

Atomic Spectra Summary

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Contents

1 Hydrogenic Atoms	1
1.1 Bohr: An Approximation	1
1.2 Rydberg Atoms	1
1.3 Exotic Atoms	2
1.4 Franck-Hertz Experiment	2
2 Lifting of Orbital Degeneracy: Alkali Metals	2
2.1 Schrödinger Equation of Alkali Metals	2
3 Fine Structure	2
3.1 Magnetic Moment of the Orbital Motion	2
3.2 Effects of an External Magnetic Field	3
3.3 Spatial Quantisation	3
3.4 Stern-Gerlach Experiment	3
3.5 Spin and Magnetic Moment of the Electron	3
3.6 Hyperfine Structure	4
4 Term Diagrams	4

The Bohr model also offers an approximation for the radius:

$$r_n = n^2 a_0 \quad (3)$$

$$a_0 = \frac{\epsilon_0 h^2}{e^2 \pi m_e} \quad (4)$$

$$r_1 = 6.2918 \times 10^{-11} \text{ m} \quad (5)$$

For a hydrogenic atom with nuclear charge Z , the energy scales with Z^2 :

$$\bar{E}_n = -\frac{Z^2 R}{n^2} \quad (6)$$

$$r_n = \frac{n^2}{Z} a_0 \quad (7)$$

The Rydberg constant, R or R_∞ and R_H for hydrogen is given:

$$R_\infty = 109737.315 \text{ cm}^{-1} \quad (8)$$

$$R_H = 109677.385 \text{ cm}^{-1} \quad (9)$$

The problem of electron and nucleus can be simplified by using **reduced mass** and assuming that the nucleus is stationary:

$$\mu = \frac{m_e M_N}{m_e + M_N} \quad (10)$$

For a specific 1-electron atom, the Rydberg constant is:

$$R_{\text{atom}} = R_\infty \frac{\mu}{m_e} \quad (11)$$

This corrects for the relative motion of the nucleus to the electron.

1 Hydrogenic Atoms

The Schrödinger equation can be solved exactly for hydrogenic atoms.

1.1 Bohr: An Approximation

The Bohr model offers a prediction of energy of a specific energy level in a one-electron system with PQN of n :

$$\begin{aligned} \bar{E}_n &= -\frac{m_e e^4}{8\epsilon_0^2 h^3 c n^2} \\ &= -\frac{R}{n^2} \end{aligned} \quad (1)$$

1.2 Rydberg Atoms

- (1) Rydberg atoms have an electron that has been excited to a high level. These atoms offers confirmation of the **Correspondence principle**.
 (2) The excited electron sees effectively a particle

with charge $+e$.

Rydberg atoms are easily ionized by applying a DC electric field, the approximate field strength necessary to remove an electron with PQN n is given by:

$$E \approx \frac{5 \times 10^9}{16n^4} \text{V cm}^{-1} \quad (12)$$

1.3 Exotic Atoms

Exotic atoms are artificial atoms where the nucleus is made up of particles other than protons and neutrons and/or the shell is made up of particles other than electrons: *i.e.* positronium (e^+e^-), muonium (μ^+e^-), anti-hydrogen (p^-e^+).

1.4 Franck-Hertz Experiment

2 Lifting of Orbital Degeneracy: Alkali Metals

The simplest multi-electron atoms are alkali atoms; they are said to be quasi-one-electron atoms.

The valence electron is screened by other inner electrons, this deviates from the Coulomb potential:

$$V_{\text{eff}} = -\frac{e^2}{4\pi\epsilon_0 r} \quad (13)$$

$$(14)$$

The above case is where the valence electron is significantly further away from the nucleus compare to the other electrons, such that the only charge it experience is $+1$. The case where the valence electron is very close to the nucleus is given below:

$$V_{\text{eff}} = -\frac{Ze^2}{4\pi\epsilon_0} \quad (15)$$

This leads to the decrease in probability density of the electron as the AMQ ℓ increases. This leads to a quantum defect and hence the loss of degeneracy for multi-electronic atoms. The

energy levels for a lithium atom can be found:

$$E_{n,\ell} = -R_{\text{Li}} \frac{1}{n_{\text{eff}}^2} \quad (16)$$

$$= -R_{\text{Li}} \left(\frac{1}{[n - \Delta(n, \ell)]^2} \right) \quad (17)$$

where $\Delta(n, \ell)$ corrects for the quantum defect. Note that Equation 17 is an empirical formula. The quantum defect increases with nuclear charge Z and decreases with ℓ .

