Развитие высокоточных методов расчёта свойств соединений тяжёлых и сверхтяжёлых элементов для фундаментальных физико-химических экспериментов

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Talk outline

- Spectra of molecules

- Nuclear magnetization distribution effect in neutral atoms and molecules

Why do we need really precise theory?

- **Prediction of spectroscopic properties to prepare experiments**

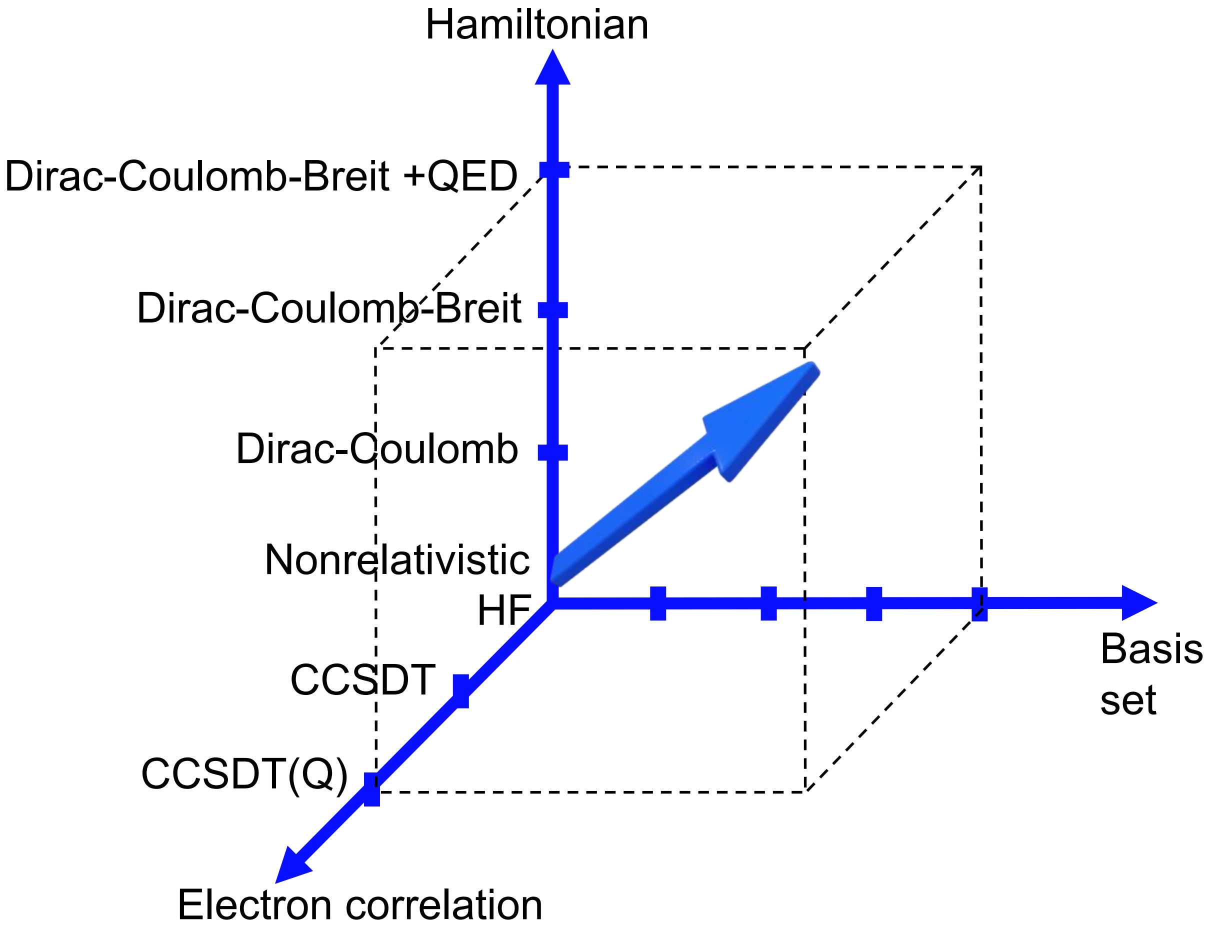
- **Study of the nuclear properties:**

- nuclear magnetic dipole moments
- nuclear electric quadrupole moments
- nuclear change radius (via isotope shifts)

- **Search for the new physics effects (nuclear Schiff moment, electron electric dipole moments)**

It is impossible to interpret experiments without a good theory

“Degrees of freedom” of electronic structure calculation



Methods: the coupled cluster theory

$$\Psi_{CC} = \mathrm{e}^{\hat{T}}\,\Phi_0$$

$$\mathrm{e}^{\hat{T}} = 1 + \hat{T} + \frac{\hat{T}^2}{2!} + \cdots$$

$$\hat{T} = \hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \cdots$$ cluster operator

$$\hat{T}_1 = \sum_{i,a} t_i^a a_a^+ a_i$$

$$\hat{T}_2 = \frac{1}{4}\sum_{ij,ab} t_{ij}^{ab} a_a^+ a_b^+ a_j a_i$$

CCSD(T) (> PT4) Complexity O(N^7)

CCSDT(Q) (> PT6) is better, but is **EXTREAMLY** expensive!
complexity O(N^9)
=> Compact basis set is required!

Multireference formulations: FS-CCSD, FS-CCSDT
in the ExpT code: http://qchem.pnpi.spb.ru/expt
[A.V. Oleynichenko, A. Zaitsevskii, E. Eliav,
Commun. Comput. Inf. Sci., 1331, 375-386 (2020)]

Methods: compact **basis sets** via the **natbas** code

CCSDT(Q): complexity: O(N^9)

- ○ Perform CCSD(T) calculations of 1-electron density matrix in a big basis set (using the generalized relativistic effective core potential)
- ○ Include all relevant atomic AND/OR molecular states

natbas:
Averaging over all density matrices
(atomic and molecular)
and atomic projections
and generating natural compact basis set

- ➢ **Natural occupations provides a systematic way to construct compact basis set**
- ➢ **Direct basis set can be optimized for a given compound**
- ➢ **With compact basis set one can use complicated CCSDT, CCSDT(Q), etc. CC models**
- ➢ **Interfaces to: CFOUR, Dirac, MRCC, Exp-T**

L.V. Skripnikov et al. Chem. Phys. Lett. 555 79 (2013)
L.V. Skripnikov J. Chem. Phys. 153, 114114 (2020)

QED in molecules

What we need for an accurate theoretical prediction of transition energy in heavy-atom molecules?

- Good basis set (CBS)

- Good treatment of the electron correlation effects

- Good Hamiltonian: Dirac-Coulomb(-Breit)

OR

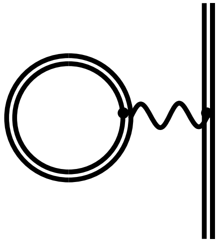
generalized relativistic effective core potential

http://qchem.pnpi.spb.ru/recp

- **QED effects should be included in order to achieve meV (~tens of cm^{-1}) of accuracy for heavy-atom molecules**

QED effects for energies

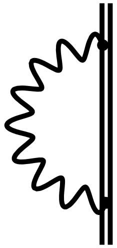
Vacuum polarization (VP)



~ Uehling potential for which a simple approximate formulas are available

Self-energy (SE)

More complicated than VP.
The method of model QED Hamiltonian is very promising.



Different expressions have been suggested for the model SE operator, e.g.:

- P. Pyykkö, L. B. Zhao, J. Phys. B **36**, 1469 (2003). (local operator)
- V. V. Flambaum, J. S. M. Ginges, Phys. Rev. A **72**, 052115 (2005).
- K.G. Dyall, J. Chem. Phys. **139**, 021103 (2013).
- V. M. Shabaev, I. I. Tupitsyn, V. A. Yerokhin, PRA **88**, 012513 (2013).

