Atomic spectra & multi-electron states

review: spin ⇒ S-electron levels split into 2!

to explain Stern-Gerlach magn. dipole moment of electron:

$$\mu_z = \frac{-e}{2m} g s_z + \text{orbital contribution}$$

classical $g=1$
actual for spin $g=2$

Pauli eqn: need two wavefcns to fully describe $\bar{e}$: $\begin{pmatrix} \psi_\uparrow(\vec{r}) \\ \psi_\downarrow(\vec{r}) \end{pmatrix}$ "spinor"

$$|\psi\rangle = |\psi_\uparrow\rangle |\uparrow\rangle + |\psi_\downarrow\rangle |\downarrow\rangle$$

$\hat{\vec{S}} = \frac{\hbar}{2}\vec{\sigma}$ with Pauli matrices for $\frac{1}{2}$ spin

$s = \frac{1}{2}$, $m_s = \pm\frac{1}{2}$ (only 2 states needed for arb. spin orientation)

joint eigenbasis for $\hat{S}_z$, $\hat{S}^2$:

$$\hat{S}^2 |s, m_s\rangle = \hbar^2 s(s+1) |s, m_s\rangle \quad \text{with } |\tfrac{1}{2}, \tfrac{1}{2}\rangle \equiv |\uparrow\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix}$$

$$\hat{S}_z |s, m_s\rangle = \hbar m_s |s, m_s\rangle \qquad |\tfrac{1}{2}, -\tfrac{1}{2}\rangle \equiv |\downarrow\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

1 Detour: perturbation theory basics

$\hat{\mathcal{H}} = \hat{\mathcal{H}}_0 + \hat{\mathcal{H}}_p$ with $\mathcal{H}_p$ "small"

$\hat{\mathcal{H}}_0$ basis $|\psi_n\rangle$ still "good enough" for $\mathcal{H}$

$E_n \rightarrow E_{0,n} + \Delta E_n$

with $\Delta E_n \approx \langle \psi_n | \hat{\mathcal{H}}_p | \psi_n \rangle$

2 spectral structure

		term in the Hamiltonian
gross structure	$\sim E_n$ ($\sim$eV)	– $V(r)$ nucl. potential
fine structure	$\sim 10^{-4}$ eV "two magnet bars"	– relativistic correction
		– spin-orbit coupling
hyperfine structure	$\sim 10^{-6}$ eV	– nucleus' spin-orbit
the Lamb shift	$= 4.3\times10^{-6}$ eV splitting of s,p levels of H	– QED

line splitting without ext. fields

QED:
mass renormalization +1017 MHz
vacuum polarization −27 MHz
anomalous magn. moment +68 MHz
total +1058 MHz

③ Spin-orbit coupling

a) field due to nuclei : $\vec{E} = \frac{1}{e}\nabla V(r) = \frac{1}{e}\frac{dV(r)}{dr}\frac{\vec{r}}{r}$

in e^- moving frame, this in part becomes B-field

$$\vec{B} = -\frac{\vec{v}\times\vec{E}}{c^2} = -\frac{\vec{v}\times\vec{r}}{ec^2 r}\frac{dV(r)}{dr} = \frac{\vec{L}}{emc^2}\frac{1}{r}\frac{dV(r)}{dr}$$

$V_{so} = -\vec{\mu}_s \cdot \vec{B}$ where $\vec{\mu}_s = \frac{-e}{2m} g \vec{S}$, => replace $\vec{S}\cdot\vec{L}$ in Q.M.

classically $V_{so} = \frac{1/2}{m^2c^2}\frac{1}{r}\frac{dV(r)}{dr}\vec{S}\cdot\vec{L}$ correct treatment gives add'l. 1/2

b) from e^-'s point of view: (e^- is not in inertial frame)

nucleus is spinning around with $\vec{L}$

B-field $\propto \vec{L}$; energy $V_{so} \propto \vec{S}\cdot\vec{L}$ internal Zeeman

c) classically : magn. dipoles interact, =>

$\vec{L}$ and $\vec{S}$ are no longer conserved

(though L^2 and S^2 are)

Q.M. : cannot use m_ℓ and m_s to label quant. states

=> solution : use total angular momentum $\vec{J} = \vec{L} + \vec{S}$

(must still be conserved)

④ Total angular momentum

eigenvalues of $\hat{J}^2$: $\hbar^2 j(j+1)$

$\hat{J}_z$: $\hbar m_j$ $\quad m_j = \underbrace{-j, \dots, 0, \dots, j}_{2j+1 \text{ values}}$

=> use n, ℓ, j, m_j to label quant. state

Q: what values can j take ? $\quad \ell - s \leq j \leq \ell + s$ (if $\ell \geq s$)

e.g. $j = \ell \pm \frac{1}{2}$ for H-like

⑤ going from $|n, \ell, m_\ell, m_s\rangle$

to $|n, \ell, j, m_j\rangle$ is "basis change"

check that we did not lose states

fixed ℓ, s : m_ℓ, m_s can take $2(2\ell+1)$ values

j, m_j can take $[2\underbrace{(\ell-\frac{1}{2})}_{j_1}+1] + [2\underbrace{(\ell+\frac{1}{2})}_{j_2}+1] =$

$= 2(2\ell+1)$

$\boxed{n^{2S+1}L_j}$

spectr. notation

⑥ other effects

relativity: $KE \neq \frac{p^2}{2m}$, instead $KE = \sqrt{(pc)^2 + (mc^2)^2} - mc^2$

$\simeq \frac{p^2}{2m} - \frac{p^4}{8m^3c^2} + \ldots$

can show that generally $E_n \to E_{n\ell}$

hyperfine structure

nuclei have magnetic dipole:

dipole-dipole interaction $\propto \vec{\mu}_p \cdot \vec{\mu}_e$

solved using same techniques as spin-orbital coupling

$\Delta E_{hyper} \sim \alpha^2 \frac{m_e}{m_p}$ in atomic units

H-atom (most dominant element in the Universe) nuclear spin electron spin

5.9×10^{-6} μeV

or 1420 MHz

21 cm wavelength

$\uparrow$ $\uparrow$

$\uparrow$ $\downarrow$

very important in radio-astronomy "21 cm line"