Fine Structure Corrections in Optical Emission Spectra of Sodium

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8.13 Experimental Physics I
MIT Department of Physics

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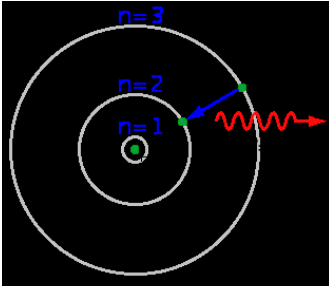
Outline



$$\begin{aligned} E_n &= -hcR_\infty \frac{Z^2}{n^2} \\ &= -\frac{m_e e^4}{2\left(4\pi\epsilon_0\right)^2 \hbar^2} \frac{Z^2}{n^2} \end{aligned}$$

- Energy and electron orbitals are quantized.
- Electron transitions emit photons, causing discrete optical spectra.

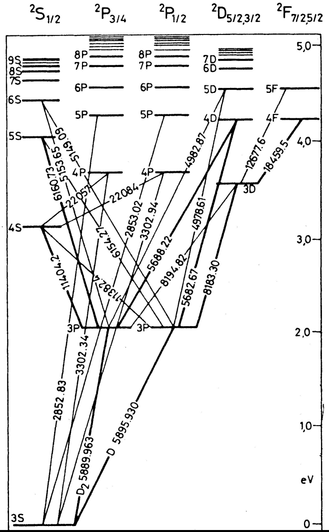
But wait!

- Electrons have angular momentum $L = 0, 1, \ldots, n-1$, $S = 1/2$
- Orbiting proton in electron frame sees a magnetic field **B**

$$H_1 = -\mu \cdot \mathbf{B} \rightarrow \left(\frac{e^2}{8\pi\epsilon_0}\right) \frac{1}{m^2 c^2 r^3} \mathbf{S} \cdot \mathbf{L} \qquad (1)$$

- Now H, L^2, S^2, and $J = L + S$ commute!
- From first-order perturbation, angular momentum terms are no longer degenerate

$$E_{nj} = -\frac{E_n}{n^2}\left[1 + \frac{\alpha^2}{n^2}\left(\frac{n}{j+1/2} - \frac{3}{4}\right)\right] \qquad (2)$$



For states specified by $|nlm\rangle$, transition probability related to

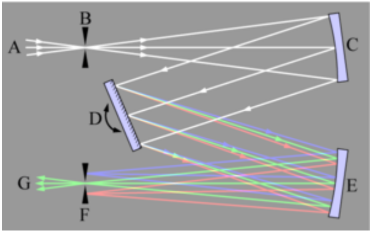
$$\langle n' l' m' | \, \mathbf{r} \, | nlm \rangle .$$

Only non-zero when,

$$\begin{aligned} \Delta l &= \pm 1 \\ \Delta m &= 0, \pm 1 \end{aligned} \qquad (3)$$

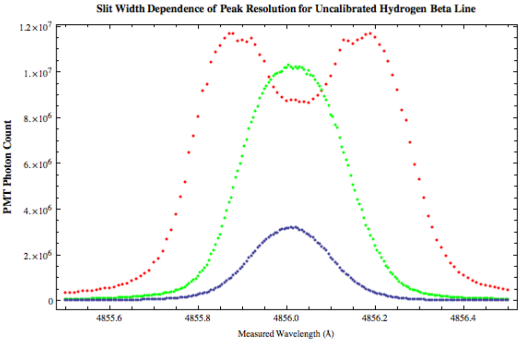
'Fine structure': Energy difference between P states

- Jobin Yvon 1250M Monochromator.
- Sources: Mercury (Hg), Hydrogen (H), Deuterium (D), and Sodium (Na) lamps
- Diffraction grating: 1800gvs/mm and 3600gvs/mm



(A) Emission source
(B) Entrance slit
(C) Collimating mirror
(D) Diffraction grating
(E) Focusing mirror
(F) Exit slit
(G) Photomultiplier Tube (950V)

Relevant parameters: entrance/exit slit width, density of the diffraction grating, and source-entrance slit distance.