Model SE operator

- The main idea of previous and present model SE operators is to rescale the Lamb shift matrix elements for the Coulomb potential

- Both **diagonal** and ***off-diagonal*** matrix elements of SE over H-like functions η_{kljm} have been calculated in [V. M. Shabaev, I. I. Tupitsyn, V. A. Yerokhin, PRA 88, 012513 (2013)] for the first time

- The following expression for SE has been introduced:

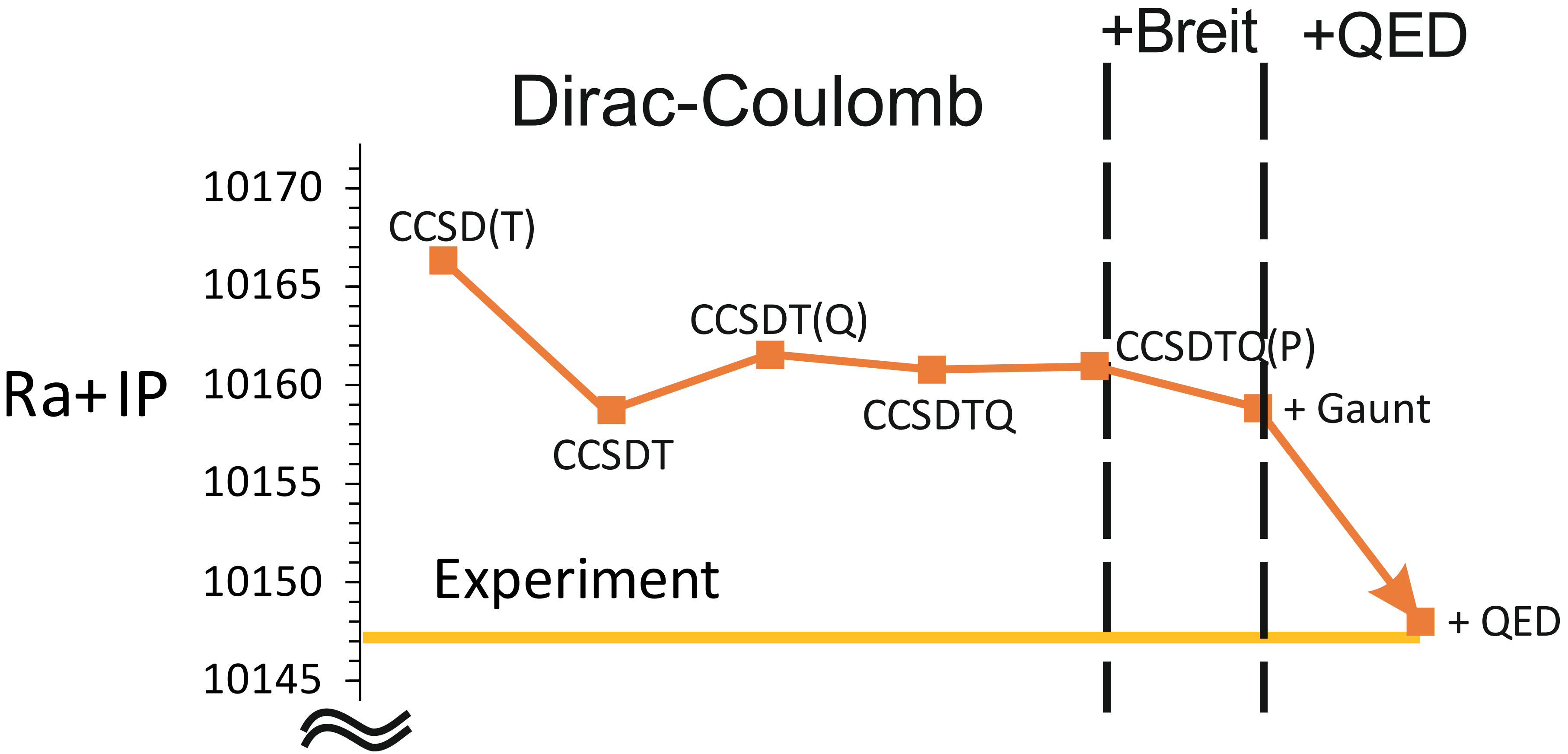
  [L.V. Skripnikov J. Chem. Phys. **154**, 201101 (2021)]

$$H_{SE} \approx \sum_{kljm,k'l'j'm'} \frac{|h_{kljm}\rangle X_{kljm,k'l'j'm'} \langle h_{k'l'j'm'}|}{\langle h_{kljm}|h_{kljm}\rangle \langle h_{k'l'j'm'}|h_{k'l'j'm'}\rangle}.$$

$\{|h_{kljm}\rangle\}$ are the orthogonal set of linear combinations of $\{|\tilde{h}_{kljm}\rangle = \eta_{kljm}\theta(R_c - |\boldsymbol{r}|)\}$,
η_{kljm} - H-like functions
The canonical orthogonalization-like procedure has been used to exclude linear dependence.

QED in Ra$^+$

units: meV ~ 8 cm^{-1}



Inclusion of QED effects allowed us to achieve a few meV level of accuracy for transitions energies and IP

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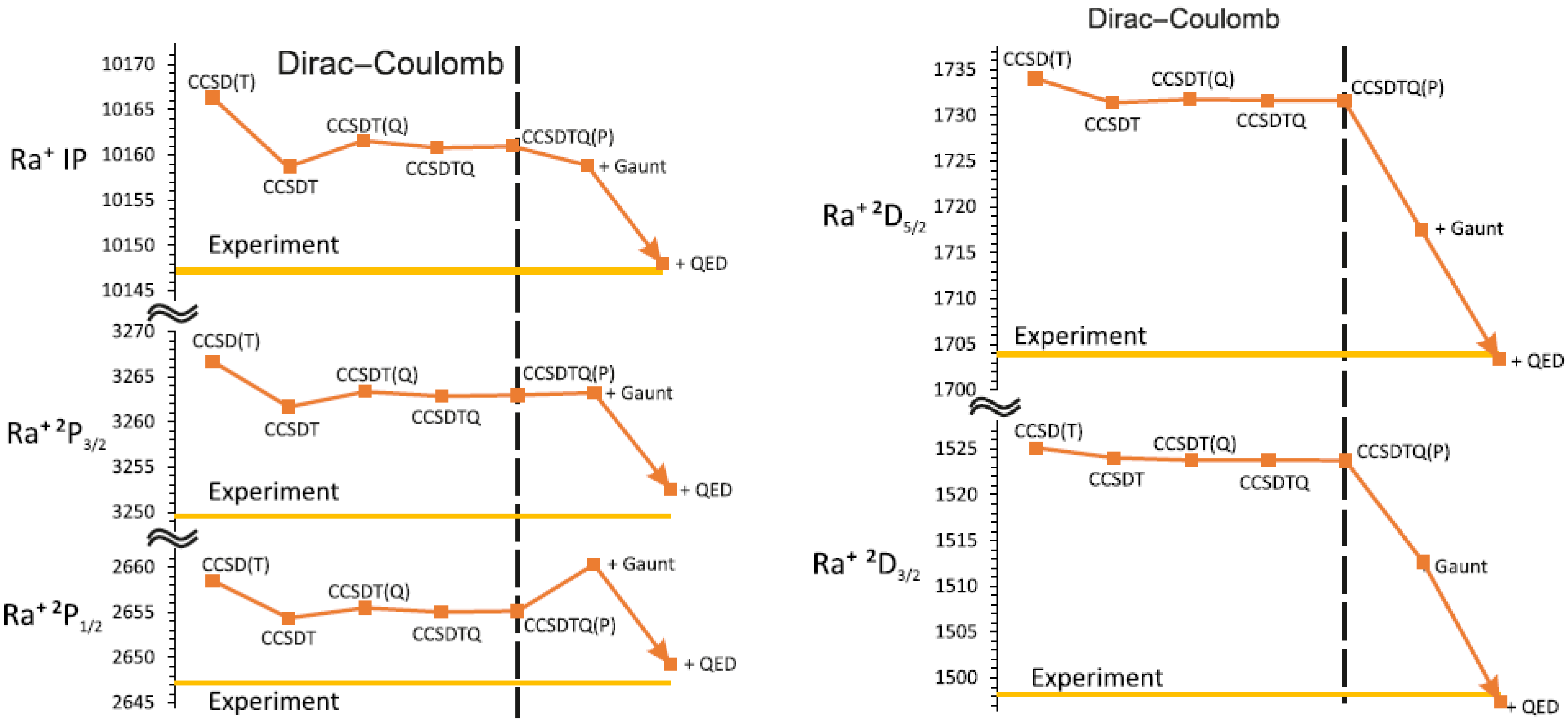
QED in Ra^+

