Lecture 11 Atomic Spectra

SCPY152, Second Semester 2021-22

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Topics

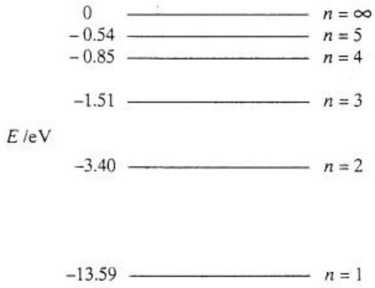
1. Principle hydrogen spectrum
2. Atom in external fields
3. Fine structure

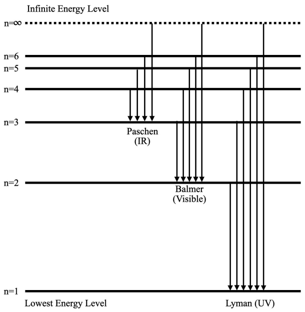
Principle spectrum

Hydrogen energy levels (from Bohr and Schrodinger)

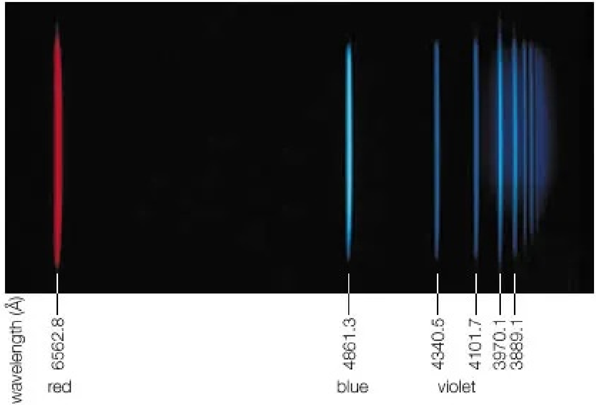
$$E_n = -\frac{1}{2}\frac{Ke^2}{a_0 n^2} = -\frac{1}{2} m_e c^2 \alpha^2 \frac{1}{n^2} = -\frac{13.6eV}{n^2} \quad (1)$$

with $a_0 = \frac{\hbar^2 c^2}{m_e c^2 Ke^2}$ and $\alpha = \frac{Ke^2}{\hbar c}$
Energy levels appear on the left, and emission transitions appear on the right





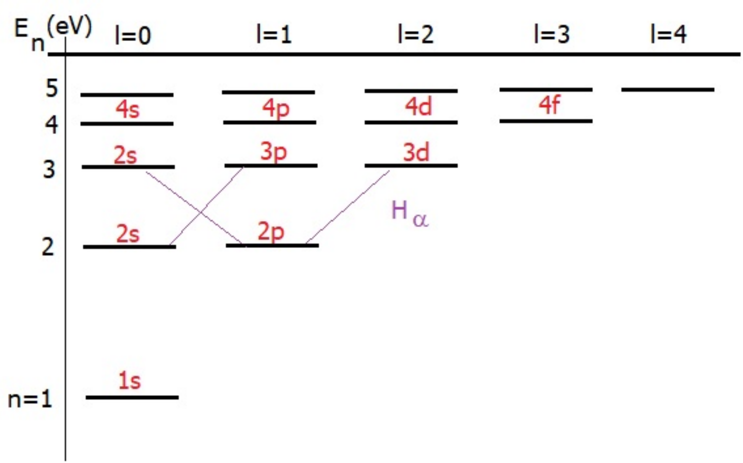
Appearance spectrum in Balmer series



Atomic transition and selection rules

Selection rules of atomic transitions (emission/absorption)

$$\Delta n = \text{any}, \ \ \Delta l = \pm 1$$



Hydrogen atom in (weak) external fields

Atom in uniform electric field $\vec{E} = E_0 \hat{z}$: Stark effect
Interaction potential energy of electron (with electric charge $-e$)

$$U = e\vec{E} \cdot \vec{r} = eE_0 r \cos\theta \quad (2)$$

Effect to the s-orbital, i.e., 1s-orbital

$$\langle U \rangle_{100} = \frac{1}{\pi a_0^3} eE_0 \int_0^\infty r^3 e^{-2r/a_0} dr \int_{-1}^{1} \cos\theta d\cos \int_0^{2\pi} \theta d\phi = 0 \quad (3)$$

No effect on s-orbital. Effect on p-orbitals

$$\langle U \rangle_{210} = \frac{eE_0}{32\pi a_0^5} \int_0^\infty r^3 e^{-r/a_0} dr \int_{-1}^{+1} \cos^3\theta d\cos\theta \int_0^{2\pi} d\phi = 0 \quad (4)$$

$$\langle U \rangle_{21\pm1} = \frac{eE_0}{64(3\pi) a_0^5} \int_0^\infty r^3 e^{-r/a_0} dr \int_{-1}^{+1} \cos\theta \sin^2\theta d\cos\theta \int_0^{2\pi} d\phi$$

$$= \frac{eE_0}{96 a_0} \int_0^\infty y^3 e^{-y} dy \int_{-1}^{1} x(1-x^2) dx = 0, \; y = \frac{r}{a_0}, \; x = \cos\theta \quad (5)$$

