

Use of molecular systems to study nuclei properties

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History

Highly charged ions can be used to test prediction of the bound state QED in large electric and magnetic fields

QED gives contribution of about 1% to the hyperfine splitting ΔE
In highly charged ions:

$$\Delta E = \Delta E_0(1-\epsilon) + \Delta E_{\text{QED}}$$

HFS in the point magnetic dipole approximation
(can be calculated accurately)

QED contribution of interest

Finite nuclear magnetization distribution contribution (hardly can be calculated accurately in ab-initio approach)

History

[V.M. Shabaev et al Phys. Rev. Lett. 86, 3959 (2001)]:

Finite nuclear distribution contribution can be cancelled in the specific difference of the hyperfine splittings of H-like and Li-like ions ^{209}Bi

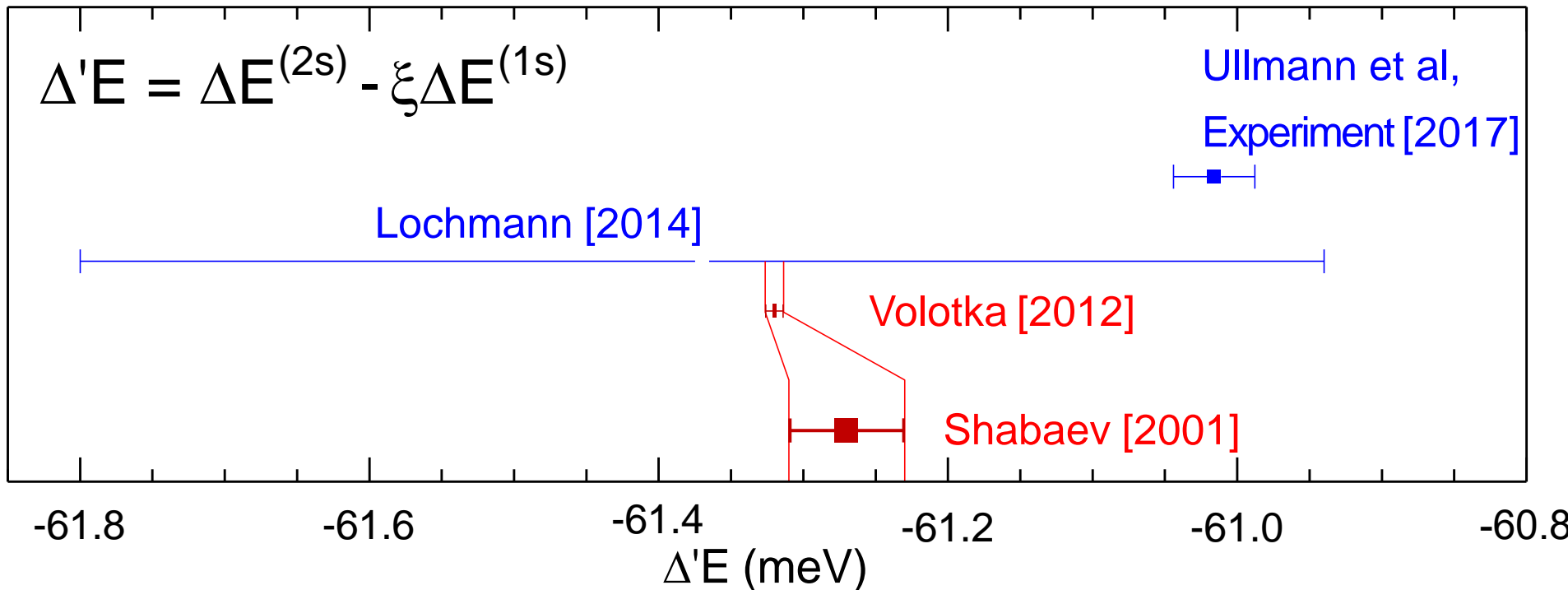
$$\Delta'E = \Delta E^{(2s)} - \xi \Delta E^{(1s)}$$

ξ is the cancellation parameter

“Hyperfine puzzle”

[V.M. Shabaev et al Phys. Rev. Lett. 86, 3959 (2001)]:

BS QED effects can be probed in a specific difference of the hyperfine (**HFS**) splitting values in H-like and Li-like $^{209}\text{Bismuth}$.