units: meV ~ 8 cm^{-1}

$$H_{SE} \approx \sum_{kljm,k'l'j'm'} \frac{|h_{kljm}\rangle X_{kljm,k'l'j'm'} \langle h_{k'l'j'm'}|}{\langle h_{kljm}|h_{kljm}\rangle \langle h_{k'l'j'm'}|h_{k'l'j'm'}\rangle}.$$



Experiment: C.A. Holliman, M. Fan, A. Contractor, M.W. Straus, A.M. Jayich, Phys. Rev. A **102**, 042822 (2020)

Inclusion of QED effects allowed us to achieve a few meV level of accuracy for transitions energies and IP

L.V. Skripnikov J. Chem. Phys. **154**, 201101 (2021)

QED in Ra^+

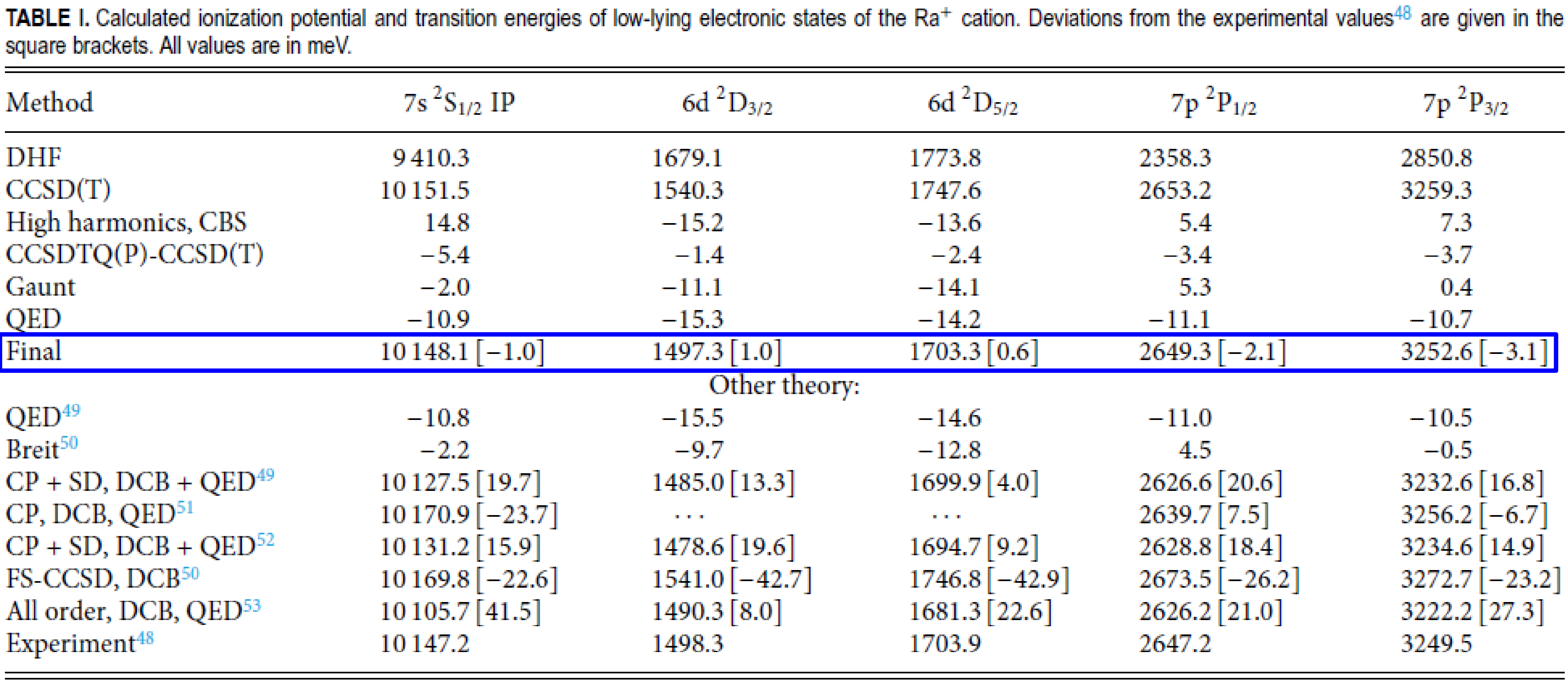


TABLE I. Calculated ionization potential and transition energies of low-lying electronic states of the Ra^+ cation. Deviations from the experimental values[48] are given in the square brackets. All values are in meV.

Method	$7s\ ^2S_{1/2}$ IP	$6d\ ^2D_{3/2}$	$6d\ ^2D_{5/2}$	$7p\ ^2P_{1/2}$	$7p\ ^2P_{3/2}$
DHF	9 410.3	1679.1	1773.8	2358.3	2850.8
CCSD(T)	10 151.5	1540.3	1747.6	2653.2	3259.3
High harmonics, CBS	14.8	−15.2	−13.6	5.4	7.3
CCSDTQ(P)-CCSD(T)	−5.4	−1.4	−2.4	−3.4	−3.7
Gaunt	−2.0	−11.1	−14.1	5.3	0.4
QED	−10.9	−15.3	−14.2	−11.1	−10.7
Final	10 148.1 [−1.0]	1497.3 [1.0]	1703.3 [0.6]	2649.3 [−2.1]	3252.6 [−3.1]
			Other theory:		
QED[49]	−10.8	−15.5	−14.6	−11.0	−10.5
Breit[50]	−2.2	−9.7	−12.8	4.5	−0.5
CP + SD, DCB + QED[49]	10 127.5 [19.7]	1485.0 [13.3]	1699.9 [4.0]	2626.6 [20.6]	3232.6 [16.8]
CP, DCB, QED[51]	10 170.9 [−23.7]	…	…	2639.7 [7.5]	3256.2 [−6.7]
CP + SD, DCB + QED[52]	10 131.2 [15.9]	1478.6 [19.6]	1694.7 [9.2]	2628.8 [18.4]	3234.6 [14.9]
FS-CCSD, DCB[50]	10 169.8 [−22.6]	1541.0 [−42.7]	1746.8 [−42.9]	2673.5 [−26.2]	3272.7 [−23.2]
All order, DCB, QED[53]	10 105.7 [41.5]	1490.3 [8.0]	1681.3 [22.6]	2626.2 [21.0]	3222.2 [27.3]
Experiment[48]	10 147.2	1498.3	1703.9	2647.2	3249.5

L.V. Skripnikov J. Chem. Phys. **154**, 201101 (2021)

