Atomic spectra (H-like atoms)

Atomic spectra – fingerprints of Q.M., played a key role in establishing of Q.M.; modern astro, AMO

Main physics

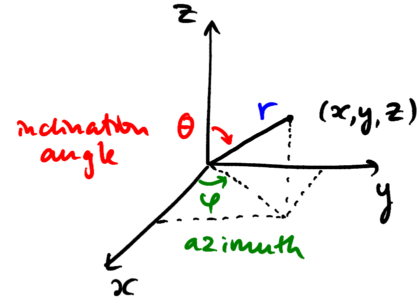
- ✱ Coulomb attraction from the nucleus
- ✱ spherical symmetry
- ✱ spin and magn. dipole moments

} QM!

① Angular momentum
in central potential $V = V(r)$

classical: $\vec{L} = \text{const}$

Q.M.: states with well-defined $\vec{L}$?



NO, but joint eigenbasis for

$$\left.\begin{aligned} \hat{L}_z &= \frac{\hbar}{i}\frac{\partial}{\partial\varphi} \\ \hat{L}^2 &= -\hbar^2 \nabla^2_{\theta,\varphi} \end{aligned}\right\} \quad [\hat{L}^2, \hat{L}_z] = 0$$

Laplacian

$$\left[\nabla^2_{\theta,\varphi} = \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right]$$

$|l, m_l\rangle = Y_l^{m_l}(\theta,\varphi)$ ← joint eigenstates (spherical harmonics)

$\hat{L}_z |l, m_l\rangle = \hbar m_l |l, m_l\rangle$ $\quad \boxed{-l \leq m_l \leq l}$

$\hat{L}^2 |l, m_l\rangle = \hbar^2 l(l+1) |l, m_l\rangle$

Mathematica example #1

Note 1: z ain't special

Note 2: normalization: $\int_0^{\pi} \sin\theta\, d\theta \int_0^{2\pi} |Y_l^m(\theta,\varphi)|^2 d\varphi = 1$

Note 3: true for any $V = V(r)$

② H-like nucleus $(H, He^{+}, Li^{2+}, Be^{3+} \ldots)$

$$V(r) = -\frac{Ze^2}{4\pi\varepsilon_0 r} \quad ; \quad \hat{\mathcal{H}} = -\frac{\hbar^2}{2m}\nabla^2 + V(r)$$

reduced mass: replace $m \to \mu = \frac{m_p m_e}{m_p + m_e}$

r – distance from the center of mass

$\hat{\mathcal{H}}$ commutes with $\hat{L}^2, \hat{L}_z$

⇒ common joint basis

$$\left.\begin{aligned} \hat{\mathcal{H}}|\psi\rangle &= E|\psi\rangle \\ \hat{L}^2|\psi\rangle &= \hbar^2 l(l+1)|\psi\rangle \\ \hat{L}_z|\psi\rangle &= \hbar m_l |\psi\rangle \end{aligned}\right\}$$

suggest $|\psi\rangle = R(r)\, Y_l^{m_l}(\theta,\varphi)$

normalization: $\int_0^{\infty} |R(r)|^2 r^2 dr = 1$

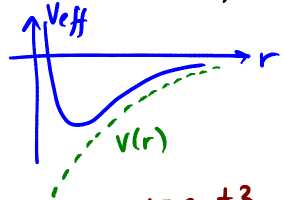
4π comes from $Y_l^{m_l}$ norm.

③ Struggle thru textbooks to reduce

$\hat{\mathcal{H}}|\psi\rangle = E|\psi\rangle$ to ODE for $R(r)$, then for $\underline{u(r)} = r \cdot R(r)$ find

$$\left[-\frac{\hbar^2}{2\mu}\frac{d^2}{dr^2} + V_{eff}(r)\right]u(r) = E\,u(r) \; ; \quad V_{eff} = V(r) + \frac{\hbar^2\,\ell(\ell+1)}{2\mu r^2} \propto \frac{L^2}{2I}$$

centrifugal potential



④ Energy levels

$$E_{n'} = -\underbrace{\frac{1}{2}\frac{Z^2 e^2}{4\pi\varepsilon_0 a_0}}_{Z^2 R_y}\frac{1}{(n'+\ell)^2}$$

$n' = 1, 2, 3, \ldots$

$1R_y = 13.6\ eV$

$$a_0 = \frac{4\pi\varepsilon_0 \hbar^2}{m e^2} \approx 0.53\,\mathring{A}$$

Bohr radius – H-atom size

principal quantum number : $n = n' + \ell$

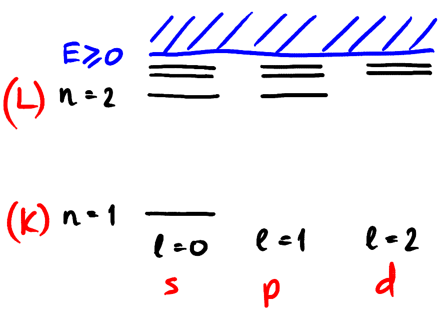
$E_n = -\frac{Z^2}{n^2}$ in units of R_y

degeneracy E_n for ℓ: $\ell = 0, 1, 2, \ldots, n-1$

'magic' of $-\frac{1}{r}$ potential

For the radial part $u(r)$ see Miller Ch10   Mathematica example #2

⑤ Notations



$n = 1, 2, 3, \ldots$ } "shell"

X-ray, Auger → K, L, M, ...

