Resolving the doublet-quartet separation in neutral boron

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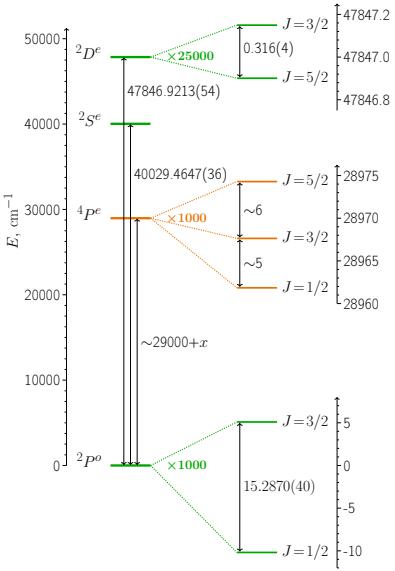
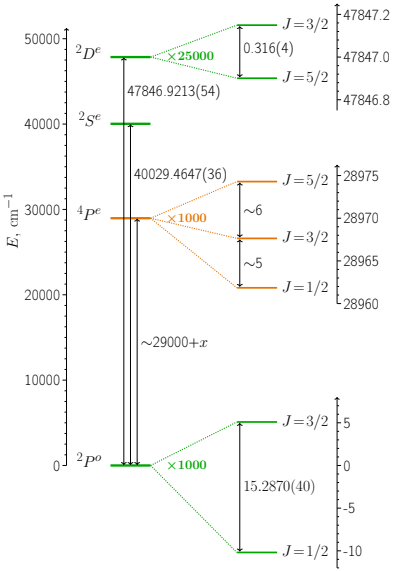
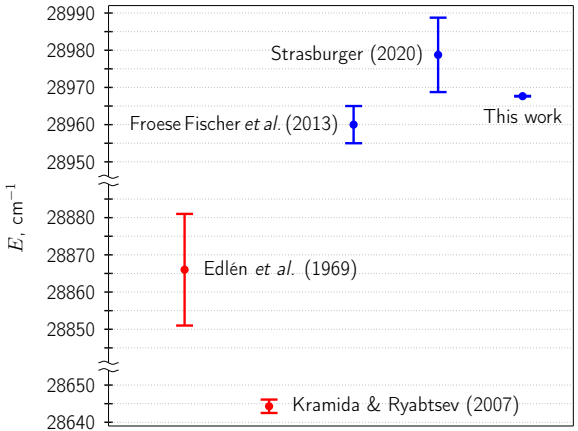
- Boron ($Z=5$): lightest atom with both **doublet** and **quartet** spin states
- The $2\,^4P^e$ is the **only** quartet state below the ionization threshold
- The $^4P^e$ state has **never been directly observed** experimentally
- Its position relative to the ground state listed with an unknown constant $\boldsymbol{x}$ in spectral databases since the 1940s
- Goal: resolve the long-standing puzzle with sub-0.1 cm^{-1} accuracy
- Advance theoretical approaches for precision spectroscopy of light atoms



- Fine structure of $^4P^e$ also largely unknown – only approximate splittings ($\sim$5–6 cm^{-1}) are available
- Previous attempts to determine the doublet–quartet separation:
  - **Experimental extrapolation** from isoelectronic sequence:
    Edlén (1969): $28\,866(15)$ cm^{-1}
    NIST ASD: $28\,644.3(1.8)$ cm^{-1}
    – *mutually inconsistent!*
  - **Ab initio calculations**:
    Froese Fischer (2013): $28\,960.0(5.0)$ cm^{-1}
    Strasburger (2020): $28\,978.8(10.0)$ cm^{-1}





- **Blue**: *ab initio* theoretical calculations
- **Red**: experimentally extrapolated values from the isoelectronic sequence
- Experimental extrapolations are **mutually inconsistent** and disagree with theory
- The B doublet–quartet gap does **not follow** the smooth isoelectronic trends
- Our result resolves the long-standing ambiguity with uncertainty $\sim$0.07 cm^{-1}

- Separate center-of-mass motion exactly from the lab-frame Hamiltonian
- All-particle approach: no Born–Oppenheimer approximation
- Spatial basis functions – Explicitly Correlated Gaussians (ECG):

$$\phi_k(\boldsymbol{r}) = \theta_k(\boldsymbol{r})\, \exp\big[- \boldsymbol{r}'(A_k \otimes \mathbf{I})\, \boldsymbol{r}\big]$$