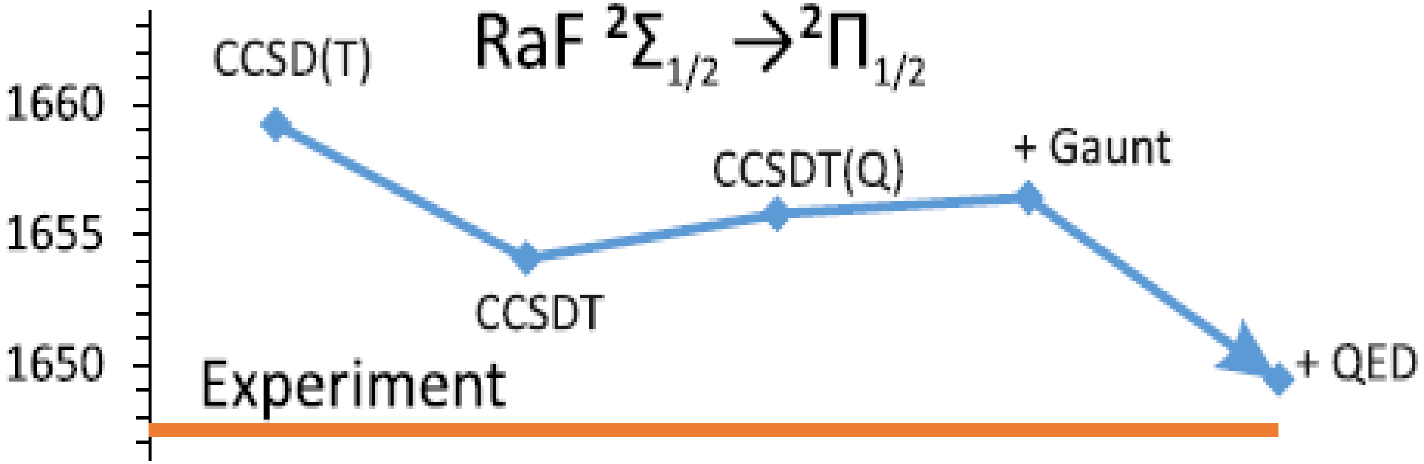
Previous calculations:

- J.S.M. Ginges, V. A. Dzuba, Phys. Rev. A 91, 042505 (2015)
- T.H. Dinh, V. A. Dzuba, V. V. Flambaum, J. S. M. Ginges, Phys. Rev. A 78, 022507 (2008)
- E. Eliav, U. Kaldor, and Y. Ishikawa, Phys. Rev. A 53, 3050 (1996)
- R. Pal, D. Jiang, M.S. Safronova, U.I. Safronova, Phys. Rev. A 79, 062505 (2009)

QED in RaF

$$H_{SE} \approx \sum_{kljm,k'l'j'm'} \frac{|h_{kljm}\rangle X_{kljm,k'l'j'm'} \langle h_{k'l'j'm'}|}{\langle h_{kljm}|h_{kljm}\rangle \langle h_{k'l'j'm'}|h_{k'l'j'm'}\rangle}.$$

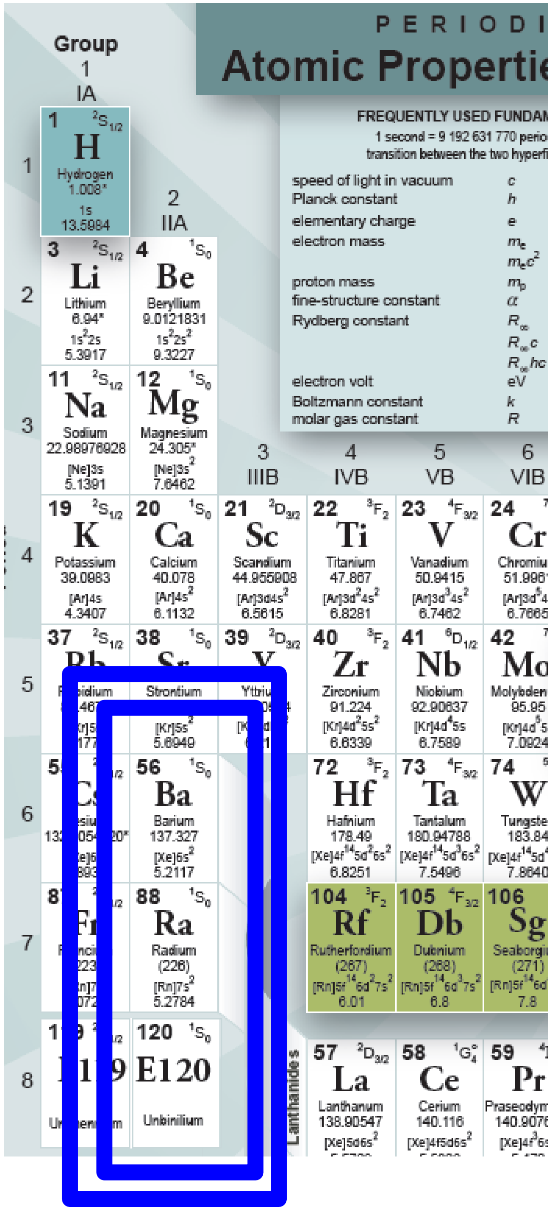
units: meV ~ 8 cm^{-1}



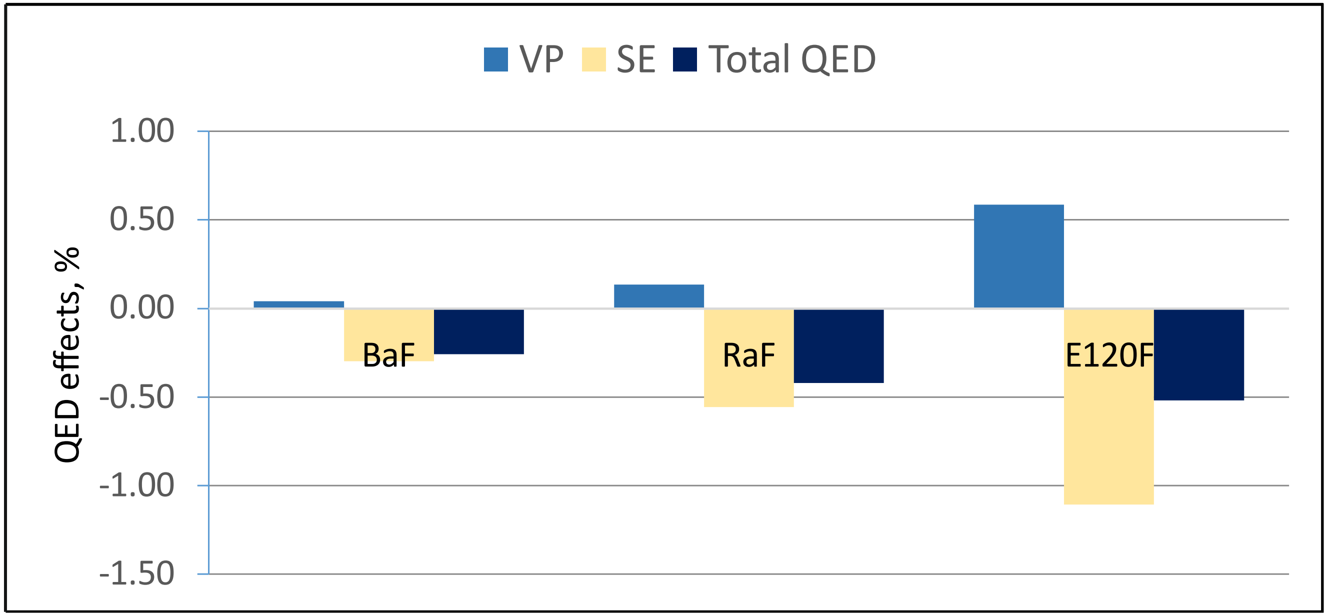
Experiment: R.G. Ruiz, R.Berger, J. Billowes, et al., Nature **581**, 396 (2020)

L.V. Skripnikov J. Chem. Phys. **154**, 201101 (2021)

QED effects in homologs of E120-F



Molecule	Excitation energy, cm^{-1} X $^2\Sigma_{1/2}$ -> $^2\Pi_{1/2}$
BaF	11,663
RaF	13,299
E120F	17,879