2.1 Schrödinger Equation of Alkali Metals

$$\hat{H}\psi_{n\ell m}(\mathbf{r}) = \left(\frac{\hat{p}^2}{2m_e} + V_s(\mathbf{r}) \right) \psi_{n\ell m}(\mathbf{r}) \quad (18)$$

... relatively easy to solve as we only need to be concerned about V_s , the screening potential.

3 Fine Structure

The fine structure is due to the interactions between the magnetic moment associated with the orbital angular momentum ℓ and the magnetic moment from the spin s of the electron.

3.1 Magnetic Moment of the Orbital Motion

The current I is given by:

$$I = \frac{ev}{2\pi r} \quad (19)$$

The magnetic moment that arises from this motion has magnitude:

$$\mu = IA = \frac{e\ell}{2m_e} \quad (20)$$

μ is proportional to the orbital angular momentum and points in the opposite direction to ℓ :

$$\mu = -\frac{e}{2m_e} \hat{\ell} \quad (21)$$

Note that ℓ is quantised and its magnitude can be written as:

$$|\ell| = \sqrt{\ell(\ell+1)}\hbar \quad (22)$$

By defining a new constant, **Bohr magneton**, the magnitude of μ of an electron orbit with orbital angular momentum ℓ is:

$$\mu_\ell = \mu_B \sqrt{\ell(\ell + 1)} \quad (23)$$

$$\mu_\ell = -g_\ell \mu_B \frac{\ell}{\hbar} \quad (24)$$

3.2 Effects of an External Magnetic Field

Under the influence of an external magnetic field, the magnetic moment will interact with the field such that it undergoes gyroscopic motion and precesses around the magnetic field. The torque acting on the atom is given by:

$$\tau = \boldsymbol{\mu} \times \mathbf{B} \quad (25)$$

The precession frequency is given by:

$$\omega = \frac{d\phi}{dt} = \frac{|\tau|}{|\ell| \sin \theta} \quad (26)$$

where ϕ is the angular displacement, and θ is the angle which ℓ makes with the \mathbf{B} field. The above equation can be rewritten using previously defined relations:

$$\omega_\ell = \frac{\mu_\ell B \sin \theta}{|\ell| \sin \theta} \quad (27)$$

$$= \frac{g_\ell \mu_B}{\hbar} B \quad (28)$$

$$= \gamma B \quad (29)$$

where γ is the gyromagnetic ratio.

3.3 Spatial Quantisation

The angular momentum vector is quantised:

$$\ell_z = m_\ell \hbar \quad (30)$$

$$m_\ell \in \{0, \pm 1, \pm 2, \dots, \pm \ell\}$$

Consequently, this leads to the quantisation of the magnetic moment:

$$(\mu_\ell)_z = -m_\ell \hbar \quad (31)$$

3.4 Stern-Gerlach Experiment

In a homogeneous magnetic field, the magnetic moment and angular momenta of atoms will precess around the field direction. In an inhomogeneous magnetic field, however, the atom

will experience another force. The potential energy of a dipole in B field is given:

$$V_B = -\boldsymbol{\mu} \cdot \mathbf{B} \quad (32)$$

The force can be given by taking the derivative of the potential energy

$$F_z = \mu_z \frac{dB}{dz} = \mu \frac{dB}{dz} \cos \theta \quad (33)$$

The inhomogeneity will lead to a non-zero $\frac{dB}{dz}$. A classical picture would make θ continuous. The Stern-Gerlach Experiment showed:

- There is directional quantisation
- The atomic magnetic moment was found to be $\mu_z = \pm \mu_B$
- The atoms that were initially investigated, all had s electron in the outer shell, which inadvertently showed the intrinsic spin of electrons.

