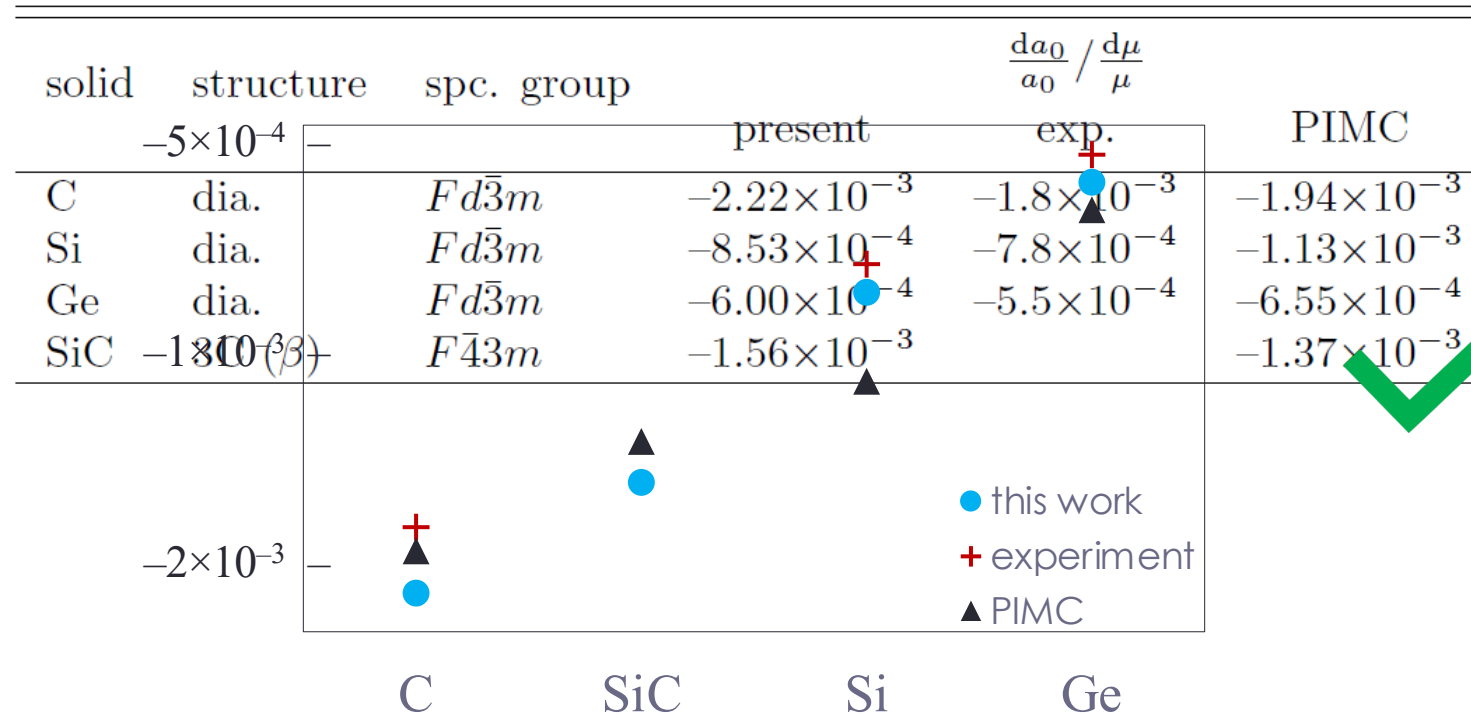
Solids: μ -dependence

solid	structure	spc. group	$\frac{da_0}{a_0} / \frac{d\mu}{\mu}$
Cu	fcc	$Fm\bar{3}m$	-1.11×10^{-3}
Ag	fcc	$Fm\bar{3}m$	-8.21×10^{-4}
Au	fcc	$Fm\bar{3}m$	-4.29×10^{-4}
C	dia.	$Fd\bar{3}m$	-2.22×10^{-3}
Si	dia.	$Fd\bar{3}m$	-8.53×10^{-4}
Ge	dia.	$Fd\bar{3}m$	-6.00×10^{-4}
Sn	dia. (α)	$Fd\bar{3}m$	-4.96×10^{-4}
	tet. (β)	$I4_1/amd$	-6.18×10^{-4}
Pb	fcc	$Fm\bar{3}m$	-5.52×10^{-4}
		$Fm\bar{3}m$	-2.08×10^{-3}
		$Im\bar{3}m$	-3.72×10^{-4}
		$P6_3/mmc$	-7.03×10^{-4}
Al ₂ O ₃	hex.	$R\bar{3}c$	-2.05×10^{-3}
SiC	3C (β)	$F\bar{4}3m$	-1.56×10^{-3}
	6H (α)	$P6_3mc$	-1.47×10^{-3}
WC	hex.	$P\bar{6}m2$	-1.26×10^{-3}

$$\frac{da_0}{a_0} / \frac{d\mu}{\mu} = -\frac{3}{16} \frac{\gamma}{BV} k_B \Theta_D$$