L.V. Skripnikov et al J. Chem. Phys. 155, 144103 (2021)

New data for the radioactive RaF molecule

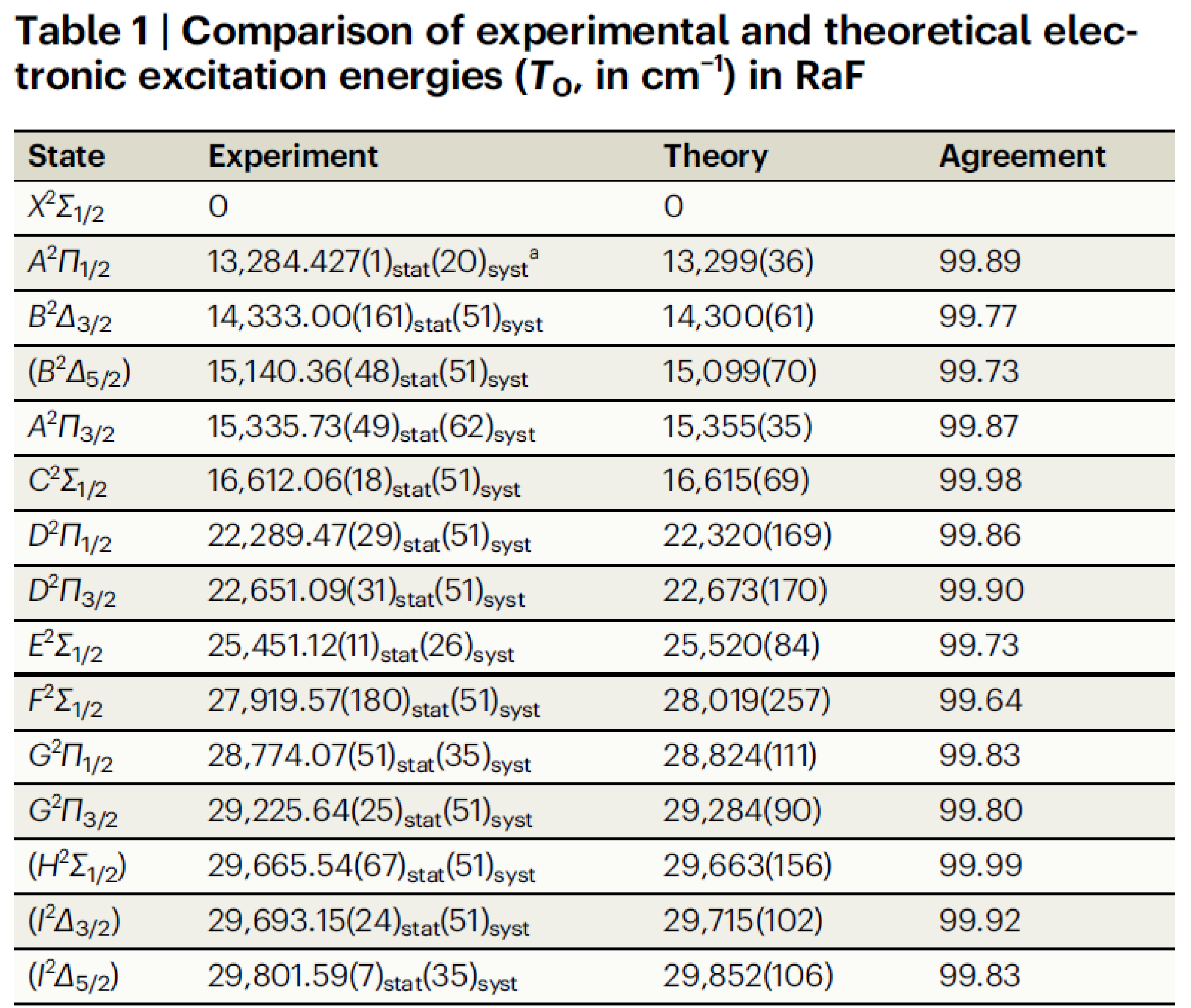
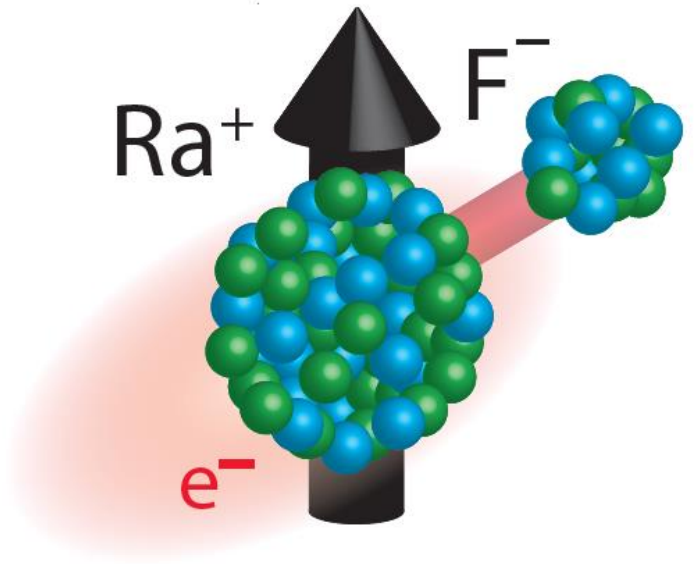


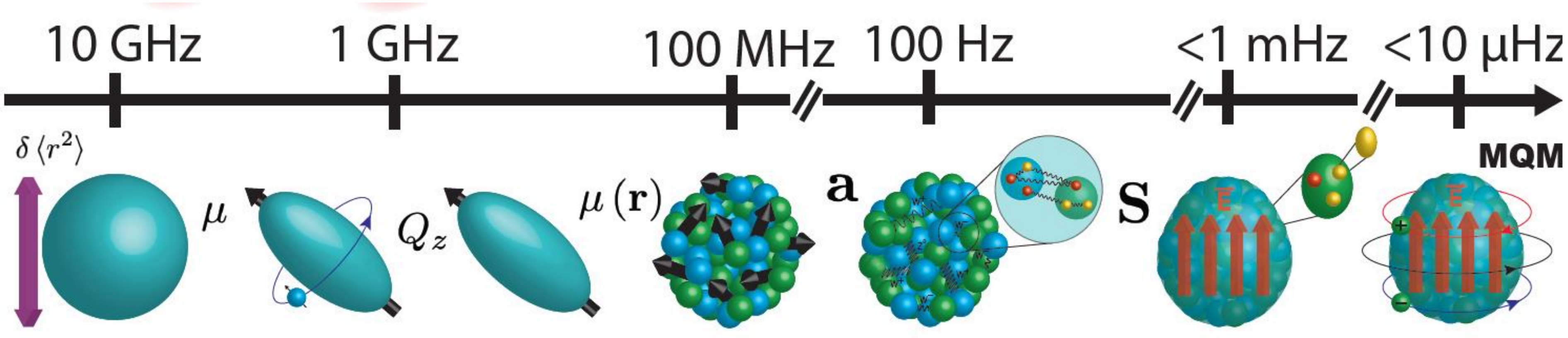
Table 1 | Comparison of experimental and theoretical electronic excitation energies (T_0, in cm^{-1}) in RaF