Resolution:

$\sigma_{1800} = 0.10 - 0.15\text{Å}$

$\sigma_{3600} = 0.06\text{Å}$

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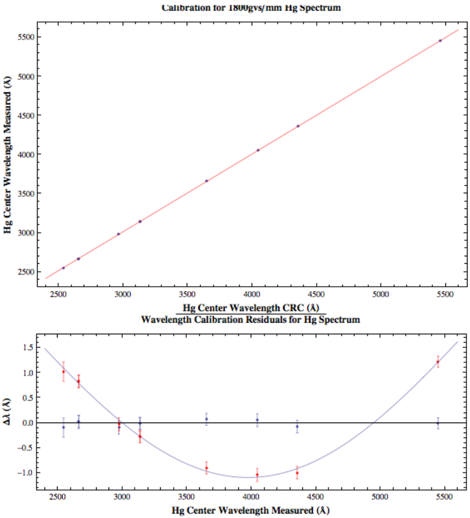
Typical 100ms integration times, 4-10μm slit widths, 0.01Å step size, and 1800gvs/mm diffraction grating.



$$\lambda_{\text{Predicted}} \sim 26.4612 + 0.9930x - 3.0940 \sin(7.4585 + 0.0009x)$$

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Standard error is $\sigma_{\text{Calib.}} \sim 0.06$Å at the 98% confidence level from χ^2 analysis.

Systematic error in our wavelength measurements are given by:

$$\sigma_\lambda^2 = \sigma_{\mathrm{FWHM}}^2 + \sigma_{\mathrm{Calib.}}^2. \tag{4}$$

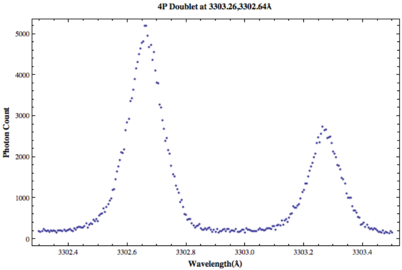
Due to finite slit width, peaks approximated as Gaussians, therefore $\sigma_{\mathrm{FWHM}} = \Delta\lambda_{\mathrm{FWHM}}/\sqrt{2\ln 2}$

$$\sigma_{\mathrm{FWHM}}^2 = \sigma_{\mathrm{slit}}^2 + \sigma_{1800}^2 + \sigma_{\mathrm{line\ width}}^2 + \sigma_{\mathrm{doppler}}^2 \tag{5}$$

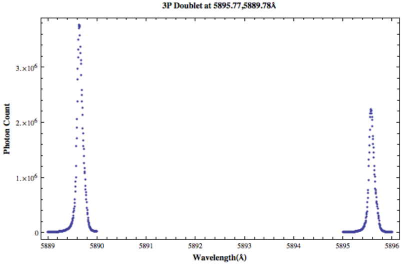
Doppler broadening for temperature $T = 2700\mathrm{K}$ and $A = 11$:

$$\Delta\lambda = \lambda \cdot 10^{-6}\sqrt{\frac{2700}{11}} = \lambda \cdot 1.57 \cdot 10^{-6}$$

For 6160Å, $\Delta\lambda =$0.001Å.



4P Doublet at
$\Delta\bar{\nu} = 5.60 \pm 0.94\mathrm{cm}^{-1}$

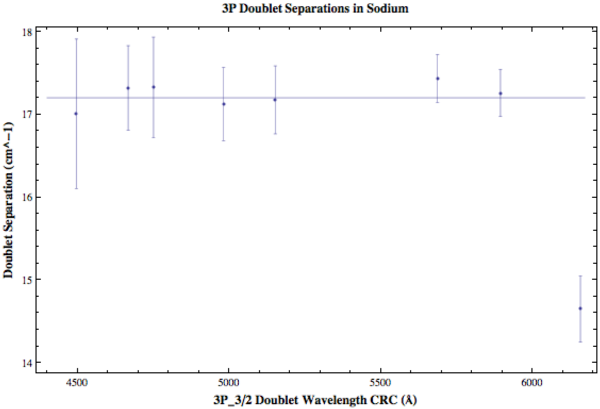


3P Doublet at
$\Delta\bar{\nu} = 17.25 \pm 0.28\mathrm{cm}^{-1}$

$$b = \mathrm{Log}_{\frac{4}{3}}[\Delta\bar{\nu}_{3\mathrm{P}}/\Delta\bar{\nu}_{4\mathrm{P}}] \quad = \quad 3.88\mathrm{Meas.} \quad 3.90\ \mathrm{NIST}$$

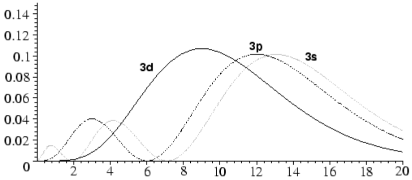
Table: Classification of sodium fine structure (in air).