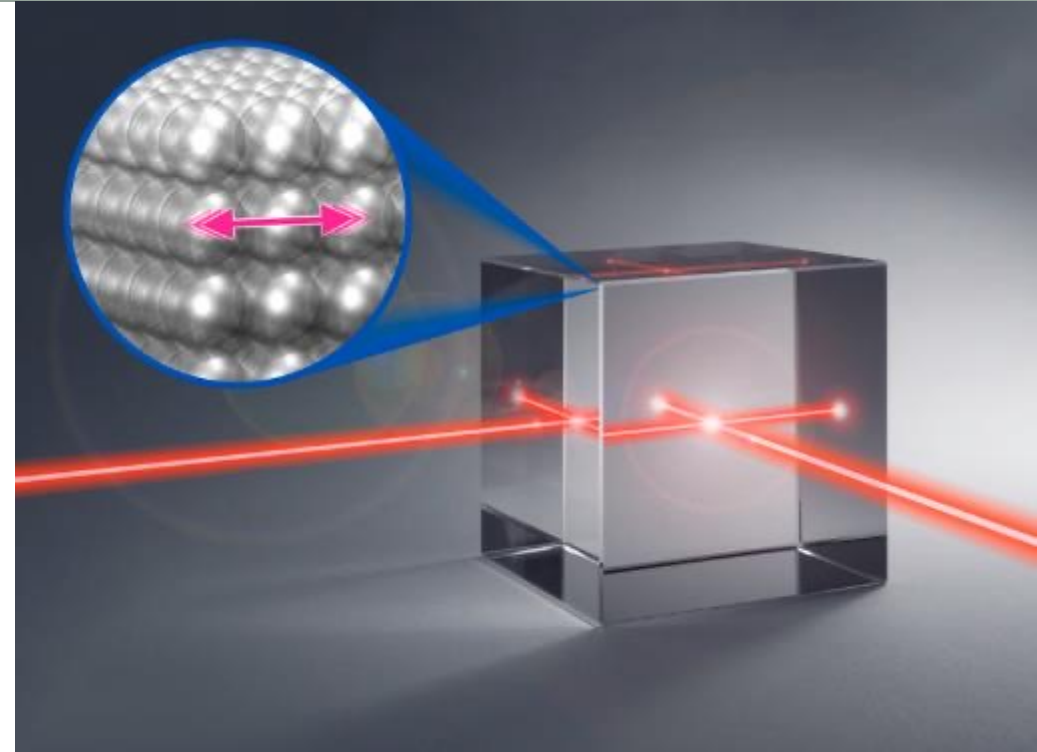
Solids: μ -dependence



In practice

- new possibility to look for drifting constants
- interferometer with 2 different arms
- 2 optical cavities
- expected effect $\sim 10^{-19} - 10^{-18}$ within current precision limits
- optical cavity/atomic clock – α -dependence suppressed

$$\omega_c \sim \frac{c}{\lambda} \sim \frac{c}{L} \sim \frac{c}{a_B} \quad \omega_a \sim \frac{e^2}{\hbar a_B} \quad \Rightarrow \quad \frac{\omega_a}{\omega_c} \sim \frac{e^2}{\hbar c} = \alpha \quad \Rightarrow \quad K = 1$$



Detecting dark matter

A grayscale image of the Cosmic Microwave Background (CMB) radiation, showing a mottled pattern of dark and light spots representing temperature fluctuations across the sky. The image is positioned at the bottom of the slide, partially obscured by the title text.