Experiment 2017: J. Ullmann, Z. Andelkovic, C. Brandau, A. Dax, W. Geithner, C. Geppert, C. Gorges, M. Hammen, V. Hannen, S. Kaufmann, K. König, Yu.A. Litvinov, M. Lochmann, B. Maaß, J. Meisner, T. Murböck, R. Sánchez, M. Schmidt, S. Schmidt, M. Steck, T. Stöhlker, R.C. Thompson, C. Trageser, J. Vollbrecht, C. Weinheimer, W. Nörtershäuser, Nat. Commun. 8, 15484 (2017). 4

Possible reasons for the hyperfine puzzle

1. QED fails
2. The magnetic moment of ^{209}Bi is different from the literature value
3. The elimination of nuclear structure contributions in the specific difference $\Delta'E$ does not work as expected

How can we obtain the magnetic moment?

$$\Delta'E = \Delta'E (\mu) !$$

In the NMR experiment one can measure Larmor frequency:

$$\nu_L = \mu_{\text{uncorrected}} * B_0 / h$$

$\mu_{\text{uncorrected}}$ - is the shielded nuclear magnetic moment

To obtain the actual value of the magnetic moment one have to calculate shielding constant:

Experiment



$$\mu = \mu_{\text{uncorrected}} / (1 - \sigma)$$

Theory

How accurately the magnetic moment of ^{209}Bi is known?

P. Raghavan, Atomic Data and Nuclear Data Tables 42, 189 (1989):

$$\mu = 4.1106(2) \mu_N$$

The value is extracted from the nuclear magnetic resonance experiment on **$\text{Bi}(\text{NO}_3)_3$ solution** using the theoretical value of σ calculated for **atomic cation Bi^{3+}**

In more recent calculation molecular environment [**$\text{Bi}(\text{NO}_3)_3$ molecule...**] contribution to σ was estimated to be **$\ll 1\%$** :

$$\mu = 4.1103(5) \mu_N \quad [\text{T. Bastug, B. Fricke, M. Finkbeiner, W. Johnson, Z. Phys. D 37, 281 (1996)}]$$

How accurately the magnetic moment of ^{209}Bi is known?

In [T. Bastug, B. Fricke, M. Finkbeiner, W. Johnson, Z. Phys. D 37, 281 (1996)] the $\text{Bi}(\text{NO}_3)_3$ molecule has been considered.

Drawbacks of the $\text{Bi}(\text{NO}_3)_3$ aqua solution:

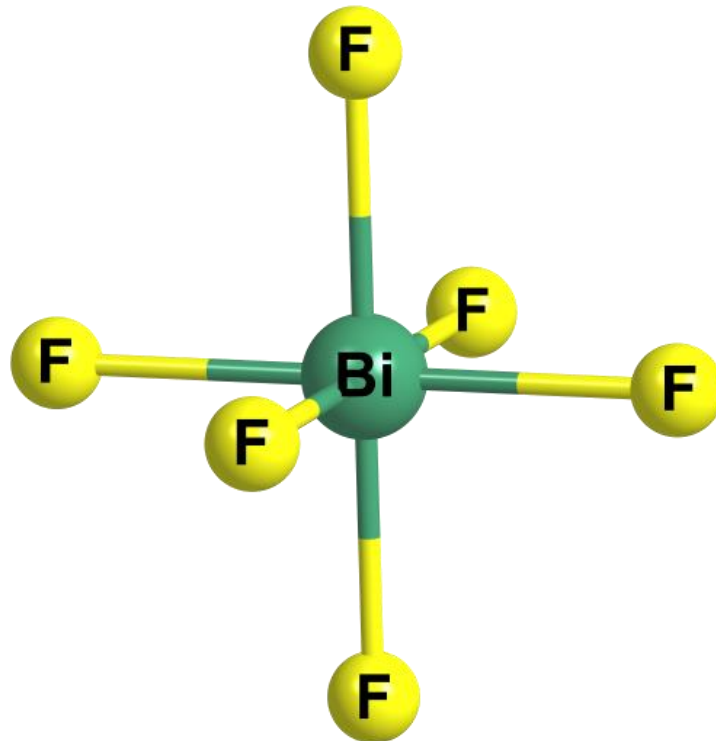
- There are no $\text{Bi}(\text{NO}_3)_3$ molecules in the aqua solution!
- $[\text{Bi}(\text{H}_2\text{O})_n]^{3+}$ but we do not know n !
- Even if we knew n the system is too complicated for an accurate calculation

How accurately the magnetic moment of ^{209}Bi is known?