Atom in uniform magnetic field $\vec{B} = B_0\hat{z}$, magnetic interaction with orbital magnetic moment of an electron is

$$U_B = -\vec{\mu}\cdot\vec{B} = -\mu_z B_0 \qquad (6)$$

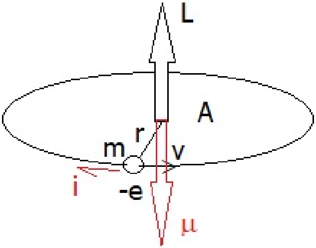
where $\vec{\mu} = i\vec{A} = -\frac{ev}{2\pi r}\pi r^2\hat{n} = -\frac{e}{2m_e}(m_e v r)\hat{n} = -\frac{e}{2m_e}\vec{L}$. Then we have from above

$$\vec{\mu} = \frac{-e}{2m_e}\vec{L}, \qquad (7)$$

$$U_B = \frac{eB_0}{2m_e}L_z \qquad (8)$$

$$\langle U_B\rangle_{nlm} = \frac{eB_0}{2m_e}m\hbar$$

$$= m\mu_B B_0 \qquad (9)$$

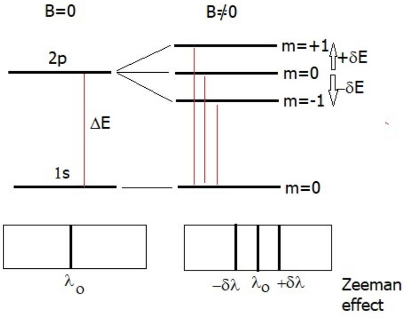


where $\mu_B = \frac{e\hbar}{2m_e} = 5.788\times 10^{-5}eV/T$ is Bohr magneton

Atomic transition with additional selection rule

$$\Delta m = 0, \pm 1$$

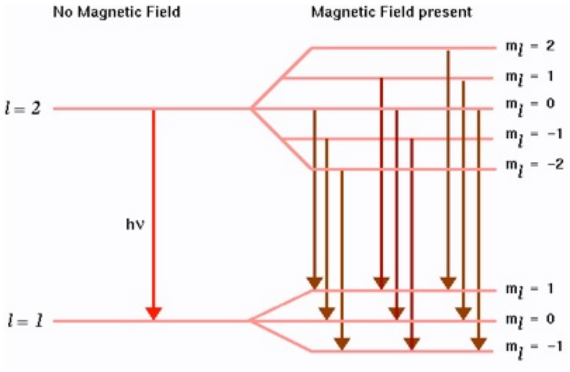
Spectral line splitting (Zeeman effect)



$$\lambda_0 = \frac{hc}{\Delta E} \mapsto \frac{\delta\lambda}{\lambda_0} = \frac{\delta E}{\Delta E} = \frac{\mu_B B_0}{\Delta E}$$

For example of L_α, $\Delta E = 10.2eV, \lambda_0 = 122.8nm$. With $B_0 = 1.0T$ we will have $\delta\lambda = 0.697 \times 10^{-3}nm$, the fourth decimal correction!

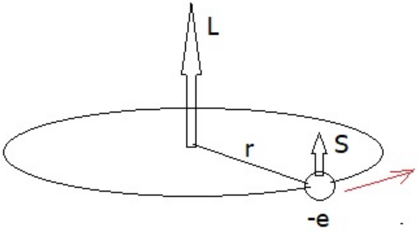
Other Zeeman splitting, i.e., H_α splitting



Can you estimate the spectral line splitting?

Fine structure

Spin-orbit coupling



Interaction potential energy is

$$\vec{\mu}_L = \frac{-e}{2m_e}\vec{L},\;\; \vec{\mu}_S = g\frac{-e}{2m_e}\vec{S},\;\; g = 2 \tag{10}$$

$$U_{LS} = -\vec{\mu}_S \cdot \vec{B}_L = g\frac{1}{2m_e^2c^2}\frac{Ke^2}{r^3}\left(\vec{L}\cdot\vec{S}\right) \tag{11}$$

Effects on atomic spectrum

$$\langle U_{LS}\rangle_{nlm,sm_s} = g\frac{Ke^2}{2m_e^2c^2}\langle\frac{1}{r^3}\rangle_{nl}\langle\vec{L}\cdot\vec{S}\rangle_{lm,sm_s} \tag{12}$$

Note that

$$\langle\frac{1}{r^3}\rangle_{nl} = \left(\frac{m_e c^2\alpha}{\hbar c}\right)^3\frac{1}{n^3}\frac{1}{l(l+1/2)l+1)},\ \ l>0 \tag{13}$$

$$\vec{J} = \vec{L}+\vec{S} \mapsto J^2 = L^2+S^2+2\vec{L}\cdot\vec{S}$$

$$\vec{L}\cdot\vec{S} = \frac{1}{2}\left(J^2-L^2-S^2\right) \tag{14}$$

with $s=1/2, l=0,1,...,n-1$ and

$$J^2 = j(j+1)\hbar^2, j = l+\frac{1}{2}, l-\frac{1}{2}$$

Combine all together, we will have

$$\langle U_{LS}\rangle_{nlm,sm_s} = \frac{1}{4}m_e c^2\alpha^4\frac{1}{n^3}\frac{1}{j+1/2}\begin{cases}\frac{1}{j}, & j=l+1/2\\ -\frac{1}{j+1}, & j=l-1/2\end{cases} \tag{15}$$

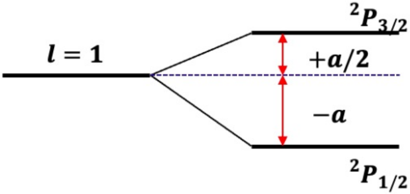


Figure 1.53: Splitting of 2*p*-state due to spin-orbit coupling.

Modified spectroscopic notation

$$nl \mapsto {}^nL_j$$

For example $1s \mapsto {}^1S_{1/2}, 2p \mapsto {}^2P_{3/2}, {}^2P_{1/2}$ or $3d \mapsto {}^3D_{5/2}, {}^3D_{3/2}$
Exercise Estimate the LS-splitting of the d-orbital.