I. Term Symbol : Understanding spectroscopic Data

- A notation to label the energy levels of <u>an atom</u>

  generally, it is about <u>the atom</u> as a whole

- Notation provides information on

  (ℓ, s, j) for H-atom

  (L, S, J) for atoms in general

Capital Letters are used for labelling <u>atoms</u>

L for quantum number of <u>total</u> orbital angular momentum

S for quantum number of <u>total</u> spin angular momentum

J for quantum number of $\vec{J} = \vec{L} + \vec{S}$

H-atom (simplest)

- One electron only (nothing to "total", e.g. electron's ℓ is atom's L)

  $\underbrace{s = 1/2 \text{ always}}$, (total spin is single electron's spin) ($S = 1/2$ H-atom)

  $2s+1 = 2$ (this will go into upper left-hand corner of term symbol)

  ℓ (single electron's ℓ is whole atom's L)

  $\ell = 0, \quad 1, \quad 2, \quad 3, \ldots$

  Notation: $s, \quad p, \quad d, \quad f, \ldots$ > H-atom

- $\vec{J} = \vec{L} + \vec{S} \Rightarrow$ Quantum number j (multiple values) [with m_j's behind j]

Atomic Term Symbol (H-atom)

$$\boxed{{}^{2s+1}\ell_j} \quad \text{labels energy levels} \qquad (28)$$

notation provides information on s, ℓ, j

e.g. H-atom ground state → 1s $(n=1, \ell=0)$

→ $\ell=0 \Rightarrow$ "S" in the middle

one electron : $2s+1 = 2$ [go to upper left-hand corner]

spin ½

$\ell=0,\ s=\frac{1}{2} \Rightarrow j=\frac{1}{2}$ only [go to lower right-hand corner]

$$\boxed{\begin{array}{l}\text{G.S. of H-atom is described by electron configuration (1s)} \\ \text{and Term Symbol } {}^{2}S_{1/2} \quad \text{OR } 1s\ {}^{2}S_{1/2}\end{array}}$$

$2\cdot\frac{1}{2}+1 \to {}^2$, $S \leftarrow \ell=0$, $\frac{1}{2} \leftarrow j=\frac{1}{2}$

An excited state : Crude description $2p \leftarrow \ell=1$ ("P" in the middle)

$j=\frac{3}{2}$, $j=\frac{1}{2}$ one-electron: $2\cdot\frac{1}{2}+1=2$ (upper LH corner)

Could be

$2p\ {}^{2}P_{1/2}$ (2 states) OR $2p\ {}^{2}P_{3/2}$ (4 states) ← Recall: fine structure [They have slightly different energies]

[Data Tables use these labels]

Making connections

This is the point of using (l, m_l, s, m_s) <u>vs</u> $(l, s, \boxed{j}, m_j)$

- Since spin-orbit interaction is always there (except for atoms with total $\vec{S}=0$)

Using $(\underbrace{l, s, j}, m_j)$ is a better choice

Term Symbol gives l, s, j

[m_j comes in only when an $\underbrace{\text{external magnetic field}}_{\text{anomalous Zeeman effect}}$ is applied]

General Atoms

- $\vec{L} = \sum_{i} \vec{l}_i$ ← orbital AM of i^{th} electron; i ← all electrons

  ↖ then L^2 can take on $L(L+1)\hbar^2$

  ; $\vec{S} = \sum_i \vec{s}_i$ ← spin AM of i^{th} electron

  ↖ then S^2 can take on $S(S+1)\hbar^2$

[Values of L? By rule of adding AM's]

$$L = 0,\ 1,\ 2,\ 3,\ \ldots$$

Notation: S, P, D, F, ...

[Values of S? By adding AM's]

$(2S+1)$ appears in upper LH corner

Definition: $\boxed{\text{Term Symbol is } \ {}^{2S+1}L_J \ \text{ for all atoms}}$ (29)

Sometimes, principle quantum number n is included as: $n\,{}^{2S+1}L_J$

J. Hydrogen Atom Data

Energy levels deduced from precise spectroscopy

Configuration	Term	J	Level(cm^{-1})
$1s$	^2S	1/2	0.0000
$2p$	^2P	1/2	82258.9191
		3/2	82259.2850
$2s$	^2S	1/2	82258.9544
$3p$	^2P	1/2	97492.2112
		3/2	97492.3196
$3s$	^2S	1/2	97492.2217
$3d$	^2D	3/2	97492.3195
		5/2	97492.3556
$4p$	^2P	1/2	102823.8486
		3/2	102823.8943
$4s$	^2S	1/2	102823.8530
$4d$	^2D	3/2	102823.8942
		5/2	102823.9095
$4f$	^2F	5/2	102823.9095
		7/2	102823.9171
$5p$	^2P	1/2	105291.6287
		3/2	105291.6521
$5s$	^2S	1/2	105291.6309
$5d$	^2D	3/2	105291.6520
		5/2	105291.6599
$5f$	^2F	5/2	105291.6598
		7/2	105291.6637
$5g$	^2G	7/2	105291.6637
		9/2	105291.6661
H	***Limit***		**109678.7717**