From the theoretical point of view we need:

- more **symmetrical** molecule
- with **definite** geometry
- **small** number of atoms

Best choice: octahedral hexafluoridobismuthate (V) ion $[\text{BiF}_6]^-$



NMR in $[\text{BiF}_6]^-$

NMR data: [K. Morgan et al J. Magn. Reson. 52, 139 (1983)] is **inconsistent**:
tesla on a 9.1-mm column of $\sim 0.1 \text{ M } (\text{CH}_3)_3\text{N}^+\text{BiF}_6^-$ in acetone). Remeasurement of a saturated solution of $\text{Bi}(\text{NO}_3)_3$ in concentrated HNO_3 gave a chemical shift value of -24 ppm with respect to BiF_6^- . The exact resonance frequency of ^{209}Bi in the aforementioned hexafluorobismuthate sample was determined to be $16,017,649 \pm 10$ Hz at 25°C in a field in which the protons in TMS resonate at exactly 100 MHz.

$$\nu_1 = \nu(^{209}\text{BiF}_6^-)$$

$$\nu_2 = \nu(^{209}\text{Bi}(\text{NO}_3)_3 \text{ solution})$$

$$\frac{\nu_2 - \nu_1}{\nu_1} = -24 \text{ ppm}$$

but also $\nu_1/\nu(^1\text{H})=0.16017649(10)$; from previous measurement [Flynn & Seymour, Proc. Phys. Soc. LXXIII, 6, 3Q] we **probably (?)** know $\nu_2/\nu(^1\text{H})$

$$\Rightarrow \frac{\nu_2 - \nu_1}{\nu_1} = +3200 \text{ ppm}$$

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One can this resolve discrepancy if we assume misprint:

$$\nu_1/\nu(^1\text{H})=0.160\mathbf{17}65(1) \quad \rightarrow \quad \nu_1/\nu(^1\text{H})=0.160\mathbf{71}65(1) \quad ???$$

How accurately the magnetic moment of ^{209}Bi is known?

New experiment has been performed in

L.V. Skripnikov, S. Schmidt, J. Ullmann, C. Geppert, F. Kraus, B. Kresse, W. Nortershauser, A.F. Privalov, B. Scheibe, V.M. Shabaev, M. Vogel, A.V. Volotka, Phys. Rev. Lett., **120**, 093001 (2018)

$$\text{Old: } \nu(^{209}\text{BiF}_6^-)/\nu(^1\text{H}) = 0.160 \mathbf{17} 65(1)$$

$$\text{New: } \nu(^{209}\text{BiF}_6^-)/\nu(^1\text{H}) = 0.160 \mathbf{71} 67(2)$$

Concentration, temperature dependences were accurately analyzed


NMR interpretation

Experiment

$$\mu = \mu_{\text{uncorrected}} / (1 - \sigma)$$

↑
Theory

$$H_{\text{NMR}} = -\mathbf{B}(1 - \sigma)\mu$$


$$\sigma_{a,b} = \left. \frac{\partial^2 E}{\partial \mu_a \partial B_b} \right|_0$$