Dark matter candidates

- scalar/axionlike oscillating DM field $\phi = \phi_0 \cos(\omega t)$ $\omega \approx \frac{m_\phi c^2}{\hbar}$
 $10^{-22} eV < m_\phi < 10^{-4} eV$

- quadratic coupling to SM fields

$$\mathcal{L}_{\text{int}} = \mp \sum_f \frac{\phi^2}{(\Lambda'_f)^2} m_f \bar{f} f \pm \frac{\phi^2}{(\Lambda'_\gamma)^2} \frac{F_{\mu\nu} F^{\mu\nu}}{4} \pm \sum_V \frac{\phi^2}{(\Lambda'_V)^2} \frac{M_V^2}{2} V_\nu V^\nu,$$

- induces effective changes in the SM

- photons

$$\mathcal{L}_\gamma = \frac{\phi^2}{(\Lambda'_\gamma)^2} \frac{F_{\mu\nu} F^{\mu\nu}}{4} \Rightarrow \alpha \rightarrow \frac{\alpha}{1 - \phi^2/(\Lambda'_\gamma)^2} \simeq \alpha \left[1 + \frac{\phi^2}{(\Lambda'_\gamma)^2} \right]$$

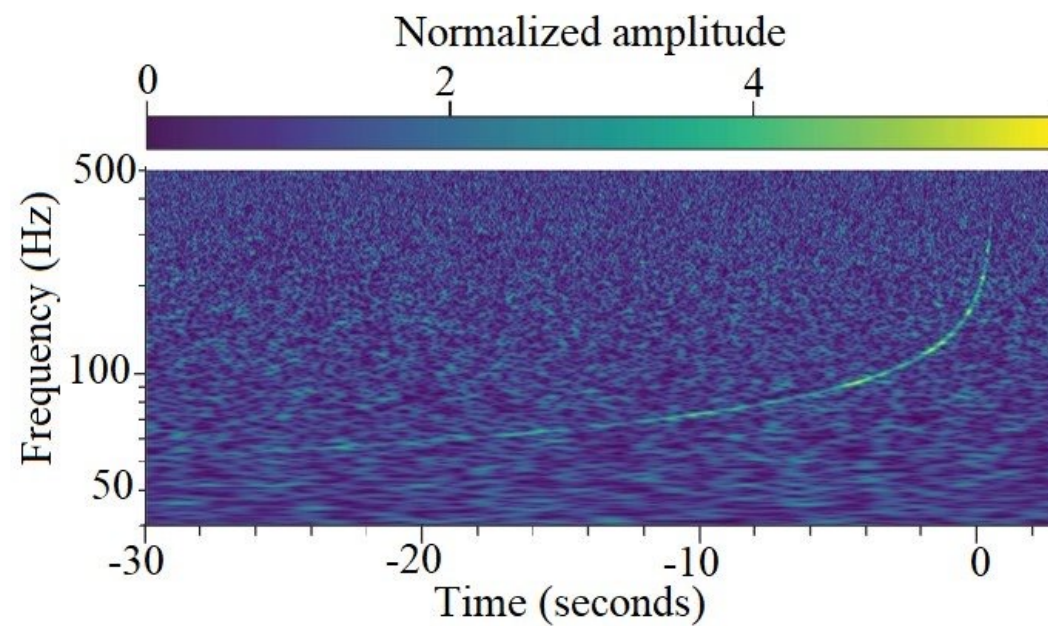
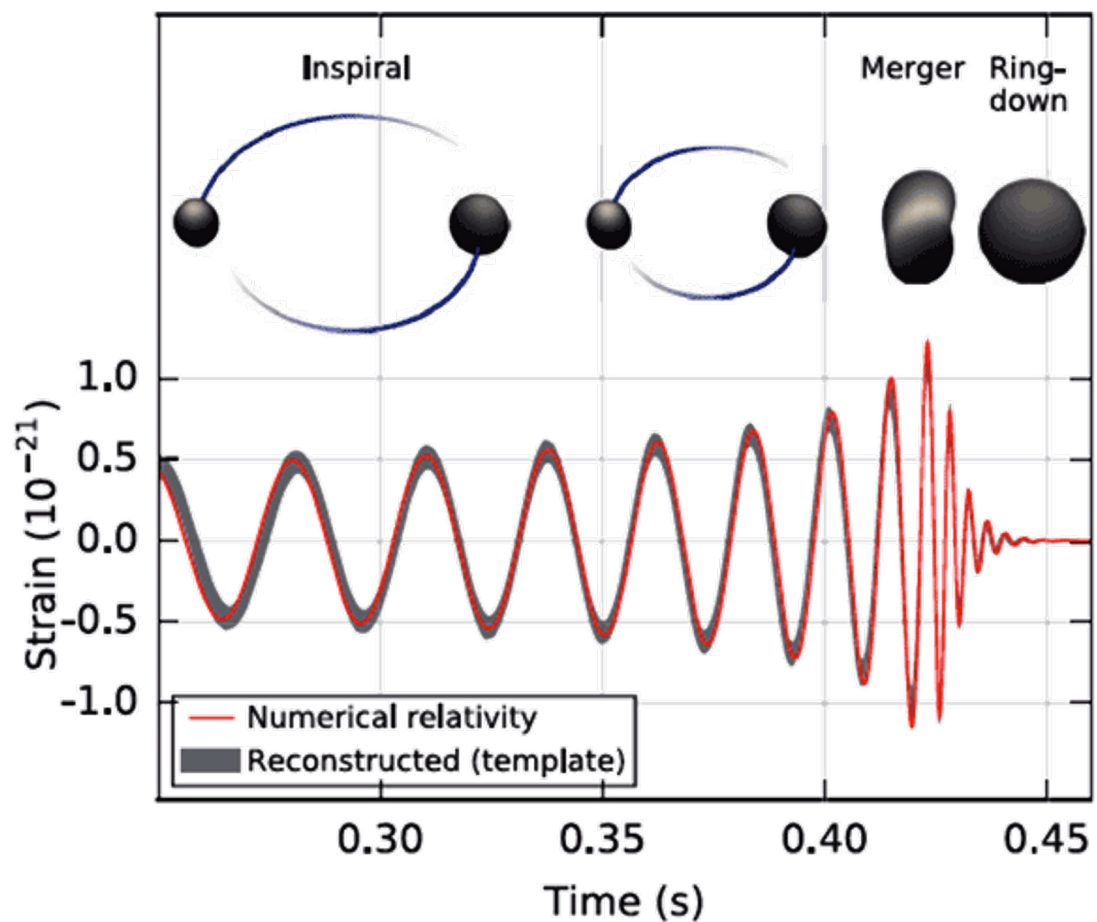
- fermions