A_k: positive definite matrix of optimized nonlinear variational parameters

θ_k: angular prefactor encoding L, M, parity

Basis sizes: up to 17 500 ECGs per state

$$\boldsymbol{r}'(A_k \otimes \mathbf{I})\boldsymbol{r} = \sum_{i=1}^{n} \beta_i^k\, r_i^2 + \sum_{i=1}^{n} \sum_{j>i}^{n} \gamma_{ij}^k\, r_{ij}^2$$

Angular prefactors:

State	$\theta_k(\boldsymbol{r})$
S^e	1
P^o	z_{i_k}
P^e	$x_{i_k} y_{j_k} - y_{i_k} x_{j_k}$
D^e	$x_{i_k} x_{j_k} + y_{i_k} y_{j_k} - 2 z_{i_k} z_{j_k}$

Total energy as a series in the fine-structure constant α:

$$E_{\mathrm{TOT}} = \underbrace{E^{(0)}}_{\mathrm{NR}} + \alpha^2 \underbrace{E^{(2)}}_{\mathrm{Rel.}} + \alpha^3 \underbrace{E^{(3)}}_{\mathrm{QED}} + \alpha^4 \underbrace{E^{(4)}}_{\mathrm{HQED}} + \cdots$$

- $E^{(0)}$: nonrelativistic energy from nearly exact variational ECG calculation
- $\alpha^2 E^{(2)}$: Expected value of the Dirac–Breit Hamiltonian
  $\mathcal{H}^{(2)}_{\mathrm{REL}} = \underbrace{\mathcal{H}_{\mathrm{MV}} + \mathcal{H}_{\mathrm{D}} + \mathcal{H}_{\mathrm{OO}} + \mathcal{H}_{\mathrm{SSF}}}_{\text{scalar relativistic}} + \underbrace{\mathcal{H}_{\mathrm{SO}} + \mathcal{H}_{\mathrm{SSNC}}}_{\text{fine structure}}$
- $\alpha^3 E^{(3)}$: leading QED (Araki–Sucher, vacuum polarization, self-energy incl. Bethe logarithm)
- $\alpha^4 E^{(4)}$: higher-order QED corrections (estimate)

First time the α^3 Ry and α^4 Ry contributions are included for the doublet–quartet separation in boron

$$\mathcal{H}^{(2)}_{\rm MV} = -\frac{1}{8}\left[\frac{1}{m_0^3}\left(\sum_{i=1}^{n}\boldsymbol{p}_i\right)^4 + \sum_{i=1}^{n}\frac{1}{m_i^3}\boldsymbol{p}_i^4\right], \quad \mathcal{H}^{(2)}_{\rm D} = -\frac{\pi}{2}\left[\sum_{i=1}^{n}\frac{q_0 q_i}{m_i^2}\delta\left(\boldsymbol{r}_i\right) + \sum_{i=1}^{n}\sum_{j\neq i}^{n}\frac{q_i q_j}{m_i^2}\delta\left(\boldsymbol{r}_{ij}\right)\right],$$

$$\mathcal{H}^{(2)}_{\rm OO} = \frac{1}{2}\sum_{i=1}^{n}\sum_{j\neq i}^{n}\frac{q_0 q_j}{m_0 m_j}\left[\frac{1}{r_j}\boldsymbol{p}_i'\boldsymbol{p}_j + \frac{1}{r_j^3}\boldsymbol{r}_j'(\boldsymbol{r}_j'\boldsymbol{p}_i)\boldsymbol{p}_j\right] - \frac{1}{2}\sum_{i=1}^{n}\sum_{j>i}^{n}\frac{q_i q_j}{m_i m_j}\left[\frac{1}{r_{ij}}\boldsymbol{p}_i'\boldsymbol{p}_j + \frac{1}{r_{ij}^3}\boldsymbol{r}_{ij}'(\boldsymbol{r}_{ij}'\boldsymbol{p}_i)\boldsymbol{p}_j\right],$$

$$\mathcal{H}^{(2)}_{\rm SSF} = -\frac{8\pi}{3}\sum_{i=1}^{n}\sum_{j>i}^{n}\frac{q_i q_j}{m_i m_j}\left(\boldsymbol{s}_i'\boldsymbol{s}_j\right)\delta(\boldsymbol{r}_{ij}),$$

$$\mathcal{H}^{(2)}_{\rm SSNC} = \sum_{i=1}^{n}\sum_{j>i}^{n}(1+a_{\rm e})^2\frac{q_i q_j}{m_i m_j}\left[\frac{(\boldsymbol{s}_i'\boldsymbol{s}_j)}{r_{ij}^3} - 3\frac{(\boldsymbol{s}_i'\boldsymbol{r}_{ij})(\boldsymbol{s}_j'\boldsymbol{r}_{ij})}{r_{ij}^5}\right],$$