NMR interpretation

$$\sigma = \left. \frac{\partial^2 E}{\partial \mu \partial B} \right|_0$$

$$H_{Hyp} = \boldsymbol{\mu} \cdot \frac{[\mathbf{r} \times \boldsymbol{\alpha}]}{r^3}$$

$$H_Z = \mathbf{B} \cdot \mu_0 [\mathbf{r} \times \boldsymbol{\alpha}]$$

One-particle approximation (or uncoupled HF approximation):

$$\sigma = 1/3 \sum_{n \neq 0} \frac{\langle 0 | [\mathbf{r} \times \boldsymbol{\alpha}] | n \rangle \langle n | \frac{\mathbf{r} \times \boldsymbol{\alpha}}{r^3} | 0 \rangle}{E_0 - E_n} + c.c.$$

n runs over both **positive** and **negative** energy states

↑
“paramagnetic”
contribution

↑
“diamagnetic”
contribution

NMR in $^{209}\text{BiF}_6^-$: DFT study

Shielding constant, ppm:

Method	Diamagnetic	Paramagnetic	Total
DHF	8618	5768	14386
DFT: LDA	8622	2433	11055
DFT: PBE	8622	2766	11387
DFT: PBE0	8621	3726	12347

DFT uncertainty ~ 1300 ppm

the coupled cluster theory

$$\Psi_{cc} = e^{\hat{T}} \Phi_0$$
$$e^{\hat{T}} = 1 + \hat{T} + \frac{\hat{T}^2}{2!} + \frac{\hat{T}^3}{3!} + \dots$$

$$\hat{T} = \hat{T}_1 + \hat{T}_2 \rightarrow \mathbf{CCSD}$$

$$\hat{T} = \hat{T}_1 + \hat{T}_2 + \hat{T}_3 \rightarrow \mathbf{CCSDT}$$

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

$$\hat{T}_2 = \frac{1}{2} \sum_{ij} \hat{t}_{ij} = \frac{1}{4} \sum_{ijab} t_{ij}^{ab} a_a^+ a_b^+ a_j a_i$$

$$\Psi_{ci} = (1 + \hat{T}) \Phi_0$$

CCSD(T) > PT4

CCSDT(Q) > PT6

- more efficient than CI: t(CISD) ~ t(CCSD)
- size extensive

Present calculation: NMR in $^{209}\text{BiF}_6^-$

We have adapted the coupled cluster theory to calculate shielding constants

BiF_6^- molecule: 138 electrons

Correlation: CCSD(T) > PT4

Shielding constant, ppm:

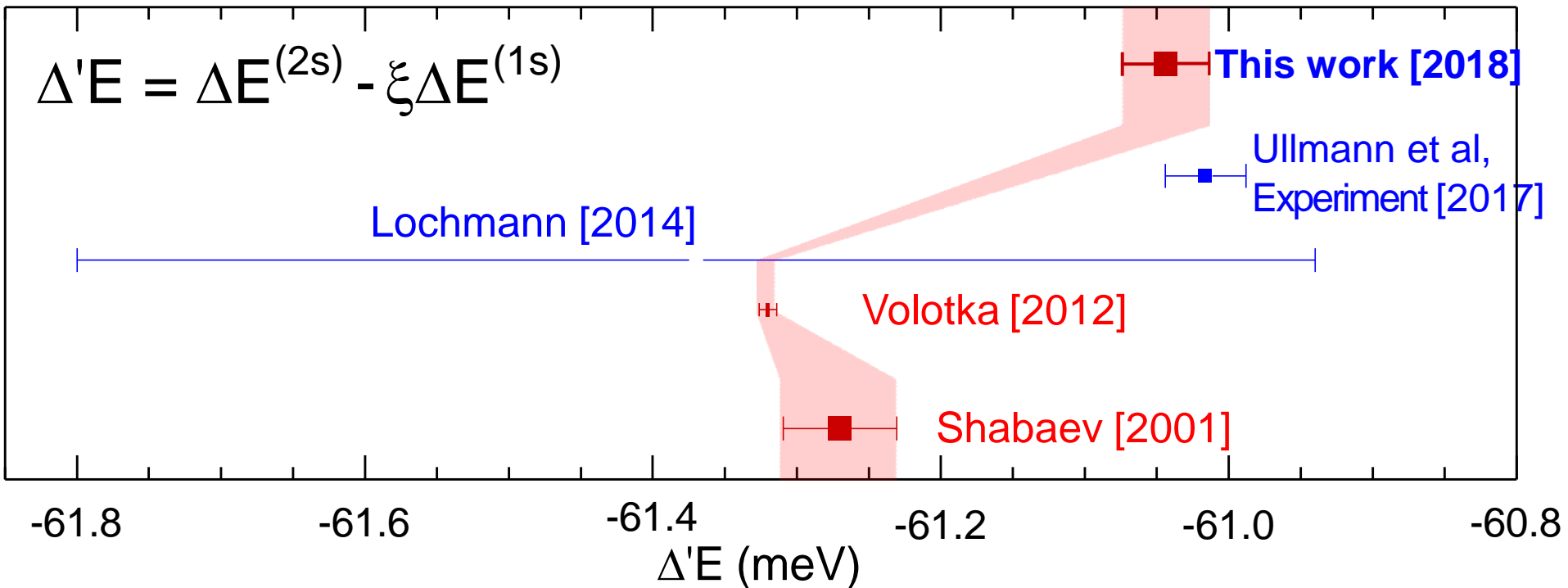
Method	Diamag.	Paramag.	Total
DFT (PBE0) _{DZ}	8621	3726	12347
DFT (PBE0) _{QZ}	8628	3763	12391
138e-CCSD		4318	
138e-CCSD(T) – 138e-CCSD		-117	
Gaunt			-37
Final			12792

