# H. Hydrogen Atom Data

Energy levels deduced from precise spectroscopy

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

| 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** |

# Same Data: Ordered in energy and Cleaver Term Symbols

| | Configuration | Term | $J$ | Level($cm^{-1}$) | |
|---|---|---|---|---|---|
| | 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)† |
| | 2s | 2s $^2S_{1/2}$ | 1/2 | 82258.9544 | |
| | 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)† |
| | 3s | 3s $^2S_{1/2}$ | 1/2 | 97492.2217 | |
| | 3p | 3p $^2P_{3/2}$ | 3/2 | 97492.3196 | same n=3, same j = 3/2 (almost identical) |
| | 3d | 3d $^2D_{3/2}$ | 3/2 | 97492.3195 | |
| | 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)† |
| | 4s | 4s $^2S_{1/2}$ | 1/2 | 102823.8530 | |
| | 4p | 4p $^2P_{3/2}$ | 3/2 | 102823.8943 | same n=4, same j = 3/2 (almost identical) |
| | 4d | 4d $^2D_{3/2}$ | 3/2 | 102823.8942 | |
| | 4d | 4d $^2D_{5/2}$ | 5/2 | 102823.9095 | same n=4, same j = 5/2 (identical) |
| | 4f | 4f $^2F_{5/2}$ | 5/2 | 102823.9095 | |
| | 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

2p
2s
2p

8 states: 2s (2 states), 2p (6 states) — same $\frac{-13.6}{4}$ eV energy

$\underbrace{\qquad\qquad}$ almost correct

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

2p $^2P_{1/2}$ (2 states, $m_j = \pm 1/2$)
2s $^2S_{1/2}$ (2 states, $m_j = \pm 1/2$)
2p $^2P_{3/2}$ (4 states, $m_j = \pm 3/2, \pm 1/2$)

slightly different in energy

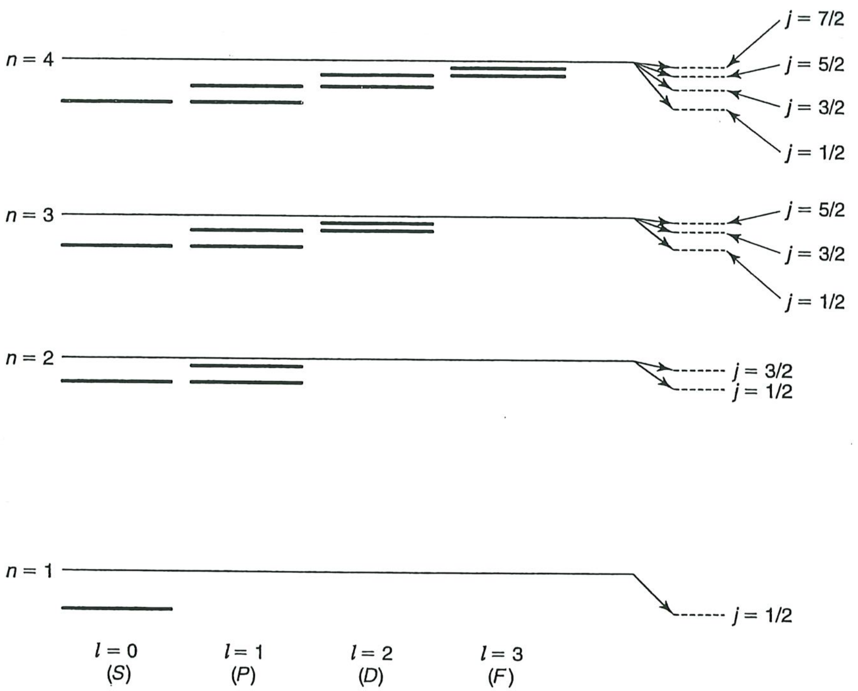
also 8 states

$\underbrace{\qquad\qquad}$ high precision spectroscopy

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

Recall[+]: $$E_n = -\frac{13.6\,(eV)}{n^2}\left[1 + \frac{\alpha^2}{n}\left(\frac{1}{j+\frac{1}{2}} - \frac{3}{4n}\right)\right] \quad (26)$$ 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)

According to (26) Same energy (fine structure only)

$2s\ {}^2S_{1/2}$ $2p\ {}^2P_{1/2}$

(same $n$, same $j$) [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)

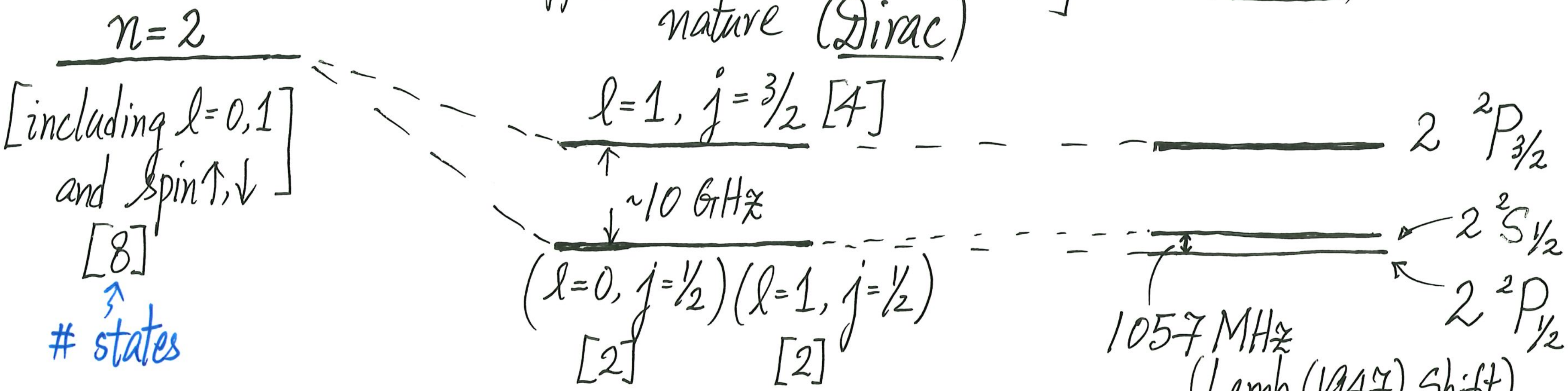
($\hat{H}_0$) Schrödinger with $-\dfrac{e^2}{4\pi\varepsilon_0 r}$ only

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)




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 $\alpha^2$
- 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
- $1^{st}$ order perturbation Theory
- Evaluating† $\left\langle \frac{1}{r^3} \right\rangle_{n\ell}$, $\left\langle \frac{1}{r^2} \right\rangle_{n\ell}$, $\left\langle \frac{1}{r} \right\rangle_{n\ell}$ for H-atom states
- 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".