Data taken from NIST (US National Institute of Standards and Technology) websites

Same Data: Ordered in energy and Cleaver Term Symbols

	Configuration	Term	J	Level(cm^{-1})	Notes
	1s	1s $^2S_{1/2}$	1/2	0.0000	
n=2	2p	2p $^2P_{1/2}$	1/2	82258.9191	same n = 2, same j = ½ (slightly different)†
n=2	2s	2s $^2S_{1/2}$	1/2	82258.9544	
n=2	2p	2p $^2P_{3/2}$	3/2	82259.2850	
n=3	3p	3p $^2P_{1/2}$	1/2	97492.2112	same n = 3, same j = ½ (slightly different)†
n=3	3s	3s $^2S_{1/2}$	1/2	97492.2217	
n=3	3p	3p $^2P_{3/2}$	3/2	97492.3196	same n=3, same j = 3/2 (almost identical)
n=3	3d	3d $^2D_{3/2}$	3/2	97492.3195	
n=3	3d	3d $^2D_{5/2}$	5/2	97492.3556	
n=4	4p	4p $^2P_{1/2}$	1/2	102823.8486	same n=4, same j = ½ (slightly different)†
n=4	4s	4s $^2S_{1/2}$	1/2	102823.8530	
n=4	4p	4p $^2P_{3/2}$	3/2	102823.8943	same n=4, same j = 3/2 (almost identical)
n=4	4d	4d $^2D_{3/2}$	3/2	102823.8942	
n=4	4d	4d $^2D_{5/2}$	5/2	102823.9095	same n=4, same j = 5/2 (identical)
n=4	4f	4f $^2F_{5/2}$	5/2	102823.9095	
n=4	4f	4f $^2F_{7/2}$	7/2	102823.9171	
	H	***Limit***		**109678.7717**	

Aside: For those who know high-school H-atom description (too) well

$$\left.\begin{matrix} 2s \\ 2p \end{matrix}\right\} \left.\begin{matrix} \underline{8 \text{ states}} \\ 2s\ (2 \text{ states}) \\ 2p\ (6 \text{ states}) \end{matrix}\right] \begin{matrix} \text{same} \\ \frac{-13.6}{4}\text{ eV} \\ \text{energy} \end{matrix}$$

$\underbrace{\hphantom{xxxxxxxxxxxx}}$ almost correct

QM: $-\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{4\pi\varepsilon_0 r} = \hat{H}_{atom}$

$$\left.\begin{matrix} 2p & {}^2P_{1/2} & (2 \text{ states}, m_j = \pm 1/2) \\ 2s & {}^2S_{1/2} & (2 \text{ states}, m_j = \pm 1/2) \\ 2p & {}^2P_{3/2} & (4 \text{ states}, m_j = \pm 3/2, \pm 1/2) \end{matrix}\right] \begin{matrix} \text{slightly} \\ \text{different} \\ \text{in} \\ \text{energy} \end{matrix}$$

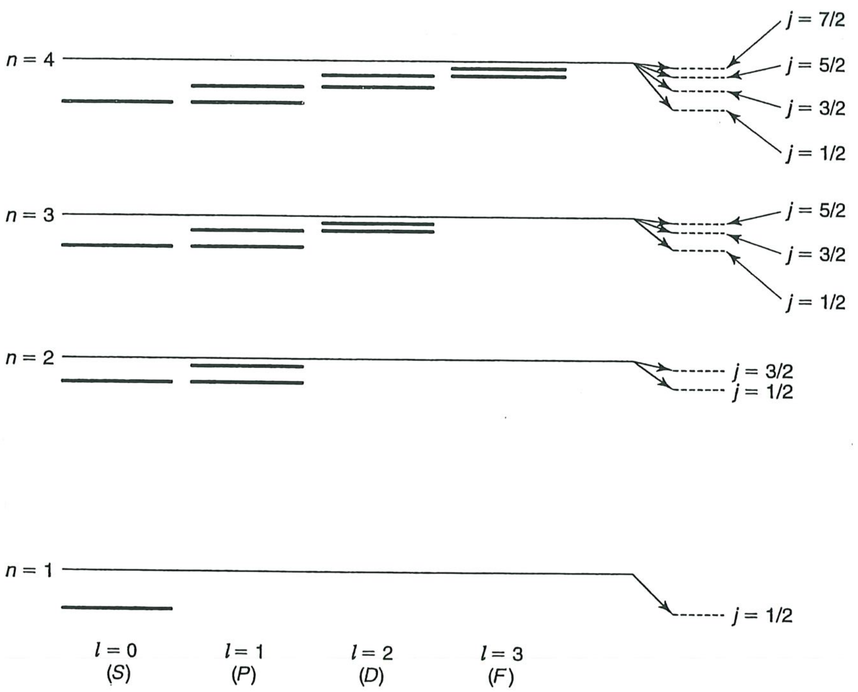
also $\underline{8 \text{ states}}$

$\underbrace{\hphantom{xxxxxxxxxxxx}}$ high precision spectroscopy

- How well $H'_{so} + H'_{rel}$ works in comparison with data?