Transition	CRC $\lambda(\text{Å})$	1800gvs/mm $\lambda(\text{Å})$	1800gvs/mm $\Delta\bar{\nu}(\text{cm}^{-1})$
$5S \rightarrow 3P_{3/2}$	6160.75	6159.65 ± 0.25	14.65 ± 0.40
$\rightarrow 3P_{1/2}$	6154.23	6154.09 ± 0.20	
$3P_{3/2} \rightarrow 3S$	5895.92	5895.77 ± 0.13	17.25 ± 0.28
$3P_{1/2} \rightarrow 3S$	5889.95	5889.78 ± 0.13	
$4D \rightarrow 3P_{3/2}$	5688.21	5688.25 ± 0.12	17.43 ± 0.29
$\rightarrow 3P_{1/2}$	5682.63	5682.61 ± 0.12	
$6S \rightarrow 3P_{3/2}$	5153.40	5153.58 ± 0.16	17.17 ± 0.41
$\rightarrow 3P_{1/2}$	5148.84	5149.03 ± 0.14	
$5D \rightarrow 3P_{3/2}$	4982.81	4983.11 ± 0.15	17.12 ± 0.44
$\rightarrow 3P_{1/2}$	4978.54	4978.86 ± 0.16	
$7S \rightarrow 3P_{3/2}$	4751.82	4752.09 ± 0.22	17.32 ± 0.61
$\rightarrow 3P_{1/2}$	4749.94	4748.18 ± 0.20	
$6D \rightarrow 3P_{3/2}$	4668.56	4668.77 ± 0.16	17.32 ± 0.51
$\rightarrow 3P_{1/2}$	4664.81	4665.00 ± 0.15	
$7D \rightarrow 3P_{3/2}$	4497.66	4497.89 ± 0.27	17.00 ± 0.90
$\rightarrow 3P_{1/2}$	4494.18	4494.45 ± 0.31	
$4P_{3/2} \rightarrow 3S$	3302.98	3303.26 ± 0.14	5.60 ± 0.94
$4P_{1/2} \rightarrow 3S$	3302.37	3302.64 ± 0.14	
$5P_{3/2} \rightarrow 3S$	2853.01	–	–
$5P_{1/2} \rightarrow 3S$	2852.81	–	



$$\sigma^2_{\Delta\bar{\nu}} = \frac{\sigma^2_{\lambda_1}}{\lambda_1^4} + \frac{\sigma^2_{\lambda_2}}{\lambda_2^4},\ \chi^2 = 0.02$$

Angular momentum L →Electrons 'see' effective charge of nucleus $Z_{\mathrm{eff}}e$

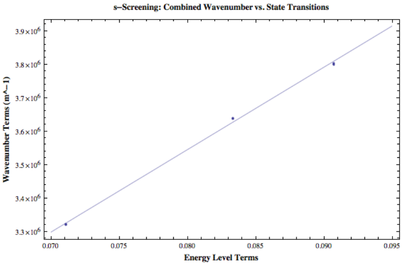


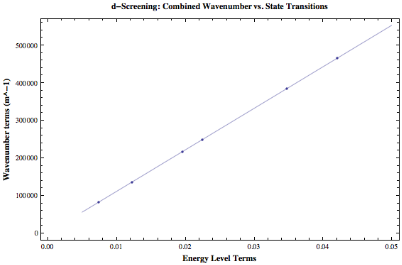
Assume final and initial states differ in Z_{eff}:

$$\frac{1}{\lambda} = -R_{\mathrm{Na}} \left(\frac{Z^2_{\mathrm{eff}_i}}{n_i^2} - \frac{Z^2_{\mathrm{eff}_f}}{n_f^2} \right) .$$

and equate common initial and final states:

$$\frac{1}{\lambda_2} \pm \frac{1}{\lambda_1} = Z^2_{\mathrm{eff}} R_{\mathrm{Na}} \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right) \tag{6}$$





$$Z_s = 1.50 \pm 0.10$$

$$Z_d = 1.00 \pm 0.09$$

$$\lambda_{\text{vac}} = \lambda_{\text{meas.}} \cdot n_{\text{air}}$$

$$n_{\text{air}} = 1.0002739$$

Summary

Table: Classification of sodium fine structure.

	Measured	CRC/NIST
$\Delta\bar{\nu}_{3P}$	$17.12 \pm 0.52 \pm 0.05\mathrm{cm}^{-1}$	$17.196\mathrm{cm}^{-1}$
$\Delta\bar{\nu}_{4P}$	$5.60 \pm 0.94\mathrm{cm}^{-1}$	$5.59\mathrm{cm}^{-1}$
Z_s	1.50 ± 0.10	1.1456
Z_d	1.00 ± 0.09	1
IE_1	$7.65 \pm 0.03\mathrm{eV}$	$5.1391\mathrm{eV}$

- We have confirmed correction to Bohr model from the spin-orbit perturbation, and have verified the angular momentum selection rules.
- Confirmed the effect of screening for outer 'shell' electrons, and

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