$$\boxed{\mathcal{H}^{(2)}_{\rm R} = \mathcal{H}^{(2)}_{\rm SR} + \mathcal{H}^{(2)}_{\rm FS}},$$

$$\mathcal{H}^{(3)}_{\rm QED} = \sum_{i=1}^{n}\sum_{j>i}^{n}\left[\left(\frac{164}{15} + \frac{14}{3}\ln\alpha\right)\delta\left(\boldsymbol{r}_{ij}\right) - \frac{7}{6\pi}\mathcal{P}\left(\frac{1}{r_{ij}^3}\right)\right] + \sum_{i=1}^{n}\left(\frac{19}{30} - 2\ln\alpha - \ln k_0\right)\frac{4q_0}{3}\delta\left(\boldsymbol{r}_i\right),$$

- The leading QED correction ($\alpha^3\,\mathrm{Ry}$) contains the **Bethe logarithm** $\ln k_0$ – notoriously difficult to compute for many-electron atoms
- To our knowledge, $\ln k_0$ has never been directly calculated for any boron state
- Our approach: estimate $\ln(k_0/q_0^2)$ from calculated values for lighter atoms (He, Li, Be) and extrapolate the observed trends

Atom	Conf.(State)	Ref.	$\ln(k_0/q_0^2)$
$^{\infty}$He	$1s^2\,(1\,^1S^e)$	Korobov 2019	2.983865862
$^{\infty}$Li	$1s^22s\,(2\,^2S^e)$	Wang 2017	2.980943(1)
	$1s^22p\,(2\,^2P^o)$	Wang 2017	2.982568(3)
$^{\infty}$Be	$1s^22s^2\,(2\,^1S^e)$	Puchalski 2014	2.97787(2)
	$1s^22s3s\,(3\,^1S^e)$	Puchalski 2014	2.97890(5)
	$1s^22s2p\,(2\,^1P^e)$	Puchalski 2014	2.97973(8)
$^{\infty}$B	$1s^22s^22p\,(2\,^2P^o)$	estimated	2.97666(77)
	$1s^22s2p^2\,(2\,^4P^e, 2\,^2D^e)$	estimated	2.97852(90)
	$1s^22s^23s\,(3\,^2S^e)$	estimated	2.97583(77)

J-dependent energy including terms up to fourth order in α:

$$E_{nLSJ} = \langle nLSJ|\mathcal{H}^{(2)}_{\rm FS}|nLSJ\rangle + \sum_{n'L'S'\neq nLS} \frac{\left|\langle n'L'S'J|\mathcal{H}^{(2)}_{\rm FS}|nLSJ\rangle\right|^2}{E_{nLS} - E_{n'L'S'}}$$
$$+ 2\sum_{n'\neq n} \frac{\langle nLSJ|\mathcal{H}^{(2)}_{\rm SR}|n'LSJ\rangle\langle n'LSJ|\mathcal{H}^{(2)}_{\rm FS}|nLSJ\rangle}{E_{nLS} - E_{n'LS}} + \langle nLSJ|\mathcal{H}^{(4)}_{\rm FS}|nLSJ\rangle$$

1st term: direct spin–orbit + dipolar spin–spin (α^2 Ry + AMM correction at α^3 Ry)

2nd term: state-mixing correction (off-diagonal $\mathcal{H}^{(2)}_{\rm FS}$ between states of different L, S)

3rd term: cross term between scalar relativistic and fine-structure operators

4th term: higher-order FS contribution $\mathcal{O}(\alpha^4\,\text{Ry})$ – estimated

State	Isotope	$\mathcal{K}$	E_{NR} (a.u.)
$2\,^2P^o$	^{11}B	17 500	$-24.652\,626\,377$
	^{11}B	∞	$-24.652\,626\,459(82)$
	Strasburger (2020)	10 304	$-24.652\,625\,854$
$2\,^4P^e$	^{11}B	16 000	$-24.520\,827\,345$
	^{11}B	∞	$-24.520\,827\,372(26)$
	Strasburger (2020)	4 672	$-24.520\,826\,909$
$3\,^2S^e$	^{11}B	17 500	$-24.470\,143\,779$
	^{11}B	∞	$-24.470\,143\,805(27)$
$2\,^2D^e$	^{11}B	16 000	$-24.434\,766\,98$
	^{11}B	∞	$-24.434\,767\,28(29)$

Results converged to a few tens of nanohartree – well beyond all previous calculations.