$$\mathcal{L}_f = -\frac{\phi^2}{(\Lambda'_f)^2} m_f \bar{f} f \Rightarrow m_f \rightarrow m_f \left[1 + \frac{\phi^2}{(\Lambda'_f)^2} \right]$$

- bosons

$$\mathcal{L}_V = \frac{\phi^2}{(\Lambda'_V)^2} \frac{M_V^2}{2} V_\nu V^\nu \Rightarrow M_V^2 \rightarrow M_V^2 \left[1 + \frac{\phi^2}{(\Lambda'_V)^2} \right]$$

Laser interferometry



Expected signals

- DM field
$$\frac{\delta m_f}{m_f} = \frac{\phi_0^2}{(\Lambda'_f)^2} \cos^2(m_\phi t) = \boxed{\frac{\phi_0^2}{2(\Lambda'_f)^2}} + \boxed{\frac{\phi_0^2}{2(\Lambda'_f)^2} \cos(2m_\phi t)}$$

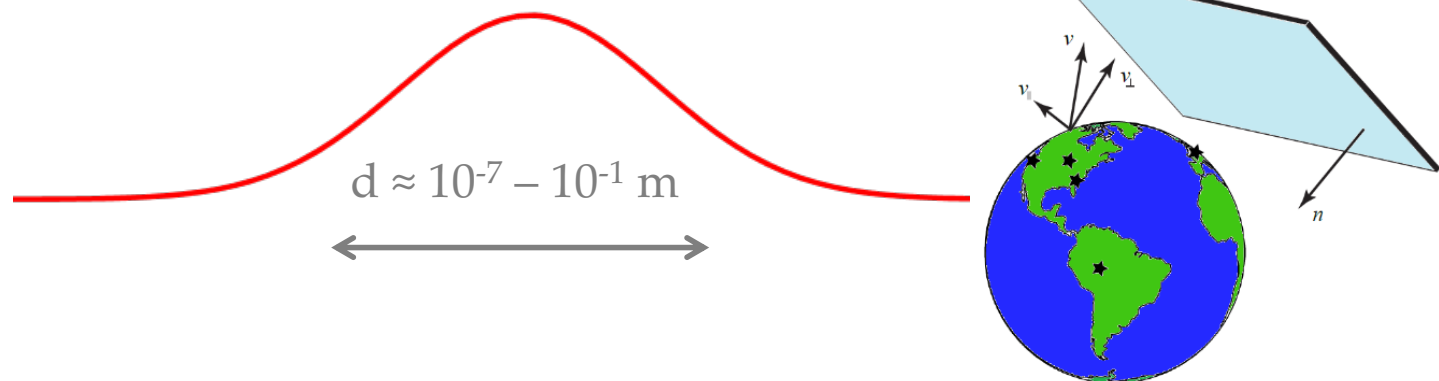
- oscillating signal



- slow drift



- topological defect



Time variation of a fundamental dimensionless constant

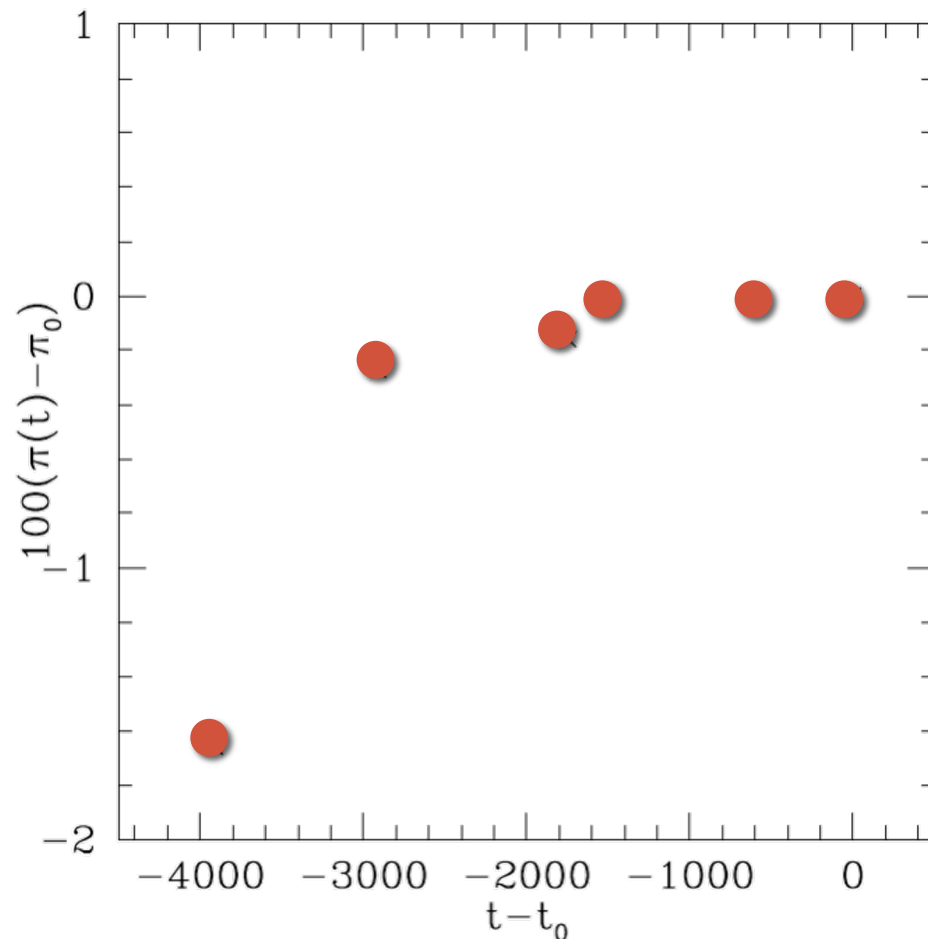
Robert J. Scherrer

Department of Physics and Astronomy, Vanderbilt University, Nashville, TN 37235

We examine the time variation of a previously-uninvestigated fundamental dimensionless constant. Constraints are placed on this time variation using historical measurements. A model is presented for the time variation, and it is shown to lead to an accelerated expansion for the universe. Directions for future research are discussed.