$\ell = 0, 1, 2, \ldots$ } "subshell"

spectroscopy → s, p, d, f, g, h, ...

E.g. 1s – ground state

2s, 2p – first excited state

etc.

⑥ Spectroscopy

transitions between energy levels → emitted light

selection rules : $\Delta\ell = \pm 1$ (angular momentum conservation, photon has $\ell = 1$)

$\Delta m_\ell = 0, \pm 1$ (more later in the course)

⑦ Atoms as dipoles

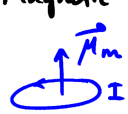
$\ell \neq 0$ levels may have electric & magnetic dipoles associated with them

$V_{int} = -\vec{E}\cdot\langle\vec{\mu}_e\rangle$
$V_{int} = -\vec{B}\cdot\langle\vec{\mu}_m\rangle$ } energy change due to ext. fields ⇒ Stark effect (elect.)

Zeeman effect (magn.)

splitting of spectral lines

⑧ Magnetic dipole moment & normal Zeeman



current I loop of area A : $|\vec{\mu}_m| = IA$

one e^- in circular orbit in xy plane

$$\mu_z = \underbrace{(-e)\frac{\omega}{2\pi}}_{\text{current}}\ \underbrace{\pi r^2}_{\text{area}} = -\frac{e}{2m} pr = -\frac{e}{2m} L_z$$

in general: $\vec{\mu}_m = \frac{-e}{2m}\vec{L}$, or Q.M. $\hat{\vec{\mu}} = -\frac{e}{2m}\hat{\vec{L}}$

$$(\mu_m)_z = -\mu_B m_\ell \quad , \; m_\ell = 0, \pm 1, \dots, \pm \ell$$

Bohr magneton $\mu_B = \frac{e\hbar}{2m}$

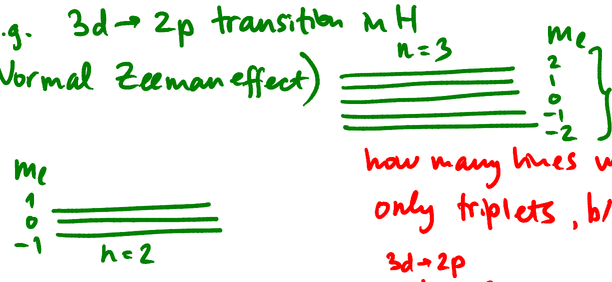
$$V_{int} = -\vec{\mu}_m \cdot \vec{B} \quad (\vec{B} \uparrow\uparrow \hat{z}) \rightarrow -B \cdot (\mu_z)_m = \frac{eB}{2m} m_\ell \hbar = \hbar \omega_L m_\ell$$

Larmor freq.

$$\Rightarrow E_{n\ell m} = -\frac{1}{2}\frac{Z^2 e^2}{4\pi\varepsilon_0 a_0 n^2} + m_\ell \hbar \omega_L$$

E.g. 3d → 2p transition in H

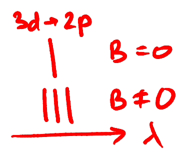
(Normal Zeeman effect)



$2\ell+1$ splitting (always odd!)

how many lines will see?

only triplets, b/c $\Delta m = 0, \pm 1$



(10) Anomalous Zeeman

splitting into even number of lines!

⇒ spin $s = \frac{1}{2}$ of electron!

(11) full H-wavefcn

$$|n\ell m_\ell m_s\rangle = R_{n\ell}(r) Y_\ell^{m_\ell}(\theta,\varphi)\,|m_s\rangle$$

joint basis for

$\hat{\mathcal{H}}|n\ell m_\ell m_s\rangle = E_n |n\ell m_\ell m_s\rangle$ with $\frac{E_n}{Ry} = -\frac{Z^2}{n^2}$; $n = 1, 2, 3, \dots$

$\hat{L}^2 |n\ell m_\ell m_s\rangle = \hbar^2 \ell(\ell+1)|n\ell m_\ell m_s\rangle$; $\ell = 0, 1, \dots, n-1$

$\hat{L}_z |n\ell m_\ell m_s\rangle = \hbar m_\ell |n\ell m_\ell m_s\rangle$; $m_\ell = -\ell, \dots, 0, \dots, +\ell$

$\hat{S}^2 |n\ell m_\ell m_s\rangle = \frac{3}{4}\hbar^2 |n\ell m_\ell m_s\rangle$; $s = \frac{1}{2}$

$\hat{S}_z |n\ell m_\ell m_s\rangle = \hbar m_s |n\ell m_\ell m_s\rangle$; $m_s = -\frac{1}{2}, +\frac{1}{2}$

(12) degeneracy : each ℓ $\quad (2\ell+1)\times 2$ ← spin

given n $\quad \sum_{\ell=0}^{n-1} 2(2\ell+1) = 2n^2$