Molecular environment contribution > 20%!

Results: “Hyperffine puzzle” solved

$$\mu(\text{old}) = 4.1106(2) \mu_N$$

$$\mu(\text{new}) = 4.092(2) \mu_N$$



L.V. Skripnikov, S. Schmidt, J. Ullmann, C. Geppert, F. Kraus, B. Kresse,
W. Nortershauser, A.F. Privalov, B. Scheibe, V.M. Shabaev, M. Vogel, A.V. Volotka,
Phys. Rev. Lett., **120**, 093001 (2018)

Results: H-like and Li-like ^{209}Bi

	Theory		Experiment
	$\mu(\text{old})$	$\mu(\text{new})$	
$\Delta E^{(1s)}$	5112 (-5/+20)	5089 (-5/+20)	5085.03 (2)(9)
$\Delta E^{(2s)}$	801.9 (-9/+34)	798.3 (-9/+34)	797.645 (4)(14)

(*) Bohr-Weisskopf effect: the most elaborated calculation by Sen'kov and Dmitriev [Nucl. Phys. A 706, 351 (2002)]

L.V. Skripnikov, S. Schmidt, J. Ullmann, C. Geppert, F. Kraus, B. Kresse, W. Nortershauser, A.F. Privalov, B. Scheibe, V.M. Shabaev, M. Vogel, A.V. Volotka, Phys. Rev. Lett., **120**, 093001 (2018)

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1. QED fails
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Magnetic moment of ^{208}Bi

If we have nuclear magnetic moment for stable isotope as well as hyperfine structure constants for 2 electronic states for both stable and short-lived isotopes **we can determine the nuclear magnetic moment of the short-lived isotope**

Note the ratio of HFS constants A_1 and A_2 :

$$\frac{A_1}{A_2} = \frac{\mu_1/I_1}{\mu_2/I_2} (1 + {}^1\Delta^2)$$

$$\frac{A_1[a] A_2[b]}{A_2[a] A_1[b]} = \frac{1 + {}^1\Delta^2[a]}{1 + {}^1\Delta^2[b]} = 1 + {}^1\delta^2[a, b]$$

$${}^1\Delta^2[b] = \frac{{}^1\delta^2[a, b]}{{}^1r^2[a, b] - {}^1\delta^2[a, b] - 1}$$

$${}^1r^2[a, b] = \frac{{}^1\Delta^2[a]}{{}^1\Delta^2[b]}$$

Magnetic moment of ^{208}Bi

[S. Schmidt, et al, Phys. Lett. B 779(10), 324-330 (2018)]:

Within the multireference CCSD theory we have calculated

$${}^{208}r^{209}[{}^4S_{3/2}, {}^4P_{1/2}] = 1.54(14) \Rightarrow {}^1\Delta^2[{}^4P_{1/2}] = 0.0049(21),$$

Using $\mu(\text{new } {}^{209}\text{Bi})$ and ${}^{208}r^{209}$ and experimental data for HFS constants

$$\mu({}^{208}\text{Bi}) = 4.570(10) \mu_N$$

$$\Delta'E({}^{208}\text{Bi}) = -67.491(5)(148)$$

Magnetic moment of ^{207}Pb

for $\text{Pb}(\text{NO}_3)_2$ in water: $\mu = 0.592\,583\,(9)\,\mu_{\text{N}}$

To obtain this results the shielding constant for the isolated Pb^{2+} ion has been used...