3.5 Spin and Magnetic Moment of the Electron

The spin of the electron, in the presence of an external magnetic field, can either point parallel or anti-parallel to the field:

$$s_z = m_s \hbar \quad (34)$$

$$m_s = \pm \frac{1}{2} \quad (35)$$

The interaction of the magnetic moment from the spin and the orbital angular momentum magnetic moment is calculated by considering the magnetic moment from ℓ to be an external field B_ℓ acting on a dipole, thus the potential energy of such interaction is:

$$V_{\ell,s} = -\boldsymbol{\mu}_s \cdot \mathbf{B}_\ell \quad (36)$$

$$V_{\ell,s} = \frac{g_s e}{2m_e} (\mathbf{s} \cdot \mathbf{B}_\ell) \quad (37)$$

Using the Biot-Savart law, the magnetic field that arises from the angular momentum is given by:

$$\mathbf{B}_\ell = \frac{Ze\mu_0}{8\pi r^3 m_e} \boldsymbol{\ell} \quad (38)$$

Substituting this in Eq 37, and approximate $g_s = 4$ **Term Diagrams**

2:

$$V_{\ell,s} = \frac{2e}{2m_e} (\mathbf{s} \cdot \mathbf{B}_\ell) \quad (39)$$

$$= \frac{Ze^2 \mu_0}{8\pi m_e^2 r^3} (\mathbf{s} \cdot \boldsymbol{\ell}) \quad (40)$$

Re writing as scalars, and defining a new constant a , the spin-orbit coupling constant:

$$V_{\ell,s} = \frac{a}{\hbar} |\boldsymbol{\ell}| |\mathbf{s}| \cos(\ell, s) \quad (41)$$

$$a = \frac{Ze^2 \mu_0 \hbar^2}{8\pi m_e^2 r^3} \quad (42)$$

By applying the law of cosine, and substitute for quantum values:

$$V_{\ell,s} = \frac{a}{2} [j(j+1) - \ell(\ell+1) - s(s+1)] \quad (43)$$

where j is the **total angular momentum quantum number**:

$$j = \ell + s \quad (44)$$

n.b.: such spin-orbit coupling is not possible when $\ell = 0$, as there is no orbital angular momentum (*i.e.* s -orbital)

By conservation of angular momentum, the following selection rules apply:

$$\Delta \ell = \pm 1 \quad (45)$$

$$\Delta j = 0, \pm 1 \quad (46)$$

3.6 Hyperfine Structure

Some atomic nuclei possess a nuclear spin, this gives rise to **hyperfine structure**. This spin is characterised by quantum number \mathbf{I} and is quantised in units of \hbar :

$$\mathbf{I} = \sqrt{I(I+1)} \hbar \quad (47)$$

$$(\mathbf{I})_z = m_I \hbar \quad (48)$$

We can treat this completely analogous to the spin-orbit coupling interaction:

$$\boldsymbol{\mu}_I = \gamma_I \mathbf{I} = \frac{g_I \mu_N}{\hbar} \mathbf{I} \quad (49)$$

$$\mu_N = \frac{e \hbar}{2m_p} = \frac{\mu_B}{1836} \quad (50)$$

where we have define a new unit, the **nuclear magneton**.

An additional energy due to hyperfine interaction is given by:

$$V = -\boldsymbol{\mu}_\ell \cdot \mathbf{B}_J \quad (51)$$

The term diagrams illustrate the energies of the orbitals taking into account the coupling interactions. The terms take the following shape:

$$^{2S+1}L_J \quad (52)$$

The set of possible S , L , and J values are determined by the **Clebsch-Gordon series**:

$$S \in \{s_1 + s_2, s_1 + s_1 - 1 \dots s_1 - s_2\} \quad (53)$$

The energies are arranged by Hund's Rule, the lower energy states will tend to:

1. Maximise S
2. Maximise L
3. If the orbitals are less than half-full, smallest J corresponds to lowest energy.
4. If more than half-filled, largest J corresponds to the lowest energy.