Atomic Physics

[Using Quantum Mechanics to understand physics of atoms]

- Various Effects introduced within the context of H-atom[†]
  - Zeeman effect [effects of applied magnetic field on spectral lines]
  - Fine structure [spin-orbit interaction, no applied field needed]
  - orbital angular momentum (AM), spin AM & total AM
  - "21-cm physics" [hyperfine structure in H-atom]

([†]These effects are applicable to other atoms)

- Other atoms and Periodic Table
  - He atom as example of multi-electron atoms
  - Idea behind self-consistent approach in independent-particle approximation
  - Anti-symmetric requirement for many-electron wavefunction and Pauli Exclusion Principle
  - Hund's rules
  - Periodic Table

A. Review[†] : Hydrogen Atom and do the results work

Does $\left[-\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{4\pi\varepsilon_0 r}\right]\psi(\vec{r}) = E\psi(\vec{r})$ really work?

- Hydrogen atom [basic form (simplest form)]

TISE: $\left[-\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{4\pi\varepsilon_0 r}\right]\psi(r,\theta,\phi) = E\,\psi(r,\theta,\phi)$ [Nucleus (proton) at (0,0,0)]

(one-electron problem)

$$\psi_{n\ell m_\ell}(r,\theta,\phi) = \underbrace{R_{n\ell}(r)}_{\text{Laguerre polynomials}} \cdot \underbrace{Y_{\ell m_\ell}(\theta,\phi)}_{\text{spherical harmonics}}$$

Allowed energies (energy eigenvalues) are $[E_n = -R_\infty/n^2]$

$$E_n \cong -\frac{13.6}{n^2}\ \text{eV}$$

depends on n only (accidental degeneracy)

[degeneracy comes from values of ℓ AND values of m_ℓ for given ℓ]

† This is a part of notes on Quantum Theory of the H-atom. This is included here for your easy references.

H-atom energy levels [from solving $\left[-\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{4\pi\varepsilon_0 r}\right]\psi = E\psi$]

many more $\vdots \quad \vdots$

$n=3$ — E_3 $\quad l=0$ (3s), $l=1$ (3p), $l=2$ (3d)

$n=2$ — E_2 $\quad l=0$ (2s)[1], $l=1$ (2p)[3]

$(1+3)\times \underset{\text{spin}}{2} = 8$ (states)

$n=1$ — E_1 $\quad l=0$ (1s)

[$Y_{lm_l}(\theta,\phi)$] for given l,

$m_l = \underbrace{-l, -l+1, \cdots, 0, \cdots, l-1, l}_{(2l+1)\text{ values}}$

Q: How correct is this in view of spectroscopic data?

Quick Answer: Almost correct! But...

Hydrogen atom data [see NIST (USA) site]

National Institute of Standards and Technology

Google "NIST database"

- Talking to experimentalist

physics students: energy eV (electron-volt) $[1.602 \times 10^{-19}\ J]$

frequency f OR ν (Hz) $[s^{-1}]$

angular frequency $\omega = 2\pi f$

EM waves/Light in vacuum $c = f \cdot \lambda = \nu \cdot \lambda$ ← wavelength [m OR cm OR nm]

Spectroscopists:

Use wave number $\left(\frac{1}{\lambda}\right)$ to represent the frequency (hence photon energy) observed in transitions and thus in spectrum

- Wave number

$\frac{1}{\lambda}$ (unit: cm^{-1}) $\boxed{\text{Meaning: How many wavelengths in one cm?}}$

e.g. $\lambda = 6.565 \times 10^{-5}$ cm $= 656.5$ nm (visible)

$\frac{1}{\lambda} \equiv \bar{\nu} = 1.523 \times 10^{4}\ cm^{-1}$ (wave number)

- Let ΔE be difference in energies between two states

photon

$\Delta E = h\nu$ (photon, Planck) [express in frequency ν]

$\frac{\Delta E}{c} = \frac{h\nu}{c} = \frac{h}{\lambda}$ (using $c = \nu \cdot \lambda$)

$\Rightarrow \frac{\Delta E}{hc} = \underbrace{\frac{1}{\lambda}}_{\text{wave number}} = \frac{\nu}{c} \equiv \bar{\nu}$ (can use $\bar{\nu} = \frac{1}{\lambda}$ to present data (ΔE))

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 (a). From 1s (assigned "0 cm^{-1}") to Limit (ionized),

$$\Delta\bar{\nu} = 109678.7717 \ cm^{-1}$$

corresponds to $\Delta E = 13.59843 \ eV$

(works very well!)

<u>Quick fix</u>

- Using reduced mass μ instead of electron mass m

  ($\because$ two-body problem although $m \ll$ mass of nucleus (proton))

$$\frac{1}{\mu} = \frac{1}{m_p} + \frac{1}{m}$$

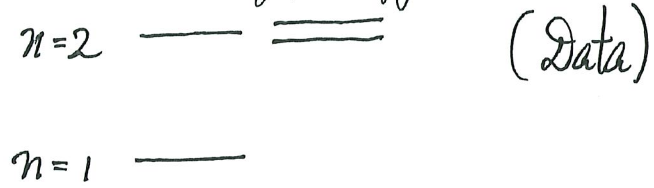
bring value closer to data (with no additional effort)

(b) Hydrogen Atom Data (from NIST, USA)

Configuration	Term	J	Level (cm^{-1})	
1s	^2S	½	0.0000	[ground state]
2p	^2P	½	82258.9191	Very close, but different!
		3/2	82259.2850	
2s	^2S	½	82258.9544	
⋮	⋮	⋮		

Almost correct! But...

Schematically (not to scale, highly exaggerated)



Why is it so?

How can these account for the n=2 (total 8) states?

$\therefore$ There are more to explore about the hydrogen atom

What can be learned from hydrogen atom are applicable to other atoms (molecules, solids)!

∴ There are more to explore in Hydrogen Atom!

- Relativistic correction? $\underbrace{-13.6\text{ eV}}_{\text{GS energy}}$ vs $\underbrace{0.511\text{ MeV}}_{\text{electron's } mc^2}$

  OR $$\underbrace{-\frac{\hbar^2}{2m}\nabla^2}_{\text{Newtonian k.e. term?}} - \frac{e^2}{4\pi\varepsilon_0 r}$$

- Electron has spin ½

  spin of electron (tiny magnetic) couples with $\underbrace{\text{electron's own motion}}_{\vec{r}\times\vec{p}=\vec{L}}$

  $\underbrace{\text{spin-orbit interaction?}}_{\text{an important concept in many modern developments in physics}}$

$\boxed{\text{To handle these problems, we need some approximation methods!}}$

Physics Ideas

- A good physical problem (H-atom here) will lead to continual development in physics
- Spectroscopy (光譜學) is a high precision experimental technique (atoms, molecules, solids)
- Physics is advanced by putting theories and accurate experiments together. It is an experimental science.