Atomic Spectra & Atomic Structure

The Spectrum of Atomic Hydrogen

ignore electron spin $E_n = -\frac{\mu e^4}{32\pi^2 \varepsilon_0^2 \hbar^2}\frac{1}{n^2}$ $n = 1, 2, \cdots$

$= -\frac{hcR_H}{n^2}$ $R_H = \frac{\mu e^4}{8\varepsilon_0^2 h^3 c}$

The energies of the transitions

$n_2 \rightarrow n_1$ wavenumber $\tilde{\nu} = \frac{\nu}{c} = \left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) R_H$

Selection rules

transition dipole moment $\mu_{fi} = \langle f|\mu|i\rangle$ $\neq 0$ allowed transition

$= 0$ forbidden transition

Laporte selection rule : only allowed are those involving a change in parity

constraints on Δl : only allowed $\Delta l = \pm 1$

constraints on Δm_l : $\Delta m_l = 0, \pm 1$

Ex : calculate the electric dipole moment for $2s \rightarrow 2p_z$ in a H for z-polarized radition

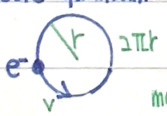
$$\psi_{2p_z} = \sqrt{\frac{Z^5}{32\pi a_0^5}}\, r\cos\theta\, e^{-\frac{Zr}{2a_0}} \qquad \psi_{2s} = \sqrt{\frac{Z^3}{32\pi a_0^5}}\,(2a_0 - Zr)\, e^{-\frac{Zr}{2a_0}}$$

$$\langle 2p_z|\mu_z|2s\rangle = -e\frac{Z^4}{32\pi a_0^5}\int_0^\infty (2a_0 - Zr) r^4 e^{-\frac{Zr}{a_0}} dr \underbrace{\int_0^\pi \cos^2\theta \sin\theta d\theta}_{\frac{2}{3}} \underbrace{\int_0^{2\pi} d\phi}_{2\pi} = -\frac{3ea_0}{Z}$$

electric dipole	$\Delta l = \pm 1$	$\Delta m_l = 0$
magnetic dipole	$\Delta l = 0$	$\Delta m_l = 0, \pm 1$
electric quadrupole	$\Delta l = 0, \pm 2$	$\Delta m_l = 0, \pm 1, \pm 2$

Orbital and spin magnetic moments

spin: $\frac{1}{2}$ spin magnetic quantum number $m_s = \pm\frac{1}{2}$

in classical picture 

$I = -\frac{e}{T} = -\frac{ev}{2\pi r}$ magnetic dipole moment $m_z = I\pi r^2$

$m_z = IA = -\frac{ev\pi r^2}{2\pi r} = -\frac{1}{2}evr = -\frac{e}{2m_e} l_z$

γ_e , magnetogyric ratio

orbital angular momentum $l_z = m_e v r$

$m_z = \gamma_e m_l \hbar$ $m_l = l, l-1, \ldots, -l$ $\vec{m} = 2\gamma_e \vec{s}$

$= g_e \gamma_e \vec{s}$

$\mu_B = -\gamma_e \hbar = \frac{e\hbar}{2m_e}$ Bohr magneton

$= 9.274 \times 10^{-24}\ JT^{-1}$

$\Rightarrow m_z = -\mu_B m_l$

NO.

DATE

Spin-Orbit Coupling

classical calculation:

particle m_e and charge $-e$ moving at v in an $\vec{E}$ experiences $\vec{B} = \frac{\vec{E}\times\vec{v}}{c^2}$

if the field is due to an isotropic electric potential φ, $\vec{E} = -\frac{\vec{r}}{r}\frac{d\varphi}{dr}$

$\Rightarrow \vec{B} = -\frac{1}{rc^2}\frac{d\varphi}{dr}\vec{r}\times\vec{v} = -\frac{1}{m_e rc^2}\frac{d\varphi}{dr}\vec{l}$ if magnetic field lies in the z

the energy of interaction between $\vec{B}$ and magnetic dipole $\vec{m}$

$$H_{so} = -\vec{m}\cdot\vec{B} = \frac{1}{m_e rc^2}\frac{d\varphi}{dr}\vec{m}\cdot\vec{l} = -\frac{e}{m_e^2 rc^2}\frac{d\varphi}{dr}\vec{s}\cdot\vec{l} = g_s\frac{e}{m}\vec{s}\cdot\vec{B}$$

this result is exactly twice the result obtained by solving the Dirac eq.
because we don't consider relativist

quantum calculation

$$H_{so} = \xi(r)\,\vec{l}\cdot\vec{s} \quad , \quad \xi(r) = -\frac{e}{2m_e^2 rc^2}\frac{d\varphi}{dr} = -\frac{e}{2m_e^2 rc^2}\frac{d}{dr}\left(\frac{Ze}{4\pi\varepsilon_0 r}\right) = \frac{Ze^2}{8\pi\varepsilon_0 m_e^2 r^3 c^2}$$

$$\langle n l m_l m_s | r^{-3} | n l m_l m_s\rangle = \frac{Z^3}{n^3 a_0^3\, l(l+\frac{1}{2})(l+1)}$$

spin-orbit coupling constant $hc\,\zeta_{nl} = \langle n l m_l m_s | \xi(r) | n l m_l m_s\rangle \hbar^2$