Recall[+]: $$E_n = -\frac{13.6(eV)}{n^2}\left[1 + \frac{\alpha^2}{n}\left(\frac{1}{j+\frac{1}{2}} - \frac{3}{4n}\right)\right] \quad (27)$$ Fine structure of Hydrogen atom

[same n and same j are expected to have the same energy]



Energy levels of hydrogen, including fine structure (not to scale). (26)

$\longleftarrow$ $2s\ ^2S_{1/2}$ $2p\ ^2P_{1/2}$ (same n, same j)

According to Eq. (27) Same energy (fine structure only)

[is it true?]

[+] Included spin-orbit interaction and relativistic correction

▪ Highly precise measurements

[Data]

82258.9544 cm^{-1} $2s\ ^2S_{1/2}$ — $2p\ ^2P_{1/2}$ 82258.9191 cm^{-1} — differ by $\underbrace{\sim 0.035\ cm^{-1}}_{\text{tiny tiny!}}$

(similar for other same n and j levels)

▪ Schrödinger Equation + Spin-orbit Interaction + Relativistic correction almost do the job! [Highly accurate already]

▪ The tiny tiny difference is called the Lamb Shift†, which requires QED (Quantum electrodynamics) beyond the scope of undergraduate courses.

Suggestion for further reading/studies (Optional)

▪ Work out everything for hydrogen atom, from Bohr to QED!

† Willis Lamb was awarded the (big) Nobel Prize in 1955 for the tiny tiny difference!

Big Picture Summarized
Hydrogen Atom

(Bohr)

($\hat{H}_0$) Schrödinger with $-\frac{e^2}{4\pi\varepsilon_0 r}$ only

With $\hat{H}'_{SO}$ and $\hat{H}'_{rel}$

[Since spin is also a relativistic effect, both are relativistic in nature (Dirac)]

QED

[effect of vacuum]

(Bethe)

$n=2$

[including $l=0,1$ and spin $\uparrow,\downarrow$]

[8]

\# states

$l=1,\ j=3/2$ [4]

~10 GHz

$(l=0,\ j=1/2)$ $(l=1,\ j=1/2)$

[2] [2]

$2\ ^2P_{3/2}$

$2\ ^2S_{1/2}$

$2\ ^2P_{1/2}$

1057 MHz

(Lamb (1947) Shift)

Our QM can explain up to this fine structure level

Need to learn quantum field theory

Understanding Fine Structure: Big Picture Summarized

- Baby level: $V(r) = -\frac{e^2}{4\pi\varepsilon_0 r}$ only, TISE $\Rightarrow E_n^{(0)} = -\frac{13.6\,(eV)}{n^2}$ Works quite well
- $$\hat{H} = \hat{H}_0 + \underbrace{\hat{H}'_{so} + \hat{H}'_{rel}}_{\text{treated perturbatively}}$$ (spin-orbit interaction and relativistic correction) [both are important in special case of H-atom]

$$E_n = -\frac{13.6\,(eV)}{n^2}\left[1 + \frac{\alpha^2}{n}\left(\frac{1}{j+\frac{1}{2}} - \frac{3}{4n}\right)\right]$$

- shift of order α^2
- predicted same energy for same n, same j
- shift depends on j

- E_n works very well with data
  - splitting accordingly to j
  - spectral line split into closely spaced lines [$\vec{B}_{ext} = 0$ though]
- Remaining tiny discrepancy with data requires quantum electrodynamics

Techniques Invoked

- Identifying $\hat{H}'$, $\vec{\mu}_s$ and $\vec{S}$, EM, mc^2
- $\vec{J} = \vec{L} + \vec{S}$, properties of angular momenta in QM
- 1st order perturbation Theory
- Evaluating† $\left\langle \frac{1}{r^3} \right\rangle_{nl}$, $\left\langle \frac{1}{r^2} \right\rangle_{nl}$, $\left\langle \frac{1}{r} \right\rangle_{nl}$ for H-atom states (optional)
- Compare with data

Refs: QM techniques, see Griffiths' book, Rae's book
Physical Picture, see Quantum Physics / Modern Physics books

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† For those who want to evaluate $\langle r^k \rangle$ for H-atom states, see (optional) discussion in Griffiths' book. Results are listed in Bransden and Joachain's "Physics of Atoms and Molecules".

Aside: What's next? Path of Further Reading/Learning

- Dirac's Equation for an electron
  - consistent with special relativity $E = \sqrt{m^2c^4 + c^2p^2}$

    what to do with $\sqrt{}$?
  - still a single-electron problem
  - Obtain Eq. (27)
- How to quantize EM field? [proton, electron interact]

  How to further change the QM Dirac Equation into a field theory?

  (quantum field theory)

Refs: A.I.M. Rae, "Quantum Mechanics" (4th ed.) has an easy-to-read section introducing the Dirac Equation.

F. Gross, "Relativistic Quantum Mechanics and Field Theory" takes you directly to research level.