NEW experiment and theory: $[\text{PbF}_6]^{2-}$ in acetonitrile

V. Fella, L.V. Skripnikov, W. Nörtershäuser, A.F. Privalov, M. Buchner, L. Deubner, F. Kraus, V.M. Shabaev, M. Vogel
Phys. Rev. Res. 2, 013368 (2020)

We used the 4c-CCSD(T) & 4c-DFT method to calculate σ .

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We used the 4c-CCSD(T) & 4c-DFT method to calculate σ .

Result: $\mu(\text{new } ^{207}\text{Pb}) = 0.591\,02(18)\,\mu_{\text{N}}$

BW effect in molecules: one of motivations

Experiments to search for the electron EDM, and other T,P-violating effects

Sensitivity:
$$\delta d_e = \frac{1}{2E_{eff}\tau\sqrt{N}}$$

Next generation of eEDM experiments will be probably performed on laser-coolable molecules such as RaF, YbOH, etc with big τ

The diagram shows the equation for electron EDM:
$$\text{electron EDM} = \frac{\Delta E}{\mathcal{E}_{eff}}$$
 The term ΔE is circled in red and labeled "Experiment". The term \mathcal{E}_{eff} is circled in blue and labeled "Theory". Arrows point from the labels to their respective terms in the equation.

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

BW effect in molecules

$$h^{\text{HFS}} = \sum_i \frac{\boldsymbol{\mu} \cdot [\mathbf{r}_i \times \boldsymbol{\alpha}_i]}{r_i^3} F(r_i) = (\boldsymbol{\mu} \mathbf{T}),$$

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

$$\mathbf{T}^{\text{BW}} = \sum_i \frac{[\mathbf{r}_i \times \boldsymbol{\alpha}_i]}{r_i^3} (1 - F(r_i)).$$

$$A_{\parallel}^{\text{BW}}(K) = \frac{\mu_K}{I\Omega} \langle \Psi_{\Omega} | T_z^{\text{BW}}(K) | \Psi_{\Omega} \rangle.$$

BW effect in molecules

$$\hbar c \left(\frac{dg_{n\kappa}}{dr} + \frac{1 + \kappa}{r} g_{n\kappa} \right) - (E_{n\kappa} + mc^2 - V) f_{n\kappa} = 0,$$

$$\hbar c \left(\frac{df_{n\kappa}}{dr} + \frac{1 - \kappa}{r} f_{n\kappa} \right) + (E_{n\kappa} - mc^2 - V) g_{n\kappa} = 0,$$

$$A^{\text{BW}} \propto \int_0^\infty gf(1 - F(r))dr \approx \int_0^{R_{\text{nuc}}} gf(1 - F(r))dr,$$

$$\begin{aligned} & \int 2p_{1/2,1/2}^\dagger T_z^{\text{BW}} 2p_{1/2,1/2} d\mathbf{r} \\ & \approx \beta \int 1s_{1/2,1/2}^\dagger T_z^{\text{BW}} 1s_{1/2,1/2} d\mathbf{r}, \end{aligned}$$

BW effect in molecules

$$\rho(\mathbf{r}|\mathbf{r}') = \sum_{p,q} \rho_{p,q} \varphi_p(\mathbf{r}) \varphi_q^\dagger(\mathbf{r}'),$$

$$\langle X \rangle = \sum_{p,q} \rho_{p,q} \int \varphi_q^\dagger X \varphi_p d\mathbf{r}.$$

$$\varphi_p(\mathbf{r}) \approx \sum_{nljm} C_{nljm}^p \eta_{nljm}(\mathbf{r}), \quad |\mathbf{r}| \leq R_c,$$