State	Experiment	Theory	Agreement
$X^2\Sigma_{1/2}$	0	0	
$A^2\Pi_{1/2}$	$13{,}284.427(1)_{\mathrm{stat}}(20)_{\mathrm{syst}}$[a]	13,299(36)	99.89
$B^2\Delta_{3/2}$	$14{,}333.00(161)_{\mathrm{stat}}(51)_{\mathrm{syst}}$	14,300(61)	99.77
$(B^2\Delta_{5/2})$	$15{,}140.36(48)_{\mathrm{stat}}(51)_{\mathrm{syst}}$	15,099(70)	99.73
$A^2\Pi_{3/2}$	$15{,}335.73(49)_{\mathrm{stat}}(62)_{\mathrm{syst}}$	15,355(35)	99.87
$C^2\Sigma_{1/2}$	$16{,}612.06(18)_{\mathrm{stat}}(51)_{\mathrm{syst}}$	16,615(69)	99.98
$D^2\Pi_{1/2}$	$22{,}289.47(29)_{\mathrm{stat}}(51)_{\mathrm{syst}}$	22,320(169)	99.86
$D^2\Pi_{3/2}$	$22{,}651.09(31)_{\mathrm{stat}}(51)_{\mathrm{syst}}$	22,673(170)	99.90
$E^2\Sigma_{1/2}$	$25{,}451.12(11)_{\mathrm{stat}}(26)_{\mathrm{syst}}$	25,520(84)	99.73
$F^2\Sigma_{1/2}$	$27{,}919.57(180)_{\mathrm{stat}}(51)_{\mathrm{syst}}$	28,019(257)	99.64
$G^2\Pi_{1/2}$	$28{,}774.07(51)_{\mathrm{stat}}(35)_{\mathrm{syst}}$	28,824(111)	99.83
$G^2\Pi_{3/2}$	$29{,}225.64(25)_{\mathrm{stat}}(51)_{\mathrm{syst}}$	29,284(90)	99.80
$(H^2\Sigma_{1/2})$	$29{,}665.54(67)_{\mathrm{stat}}(51)_{\mathrm{syst}}$	29,663(156)	99.99
$(I^2\Delta_{3/2})$	$29{,}693.15(24)_{\mathrm{stat}}(51)_{\mathrm{syst}}$	29,715(102)	99.92
$(I^2\Delta_{5/2})$	$29{,}801.59(7)_{\mathrm{stat}}(35)_{\mathrm{syst}}$	29,852(106)	99.83

M. Athanasakis-Kaklamanakis, S.G. Wilkins, L.V. Skripnikov et al, Nature Communications, **16**, 2139 (2025)

Что можно узнать о ядре, изучая молекулы?





1 GHz ~ $4*10^{-6}$ eV

Hyperfine structure and nuclear magnetization distribution effect in molecules and atoms

$$\Delta E = \Delta E_0 - \Delta E_{BW}$$

- ✓ Test of the electronic structure theory for problems of New physics search

Experiment

$$\text{electron EDM} = \frac{\Delta E}{\mathcal{E}_{\text{eff}}}$$

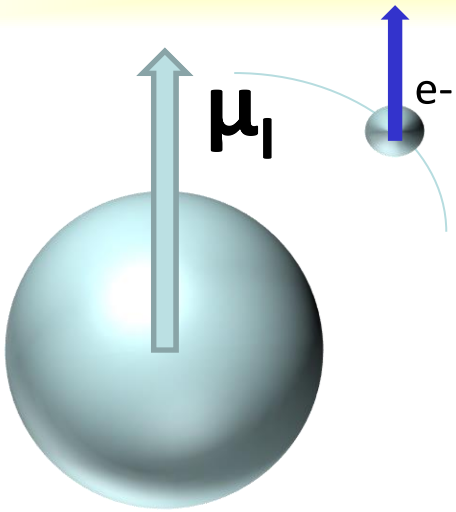
Theory

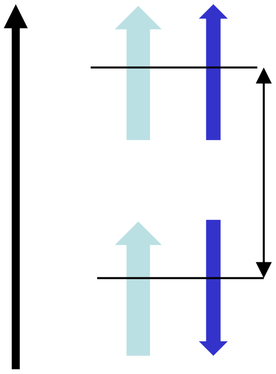
To test the accuracy of E_{eff} calculation one usually calculates molecular HFS constants

- ✓ Tests of bound-state QED methods

- ✓ Study of the nuclear structure: valence nucleon configuration, many-body effects, etc.

The hyperfine structure





$$\Delta E_{HFS} \sim \boldsymbol{I} \cdot \boldsymbol{A} \cdot \boldsymbol{S}$$

$$\Delta E = \Delta E_0 - \Delta E_{BW}$$

HFS in the point magnetic dipole approximation

Finite nuclear magnetization distribution contribution: **B**ohr-**W**eisskopf effect (**BW**)

$$\Delta E \sim \mu_I$$

What is the nuclear magnetization distribution effect?

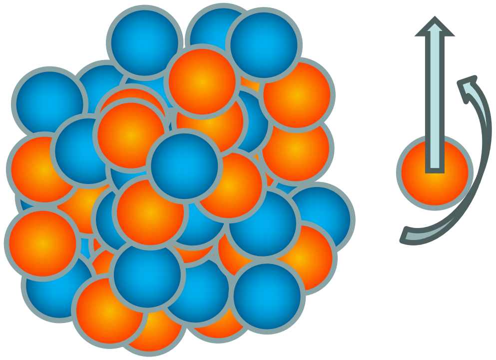
The nuclear magnetic dipole moment operator:

$$\boldsymbol{\mu} = \sum_{i}^{A} g_s \boldsymbol{s}(i) + g_l \boldsymbol{l}(i)$$

Odd-A nucleus: $\boldsymbol{\mu} = g_s \boldsymbol{s} + g_l \boldsymbol{l}$

- Nucleon spin produces vector potential $A_S(\boldsymbol{r})$ that interacts with electrons and contributes to atomic HFS $\sim\int d\boldsymbol{r}\psi^{\dagger} e\boldsymbol{\alpha}\boldsymbol{A}_S(\boldsymbol{r})\psi$

- Nucleon orbital motion produces vector potential $A_L(\boldsymbol{r})$ that interacts with electrons, which contributes $\sim\int d\boldsymbol{r}\psi^{\dagger} e\boldsymbol{\alpha}\boldsymbol{A}_L(\boldsymbol{r})\psi$



Electronic wave function penetrates inside the nucleus

$$\boldsymbol{\mu} \rightarrow \boldsymbol{\mu}(\boldsymbol{r})$$

BW effect factorization: summary

$$A = A^{(0)} - A^{BW}$$

$$\boxed{A^{BW} = \frac{\mu}{I\Omega}\left(\mathcal{P}_s + \beta\mathcal{P}_p\right) B_s}$$

Pure electronic part

Nuclear model-dependent parameter

$$B_s = \frac{1}{2\mu} A_{BW}(\mathrm{H-like\ ion})$$

The BW effect can be factorized into the pure electronic and nuclear depended parts due to:

1.) only $s_{1/2}$ and $p_{1/2}$ functions contribute to the BW effect

2.) all $s_{1/2}$-type functions proportional to $1s_{1/2}$ H-like function inside the nucleus
all $p_{1/2}$-type functions proportional to $2p_{1/2}$ H-like function inside the nucleus

3.) Two special symmetry properties of the hyperfine interaction operator

- ✓ **If any of these properties is violated, then the accurate factorization for any state in heavy-atom compound would be impossible**

L.V. Skripnikov, J. Chem. Phys. **153**, 114114 (2020)

