

Emission Spectra: The principal series can be observed in emission as well as in absorption.

The strongest line \rightarrow for the transition $n_p \rightarrow n_1$ called a resonance line

Spin-orbit coupling \rightarrow The resonance lines are doublets

The resonance lines of the alkali metals: Li, Na, K, Rb, Cs

Li	6708	K	7655	Cs	8543
			7665		8521
Na	5896	Rb	7946		
	5890		7800		

\downarrow
The yellow lines in this doublet \rightarrow Fraunhofer D-lines in the spectrum of sunlight.

Other series of emission lines

Sharp series $\Rightarrow n_s \rightarrow n_0 p$ transitions

Diffuse series $\Rightarrow n_d \rightarrow n_0 p$ transitions

fundamental series $\Rightarrow n_f \rightarrow n_0 d$ transitions

The energy levels of sequence like Li I, Be II, B III, C IV, ... where I \rightarrow neutral atom, II for a singly ionized atom and so forth.

$$\bar{E}_{nl} = -\frac{1}{2} \frac{\tilde{Z}^2}{[n - \alpha(l)]^2} \text{ e.u.}$$

where $\tilde{Z} = Z - N + 1$, Z nuclear charge, N ~~total~~ number of electrons

The quantum defect $\alpha(l)$ decreases smoothly during such a sequence so that for large Z , spectrum becomes hydrogenic

Spin-orbit Interactions fine structure

For the one-electron atoms the non-relativistic Hamiltonian $H = \frac{p^2}{2\mu} - \frac{Ze^2}{(4\pi\epsilon_0)r}$ — (1)

$\frac{p^2}{2\mu}$ → non-relativistic K.E. in the centre of mass system
 $-\frac{Ze^2}{(4\pi\epsilon_0)r}$ → electrostatic (Coulomb) interaction between the electron and the nucleus.

Very precise measurements in atomic physics → demonstrate several effects → can't be derived by this Hamiltonian, requires the addition of correction terms

Relativistic corrections → splitting of the energy levels
 ↓
fine structure.

Additional splitting of energy levels → Lamb shift
 → displaces the fine structure components.

Various small corrections → hyperfine structure splitting

Volume effect → Nucleus is not simply a point charge but has a finite

~~size~~ size, and may possess an intrinsic angular momentum (spin), a magnetic dipole moment, an electric quadrupole moment and higher moments.

Fine structure of hydrogenic atoms:

fine structure of the energy levels of hydrogen atoms → due to relativistic effects

Required → Basis wavefunctions → which satisfies the requirements of special relativity as well as quantum mechanics.

Dirac eqⁿ → correct relativistic wave eqⁿ for electrons.

↓
To solve Dirac eqⁿ for an electron in the central field $V(r) = -ze^2 / (4\pi\epsilon_0 r)$ of the nucleus assumed to be of infinite mass and at the origin of the coordinates.

Simple way to solve → perturbation theory, keeping terms up to order v^2/c^2 in the Dirac Hamiltonian.

We start with Hamiltonian

$$H = H_0 + H' \quad \text{--- (2)}$$

where $H_0 = \frac{p^2}{2m} - \frac{ze^2}{(4\pi\epsilon_0)r}$ --- (3) [with $\mu = m$
in eqⁿ (1)]

and $H' = H'_1 + H'_2 + H'_3$ --- (4)

with $H'_1 = -\frac{p^4}{8m^3c^2}$ --- (5)

$$H'_2 = \frac{1}{2m^2c^2} \frac{1}{r} \frac{dV}{dr} \text{ L.S.} \quad \text{--- (6)}$$

and $H'_3 = \frac{\pi\hbar^2}{2m^2c^2} \left[\frac{ze^2}{4\pi\epsilon_0} \right] \delta(r)$ --- (7)

$H_1' \rightarrow$ relativistic correction to the kinetic energy (30)

$H_2' \rightarrow$ spin-orbit interaction

$H_3' \rightarrow$ Darwin term.

Schödinger theory \rightarrow does not include the spin of electron.

Spin - Orbit term

$$H_2' = - \frac{1}{2m^2c^2} \frac{1}{r} \frac{dV}{dr} L \cdot S$$

more simply $H_2' = \xi(r) L \cdot S \quad \text{--- (8)}$

where $\xi(r) = \frac{1}{2m^2c^2} \frac{1}{r} \frac{dV}{dr} \quad \text{--- (9)}$

In the case $V(r) = -Ze^2 / (4\pi\epsilon_0 r)$

$$\xi(r) = \frac{1}{2m^2c^2} \frac{Ze^2}{4\pi\epsilon_0} \frac{1}{r^3} \quad \text{--- (10)}$$

Since operator L^2 does not act on the radial variable r nor on the spin variable, and commutes with the components of L , we see from eqⁿ (8) that L^2 commutes with H_2' .

To calculate corrections involving the spin operator - such as those arising from H_2' , we begin with 'unperturbed' eqⁿ

$$H_0 \psi_{nlm_l m_s} = E_n \psi_{nlm_l m_s} \quad \text{--- (11)}$$

$E_n \rightarrow$ Schödinger eigenvalues (with $l=m$) and zero-order wavefunctions $\psi_{nlm_l m_s}$ are modified (two-component) Schödinger wave functions. (Pauli wavefn or 'spin orbitals')

$$\psi_{nlm m_s}(r) = \psi_{nlm}(r) \chi_{1/2, m_s} \quad \text{--- (12)} \quad (21)$$

Space and spin variables

$$m_l \rightarrow -l, -l+1, \dots, +l$$

$\psi_{nlm}(r) \rightarrow$ one-electron Schrödinger wave function. Such that

$$H_0 \psi_{nlm}(r) = E_n \psi_{nlm}(r) \quad \text{--- (13)}$$

and $\chi_{1/2, m_s} \rightarrow$ Spin eigenfunctions for spin one half ($s=1/2$), with $m_s = \pm 1/2$.

$\chi_{1/2, m_s} \rightarrow$ two-component spinor and the normalized spinors corresponding to 'spin up' ($m_s = +1/2$) and 'spin-down' ($m_s = -1/2$) are denoted by

$$\alpha = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \text{ and } \beta = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

$H_0 \rightarrow$ does not operate the spin variable, the two-component wave functions are separable in space and spin variables. (14)

Now we have four quantum numbers (n, l, m_l, m_s) to describe one-electron atom.

Effect of spin on the 'unperturbed' solⁿ

\rightarrow to double the degeneracy, each Schrödinger energy level E_n is now $2n^2$ degenerate