PACS numbers: 98.80.Cq

Location	Time	$\pi(t)$
Babylon	1900 BC	3.125
India	900 BC	3.139
China	263 AD	3.14
China	500 AD	3.1415926
India	1400 AD	3.14159265359



Thank you

- Experiment

Ronald Garcia-Ruiz, MIT
 Shane Wilkins, MIT
 Benoît Darquié, LPL Paris
 Yuval Shagam, Technion Haifa
 David Leibrant, UCLA
 David Leimbach, CERN
 Eric Norrgard, NIST
 Nick Hutzler, CalTech
 Richard Mawhorter, Pomona CA
 Rick Bethlem, VU Amsterdam
 Wim Ubachs, VU Amsterdam
 Steve Jones, RUG NL
 Roman Bause, RUG, NL

- Theory

Ephraim Eliav, Tel Aviv U
 Rob Timmermans, RUG NL
 Trond Saue, CNRS Toulouse
 Shirin Faraji, RUG NL
 Agustin Aucar, UNNE Argentina



Peter Schwerdfeger



Anastasia Borschevsky



Victor Flambaum



- Students & postdocs

Sasha Kyuberis
 Eifion Prinsen
 Pi Haase
 Odile Smits

Yuly Chamorro
 Eduardus
 Yangyang Guo
 Marit Fiechter

Martijn Reitsma
 Radka Hlaváčová
 Yongliang Hao