BW effect in $^{225}Ra^+$

$$A^{BW} = A^{(0)}_{theory} - A(Ra^+)_{exp} \Rightarrow B_s(^{225}Ra)$$

BW effect in any system

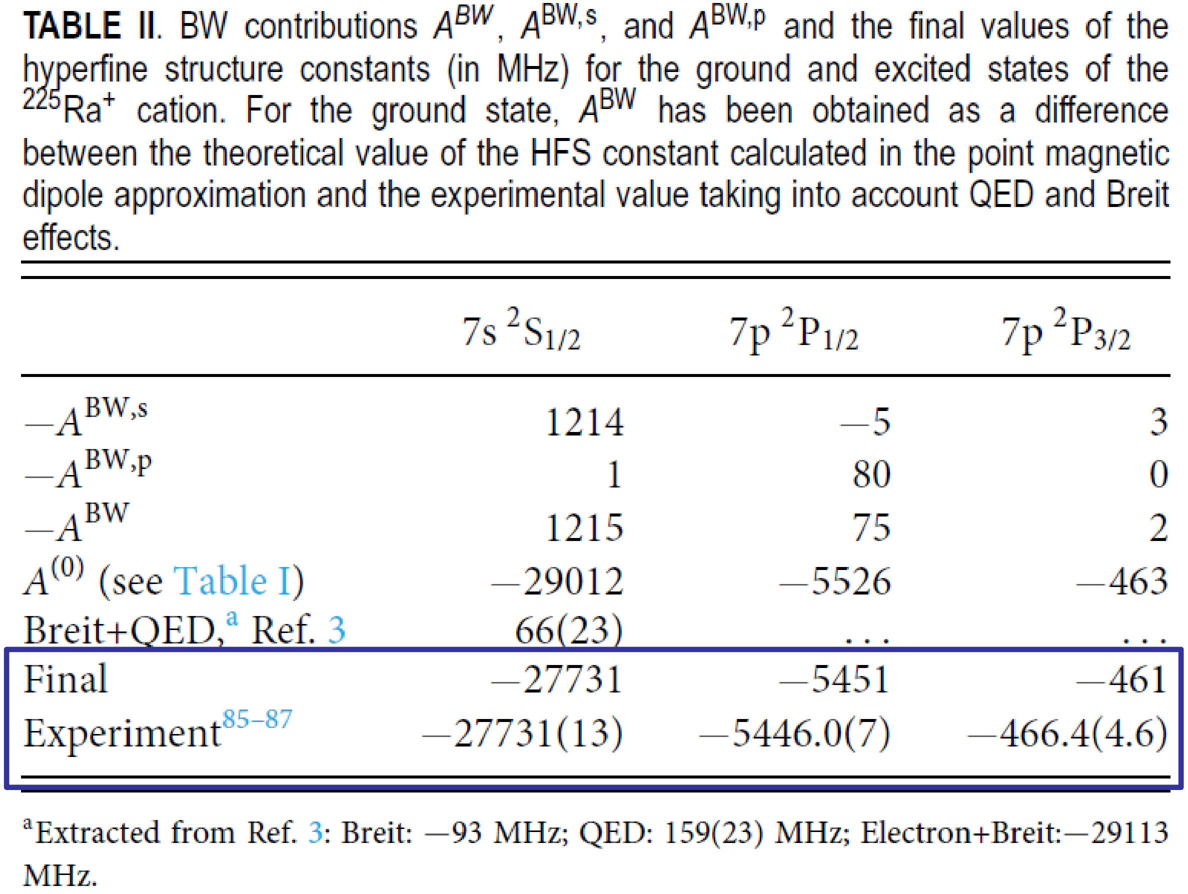


TABLE II. BW contributions A^{BW}, $A^{BW,s}$, and $A^{BW,p}$ and the final values of the hyperfine structure constants (in MHz) for the ground and excited states of the $^{225}Ra^+$ cation. For the ground state, A^{BW} has been obtained as a difference between the theoretical value of the HFS constant calculated in the point magnetic dipole approximation and the experimental value taking into account QED and Breit effects.

	$7s\ ^2S_{1/2}$	$7p\ ^2P_{1/2}$	$7p\ ^2P_{3/2}$
$-A^{BW,s}$	1214	−5	3
$-A^{BW,p}$	1	80	0
$-A^{BW}$	1215	75	2
$A^{(0)}$ (see Table I)	−29012	−5526	−463
Breit+QED,[a] Ref. 3	66(23)	…	…
Final	−27731	−5451	−461
Experiment[85–87]	−27731(13)	−5446.0(7)	−466.4(4.6)

[a] Extracted from Ref. 3: Breit: −93 MHz; QED: 159(23) MHz; Electron+Breit: −29113 MHz.

L.V. Skripnikov, J. Chem. Phys. **153**, 114114 (2020).

BW effect in ^{225}RaF

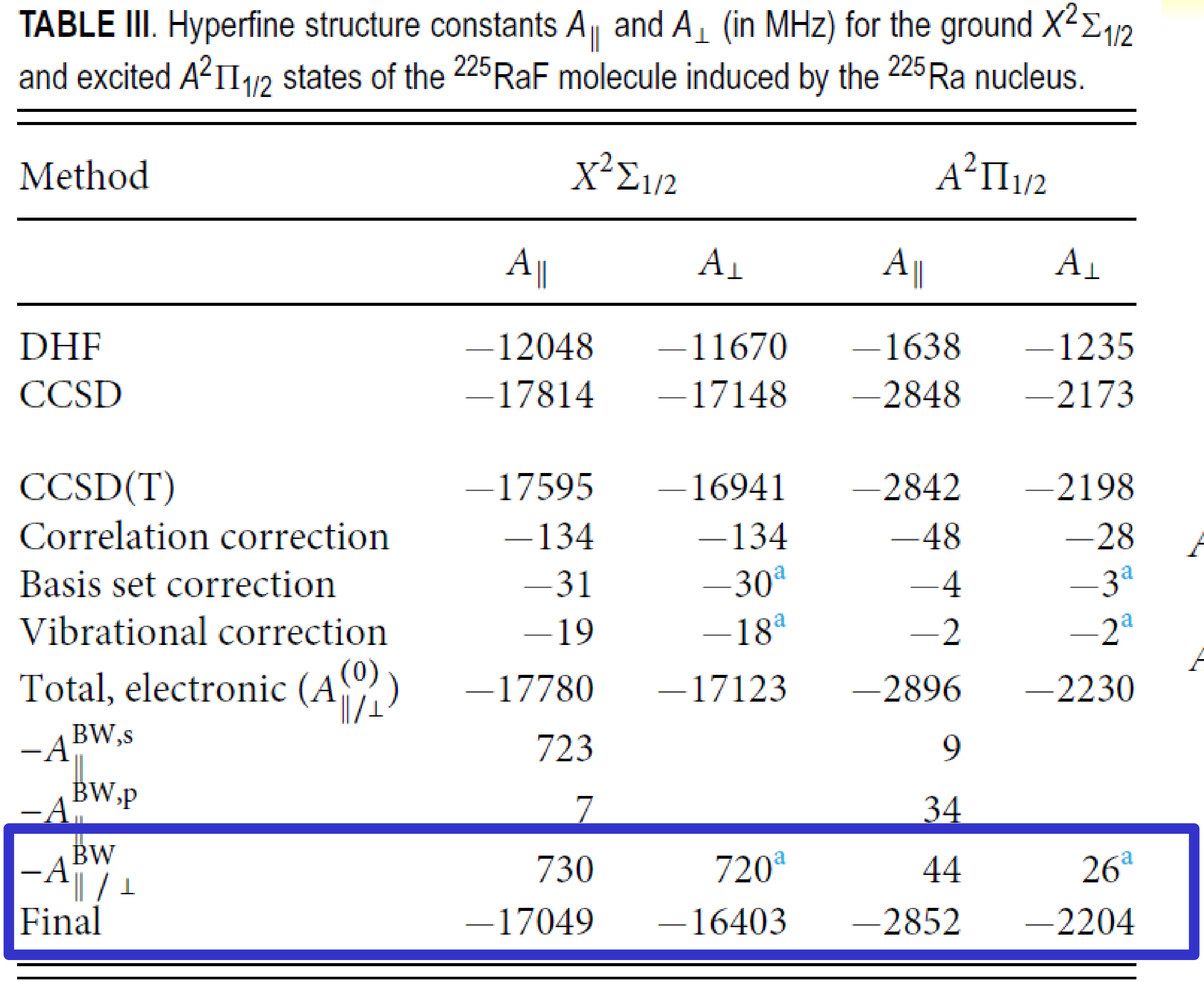


TABLE III. Hyperfine structure constants $A_{\parallel}$ and $A_{\perp}$ (in MHz) for the ground $X^2\Sigma_{1/2}$ and excited $A^2\Pi_{1/2}$ states of the ^{225}RaF molecule induced by the ^{225}Ra nucleus.