Doublet–quartet separation in the boron atom (centroid values) in cm^{-1}

State	Contrib.	$^{\infty}$B	^{11}B	^{10}B	N.M.
$2\,^4P^e$	α^0	28 932.633(19)	28 926.556(19)	28 925.951(19)	28 926.437(19)
	α^2	44.4573(49)	44.4566(49)	44.4565(49)	44.4566(49)
	α^3	−3.162(48)	−3.162(48)	−3.162(48)	−3.162(48)
	α^4	−0.195(49)	−0.195(49)	−0.195(49)	−0.195(49)
	E_{FNS}	—	−0.005 60(15)	−0.006 12(8)	−0.005 70(13)
	Total	28 973.733(71)	28 967.650(71)	28 967.045(71)	28 967.531(71)
Strasburger	$\alpha^0+\alpha^2$	28 984.8(100)	28 978.8(100)	28 978.2(100)	28 978.6(100)
Froese Fischer	$\alpha^0+\alpha^2$	28 966.1(50)	28 960.0(50)	28 959.4(50)	28 959.9(50)
Edlén *et al.*	—	—	—	—	28 866(15)*
NIST ASD	—	—	—	—	28 644.3(18)

Two orders of magnitude improvement in accuracy over previous results!

$2\,^2P^o$–$2\,^2D^e$ separation in the boron atom (centroid values) in cm^{-1}

State	Contrib.	$^{\infty}$B	^{11}B	^{10}B	N.M.
$2\,^2D^e$	α^0	47 820.331(67)	47 814.564(67)	47 813.990(67)	47 814.451(67)
	α^2	35.0287(70)	35.0370(71)	35.0379(71)	35.0372(71)
	α^3	−2.525(48)	−2.525(48)	−2.525(48)	−2.525(48)
	α^4	−0.152(38)	−0.152(38)	−0.152(38)	−0.152(38)
	E_{FNS}	—	−0.004 46(12)	−0.004 87(6)	−0.004 54(11)
	Total	47 852.682(91)	47 846.919(91)	47 846.345(91)	47 846.806(91)
Strasburger	—	47 861.4(100)	47 855.6(100)	47 855.0(100)	47 855.5(100)
NIST ASD	—		47 846.858(5)	47 846.289(5)	47 846.744(4)

For ^{11}B states with known experimental values, our results show excellent agreement:

State	$3\,^2S^e$	$2\,^2D^e$
This work	$40\,029.474(55)$	$47\,846.919(91)$
NIST ASD	$40\,029.4647(36)$	$47\,846.9213(54)$

- Deviations from experiment: < 0.01 cm^{-1} – several times better than our estimated uncertainties.
- This validates:
  - The ECG wave function quality
  - Our Bethe logarithm estimation procedure
  - The overall perturbative approach up to α^4
- Suggests our uncertainty of $\sim$0.07 cm^{-1} for the $^4P^e$ state is **conservative**; true accuracy is likely $\sim$0.01 cm^{-1}

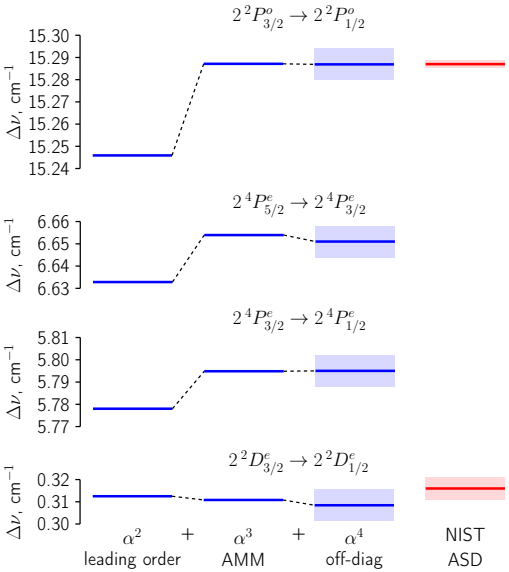
Transition	Contrib.	^{11}B	^{10}B	N.M.
$2\,^2P^o_{3/2} \to 2\,^2P^o_{1/2}$	α^2	15.246 006 7(90)	15.245 911 0(94)	15.245 987 9(91)
	α^3	0.041 139 981(12)	0.041 139 912(12)	0.041 139 968(12)
	α^4 mixing	−0.001 211 7(83)	−0.001 211 7(83)	−0.001 211 7(83)
	Total	15.2859(6)(70)	15.2858(6)(70)	15.2859(6)(70)
NIST ASD		15.2870(18)	15.287(4)	15.287(3)
ECG [2]	$\alpha^2 + \alpha^3 + \alpha^4$	15.288(2)	—	—
MCHF [1]	α^2	—	—	15.39
$2\,^2D^e_{3/2} \to 2\,^2D^e_{5/2}$	α^2	0.312 506(29)	0.312 522(28)	0.312 510(29)
	α^3	−0.001 679 835(79)	−0.001 679 814(78)	−0.001 679 831(78)
	α^4 mixing	−0.002 375 89(75)	−0.002 375 97(75)	−0.002 375 91(75)
	Total	0.3085(7)(70)	0.3085(7)(70)	0.3083(7)(70)
MCHF [1]		—	—	0.27
NIST ASD		0.316(5)	0.316(5)	0.316(4)