$$\eta_{nljm}(\mathbf{r}) \approx k_{nljm} \eta_{ljm}(\mathbf{r}), \quad |\mathbf{r}| \leq R_c,$$

$$\langle X \rangle \approx \sum_{ljm;l'j'm'} \mathcal{P}_{ljm,l'j'm'} \int_{|\mathbf{r}| < R_c} \eta_{l'j'm'}^\dagger X \eta_{ljm} d\mathbf{r},$$

where

$$\mathcal{P}_{ljm,l'j'm'} = \sum_{p,q,n,n'} \rho_{p,q} C_{nljm}^p k_{nljm} C_{n'l'j'm'}^{q*} k_{n'l'j'm'}^*.$$

BW effect in molecules

$$\int \eta_{ljm}^\dagger T_z^{\text{BW}} \eta_{ljm} d\mathbf{r} = - \int \eta_{lj-m}^\dagger T_z^{\text{BW}} \eta_{lj-m} d\mathbf{r}.$$

$$\mathcal{P}_s = \mathcal{P}_{1s_{1/2,1/2}, 1s_{1/2,1/2}} - \mathcal{P}_{1s_{1/2,-1/2}, 1s_{1/2,-1/2}},$$

$$\mathcal{P}_p = \mathcal{P}_{2p_{1/2,1/2}, 2p_{1/2,1/2}} - \mathcal{P}_{2p_{1/2,-1/2}, 2p_{1/2,-1/2}},$$

$$B_s = \int_{|\mathbf{r}| \leq R_{\text{nuc}}} \eta_{1s_{1/2,1/2}}^\dagger T_z^{\text{BW}} \eta_{1s_{1/2,1/2}} d\mathbf{r},$$

$$B_p = \int_{|\mathbf{r}| \leq R_{\text{nuc}}} \eta_{2p_{1/2,1/2}}^\dagger T_z^{\text{BW}} \eta_{2p_{1/2,1/2}} d\mathbf{r},$$

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

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

BW effect in Ra^+

TABLE I. Hyperfine structure constant (in MHz) for the ground and excited states of the $^{225}\text{Ra}^+$ cation calculated in the point magnetic dipole approximation.

Method	$7s\ ^2S_{1/2}$	$7p\ ^2P_{1/2}$	$7p\ ^2P_{3/2}$
DHF	−21976	−3657	−276
CCSD	−29160	−5484	−459
CCSD(T)	−28896	−5498	−463
Correlation correction	−117	−31	0
Basis set correction	2	3	0
Total, electronic ($A^{(0)}$)	−29012	−5526	−463

TABLE II. BW contributions A^{BW} , $A^{\text{BW},s}$, and $A^{\text{BW},p}$ and the final values of the hyperfine structure constants (in MHz) for the ground and excited states of the $^{225}\text{Ra}^+$ 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.

	$7s\ ^2S_{1/2}$	$7p\ ^2P_{1/2}$	$7p\ ^2P_{3/2}$
$-A^{\text{BW},s}$	1214	−5	3
$-A^{\text{BW},p}$	1	80	0
$-A^{\text{BW}}$	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)

^aExtracted from Ref. 3: Breit: −93 MHz; QED: 159(23) MHz; Electron+Breit: −29113 MHz.

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

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

$$B_s = \int_{|\mathbf{r}| \leq R_{\text{nuc}}} \eta_{1s_{1/2,1/2}}^{\dagger} T_z^{\text{BW}} \eta_{1s_{1/2,1/2}} d\mathbf{r},$$

BW effect in 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 ($A_{\parallel/\perp}^{(0)}$)	-17780	-17123	-2896	-2230
$-A_{\parallel}^{\text{BW},s}$	723		9	
$-A_{\parallel}^{\text{BW},p}$	7		34	
$-A_{\parallel/\perp}^{\text{BW}}$	730	720 ^a	44	26 ^a
Final	-17049	-16403	-2852	-2204

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

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

$$B_s = \int_{|\mathbf{r}| \leq R_{\text{nuc}}} \eta_{1s_{1/2,1/2}}^{\dagger} T_z^{\text{BW}} \eta_{1s_{1/2,1/2}} d\mathbf{r},$$

Thank you!