Method	$X^2\Sigma_{1/2}$		$A^2\Pi_{1/2}$	
	$A_{\parallel}$	$A_{\perp}$	$A_{\parallel}$	$A_{\perp}$
DHF	−12048	−11670	−1638	−1235
CCSD	−17814	−17148	−2848	−2173
CCSD(T)	−17595	−16941	−2842	−2198
Correlation correction	−134	−134	−48	−28
Basis set correction	−31	−30[a]	−4	−3[a]
Vibrational correction	−19	−18[a]	−2	−2[a]
Total, electronic ($A^{(0)}_{\parallel/\perp}$)	−17780	−17123	−2896	−2230
$-A_{\parallel}^{\mathrm{BW,s}}$	723		9	
$-A_{\parallel}^{\mathrm{BW,p}}$	7		34	
$-A_{\parallel\,/\,\perp}^{\mathrm{BW}}$	730	720[a]	44	26[a]
Final	−17049	−16403	−2852	−2204

$$A^{\mathrm{BW}} = A^{(0)} - A.$$

$$A_{\parallel}^{\mathrm{BW}}(K) \approx \frac{\mu_K}{I\Omega}(\mathcal{P}_s + \beta\mathcal{P}_p)B_s$$

Thus, BW effect contribution about 4% to the HFS of RaF and should be taken into account

L.V. Skripnikov, J. Chem. Phys. **153**, 114114 (2020).

^{225}RaF hyperfine structure experiment

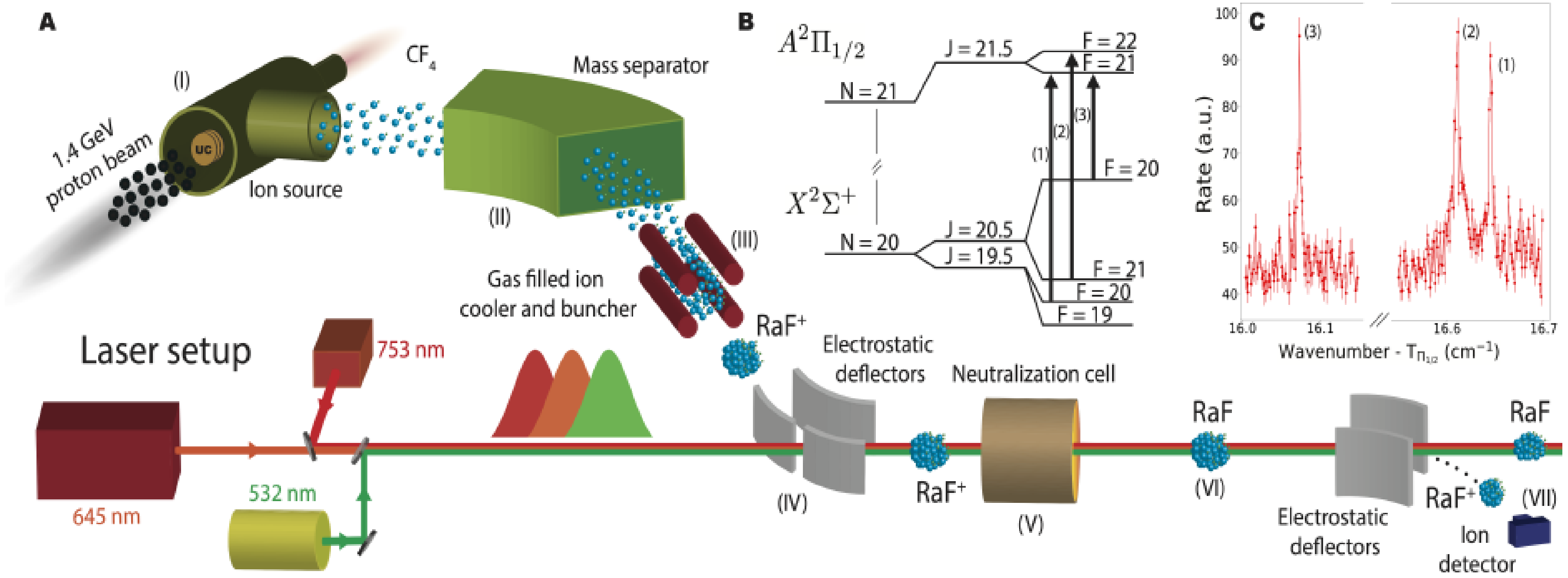


FIG. 1. **Experimental setup.** (**A**) Radium fluoride molecules are produced by impinging 1.4-GeV protons on a high-temperature (T= 2000 K) uranium carbide target, injected with CF$_4$ gas, then surfaced ionized and extracted using electrostatic fields (I). ^{225}RaF is mass-selected (II) and trapped in a He-filled radiofrequency quadrupole (T = 300 K) for up to 20 ms (III). The bunched RaF ions are guided using electrostatic deflectors (IV), neutralized in a Na-filled charge-exchange cell (V), then overlapped with 3 pulsed lasers in a collinear geometry (VI). The resulting RaF ions are deflected and detected using an ion detector (VII). (**B**) Example of energy levels involved in a transition between hyperfine levels in an R-branch (not to scale). N, J and F correspond to the rotational, electronic and total angular momentum quantum numbers of the molecule (N and J are not good quantum numbers when $I > 0$). Experimentally observed transitions are shown by upwards-pointing arrows and numbered. (**C**) Example of measured spectra showing the ion rate in arbitrary units (a.u.) as a function of the wavenumber of the first laser, Doppler corrected to the molecular rest frame and shifted by T_Π. The error bars show one standard deviation statistical uncertainty. Data points are connected by straight lines to guide the eye. The numbering on the individual peaks corresponds to the transitions shown in (**B**).

Science, accepted (2025); arXiv:2311.04121 [nucl-ex]

“Observation of the distribution of nuclear magnetization in a molecule”

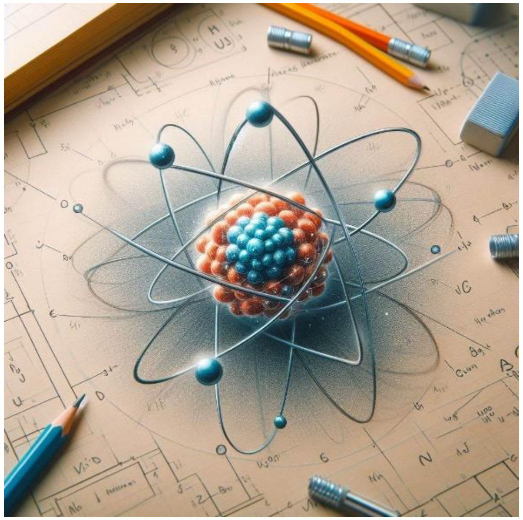
HFS constants for the ground electronic states of ^{225}RaF in MHz

	No BW , theory 2020	**With BW, theory 2020**	**Experiment 2025 ***
$A_{II}(^{225}\mathrm{RaF})$	-17**780**	-17**049**(170)	-17**064**(62)
$A_{perp}(^{225}\mathrm{RaF})$	-1**7123**	-1**6403**(164)	-1**6324**(25)

* Science, accepted (2025); arXiv:2311.04121 [nucl-ex] – experiment in ISOLDE/CERN &, theory in PNPI

The BW effect was “observed” in a molecule for the first time

Thank you!



Other topics on which our group is working on:

- ✓ Search for the New physics using atoms, molecules and solids

  electron electric dipole moment, axion-like-particle-induced interactions, nuclear T,P-violating moments, etc.
- ✓ Isotope shifts, nuclei radii: Tl, Au, Si, Po, Ag, Al (towards test unitarity of the CKM matrix), etc