[1] C. Froese Fischer and G. Tachiev, ADNDT 87, 1 (2004)

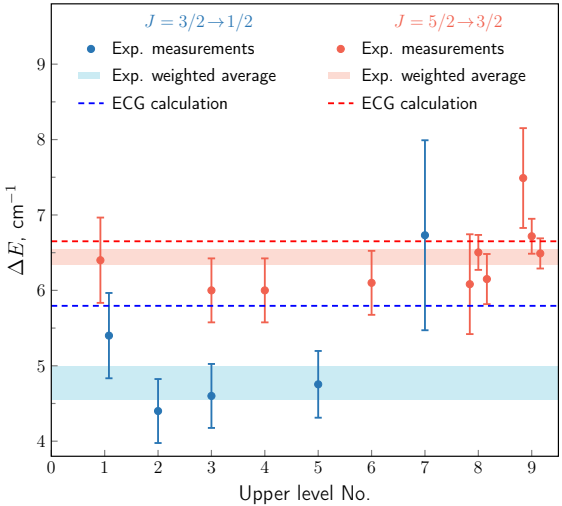
[2] M. Puchalski, J. Komasa, K. Pachucki, PRA 92, 062501 (2015)

Transition	Contrib.	^{11}B	^{10}B	N.M.
$2\,^4P^e_{3/2} \to 2\,^4P^e_{1/2}$	α^2	5.778 012 62(84)	5.777 959 42(89)	5.778 002 17(85)
	α^3	0.016 832 485 7(29)	0.016 832 406 3(34)	0.016 832 470 1(30)
	α^4 mixing	0.000 175 906 9(82)	0.000 175 901 4(82)	0.000 175 905 8(82)
	Total	5.7950(2)(70)	5.7950(2)(70)	5.7950(2)(70)
MCHF [1]	α^2		—	5.82
NIST ASD		—	—	4.64(21)
New eval.*		—	—	4.78(22)
$2\,^4P^e_{5/2} \to 2\,^4P^e_{3/2}$	α^2	6.632 825 9(16)	6.632 763 9(17)	6.632 813 7(16)
	α^3	0.021 098 700 8(26)	0.021 098 629 2(24)	0.021 098 686 7(25)
	α^4 mixing	−0.002 911 844 9(65)	−0.002 911 810 7(66)	−0.002 911 838 2(65)
	Total	6.6510(3)(70)	6.6510(3)(70)	6.6510(3)(70)
MCHF [1]		—	—	6.70
NIST ASD		—	—	6.33(13)
New eval.*		—	—	6.44(10)
MCHF [1]		—	—	0.27
NIST ASD		0.316(5)	0.316(5)	0.316(4)

[1] C. Froese Fischer and G. Tachiev, ADNDT 87, 1 (2004)



- Our theoretical uncertainty for $^2D^e$ is comparable to the current experimental uncertainty
- For $^4P^e$: experimental uncertainties ($\sim$1.8 cm^{-1}) exceed the plot scale by $\sim$2 orders of magnitude — our predictions serve as a **direct guide** for future spectroscopic searches



Experimental and theoretical fine-structure intervals of the $^4P^e$ term in boron.

Key results:

- Determined the $^2P^o - {}^4P^e$ separation in boron with sub-0.1 cm^{-1} accuracy:

$$E(2\,{}^4P^e) - E(2\,{}^2P^o) = 28\,967.650(71)\ \text{cm}^{-1} \qquad ({}^{11}\text{B})$$

- Resolves a puzzle in the boron spectrum that has persisted since the 1940s
- First accurate fine-structure splittings of the $^4P^e$ manifold
- Achieved through massive ECG expansions (16 000–17 500 basis functions) + relativistic and QED corrections up to α^4

Outlook:

- Our predictions can guide future laser spectroscopy experiments targeting the quartet state
- Direct calculation of the Bethe logarithm for boron is necessary for further improvements

THANK YOU!