$$\Rightarrow \zeta_{nl} = \frac{Z^4 e^2 \hbar^2/hc}{8\pi\varepsilon_0 m_e^2 c^2 n^3 a_0^3\, l(l+\frac{1}{2})(l+1)} = \frac{\alpha^2 R_\infty Z^4}{n^3 l(l+\frac{1}{2})(l+1)}$$

fine-structure const. $\alpha = \frac{e^2}{4\pi\varepsilon_0\hbar c}$

Rydberg constant

$\zeta \propto Z^4$ spin-orbit coupling are very much larger in heavy atoms than in light atoms

for H, $Z=1$, 2p, $\zeta = \frac{\alpha^2 R_\infty}{24} = 2.22\times10^{-6} R_\infty$

Ex: H, $n=2$ $l=1$ $H_{s.o.}$?

$V(r) = -\frac{e^2}{4\pi\varepsilon_0 r}$, $\frac{dV}{dr} = \frac{e^2}{4\pi\varepsilon_0 r^2}$,

$$H_{s.o.} = \frac{1}{4\pi\varepsilon_0}\frac{e^2}{2\mu^2 c^2 \langle r^3\rangle}\hat{S}\cdot\hat{L} = \frac{1}{4\pi\varepsilon_0}\frac{e^2}{2\mu^2c^2}\left(\frac{\mu e^2}{12\pi\varepsilon_0\hbar^2}\right)^3\hbar^2$$

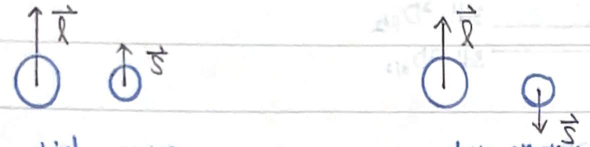
$\sqrt{l(l+1)}\,\hbar = \sqrt{2}\,\hbar$

$\sim\left(\frac{1}{3a_0}\right)^3 = \left(\frac{\mu e^2}{3\cdot 4\pi\varepsilon_0\hbar^2}\right)^3$ $\quad \hbar\sqrt{s(s+1)} = \frac{\sqrt{3}}{2}\hbar$

$$= \frac{\mu e^8}{54\times(4\pi\varepsilon_0)^4 c^2\hbar^4} \sim 10^{-23}\,\text{J} \sim 10^{-4}\,\text{eV}$$

$\Delta E \sim 2\times10^{-4}$ eV

The Fine-Structure of Spectra



high energy   low energy

because the so interaction is so weak in comparison with the energy-level separations of atom
we can use first-order perturbation

$$E_{so} = \langle ls; j m_l | H_{so} | ls; j m_l \rangle = \langle ls; j m_l | \xi(r) \vec{l} \cdot \vec{s} | ls; j m_j \rangle$$

$$= \frac{1}{2}\hbar^2 \left[j(j+1) - l(l+1) - s(s+1)\right] \langle ls; j m_j | \xi(r) | ls; j \rangle$$

$$= \frac{1}{2} hc\zeta_{nl} \left[j(j+1) - l(l+1) - s(s+1)\right]$$

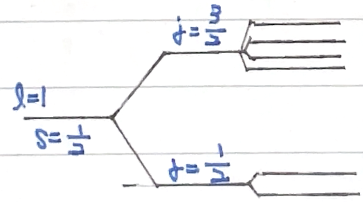
$$= Z^4 \alpha^2 hc R_\infty \frac{j(j+1) - l(l+1) - s(s+1)}{2n^3 l(l+\frac{1}{2})(l+1)}$$

$$\boxed{\begin{aligned} \hat{j}^2 &= (\hat{l} + \hat{s})(\hat{l} + \hat{s}) \\ &= \hat{l}^2 + \hat{s}^2 + 2\hat{s}\cdot\hat{l} \\ \hat{s}\cdot\hat{l} &= \frac{1}{2}(\hat{j}^2 - \hat{l}^2 - \hat{s}^2) \\ &= \frac{\hbar^2}{2}\left[j(j+1) - l(l+1) - s(s+1)\right] \end{aligned}}$$

Ex: for p $j = \frac{3}{2}$ or $\frac{1}{2}$,

$j = \frac{3}{2}$ $2j+1 = 4$ degenerate states

$j = \frac{1}{2}$ $= 2$



Term Symbols and spectral details

spectral lines arise from transitions between "terms"

wavenumber $\tilde{\nu} = T' - T$ emission $T' \rightarrow T$ absorption $T' \leftarrow T$

Configuration — the orbitals that the e⁻ occupy $2p^1$

split by electrostatic interactions

$L =$ S, P, D, F ...
0, 1, 2, 3 ...

$\boxed{^{2S+1}L}$ $\boxed{}$ $\boxed{\text{Terms}}$ ^2P

split by spin-orbit intera.

$\boxed{^{2S+1}L_J}$ $\boxed{}$ $\boxed{\text{Levels}}$ $^2P_{3/2}$ $j = \frac{3}{2}$ $j = \frac{1}{2}$

split by external fields

$\boxed{^{2S+1}L_J^{M_J}}$ $\boxed{}$ $\boxed{\text{States}}$