# Astro 501: Radiative Processes
## Lecture 28
April 1, 2013

Announcements:
- **Problem Set 8** due 5pm today
- **Problem Set 9** due 5pm next Monday

Last time: finished continuum emission processes

Today and henceforth:
radiation and bound states

# Atomic Structure

# Atomic Structure: Order of Magnitude

Atoms and molecules inherently *quantum* systems

Cowgirl/cowboy view of hydrogen:
*quantum* bound state of electron around proton, with energy

$$E = \frac{p^2}{2m_e} - \frac{e^2}{r} \tag{1}$$

but Heisenberg: $rp \geq \hbar/2$

Wild West: cowgirl/cowboy approximation $p \sim \hbar/r$

$$E = \frac{\hbar^2}{2m_e r^2} - \frac{e^2}{r} \tag{2}$$

*Q: so how to find ground state?*

## Heisenberg-ized sketch of hydrogen energy

$$E = \frac{\hbar^2}{2m_e r^2} - \frac{e^2}{r} \tag{3}$$

ground state: $E$ is *minimum*

$$\partial_r E = -\frac{\hbar^2}{m_e r^3} + \frac{e^2}{r^2} = 0 \tag{4}$$

gives electron radius $r_{\text{min}} \equiv a_0$:

$$a_0 = \frac{\hbar^2}{e^2 m_e} = 0.05 \text{ nm} \tag{5}$$

and electron energy $E(r_{\text{min}}) \equiv E_1$:

$$E_1 = -\frac{e^4 m_e}{2\hbar^2} = -\frac{1}{2}\alpha^2 m_e c^2 = 13.7 \text{ eV} \tag{6}$$

where $\alpha = e^2/\hbar c \approx 1/137$

*Q: how do these compare with results of honest calculation?*

# Hydrogen Atom: Honest Non-Relativistic Results

*non-relativistic* Schrödinger ignores relativistic effects

- electron (and proton) spins absent from Hamiltonian
  $\rightarrow$ electron orbit properties independent of spin

for hydrogen-like species: single electron, nuclear charge $Z$

*ground state* properties

- energy $E_1 = -Z^2 e^4 m_e / 2\hbar^2$
- mean radius $\langle r_1 \rangle = a_0 / Z$
- electron expected speed $\langle v_1 \rangle = Ze^2/\hbar = Z\alpha c$
  so that $\beta_1 = v_1/c = Z\alpha \approx Z/137 \ll 1$ for most atoms
  if not: non-relativistic is bad approximation!

*Q: what about excited states: how many? Q: how do $E_n, r_n, v_n$ vary with $n$?*

excited states, ignoring spin effects (*non-relativistic*):
for each integer $n = 1, 2, 3, \ldots$

- $E_n = E_1/n^2$
- $\langle r \rangle_n = n^2 r_1$
- $\langle v \rangle_n = v_1/n$

Lessons

- H has an infinite "tower" of bound states
- $\langle r \rangle_n \propto n^2$: *principal quantum number* $n$
  controls *radial* part of wavefunction
- as $n \to \infty$: bigger radius, slower, more weakly bound

*hydrogen wavefunction*: 3-D system → need 3 quantum numbers
*Q: what are the other two?*

Non-relativistic hydrogen wavefunction: states specified by

- *principal* quantum number $n = 1, 2, \ldots$
  controls wavefunction dependence on $r$
- *orbital angular momentum* $\ell = 0, 1, \ldots, n-1$
  $\hat{L}^2 \psi = \ell(\ell+1)\hbar^2 \psi$
  controls wavefunction dependence on $\theta$
- *$z$-projection of $\hat{L}$* $m = -\ell, \ldots, +\ell$
  controls wavefunction dependence on $\phi$

in non-relativistic case: energy only depends on $n$
all states with fixed $n$ are *degenerate* (same energy)

- at each $\ell$ value: $2\ell + 1$ “substates” of different $m$
- each of which has 2 possible $e$ spin states: $s_z = \pm 1/2$
- at each $n$: a total of $2 \sum_{\ell=0}^{n-1} 2\ell + 1 = 2n^2$ states
  all with the same energy

*Q: effect of full relativistic treatment?*

# Realistic Atoms

for *hydrogen*

Schrödinger: $v_n/c = \alpha/n \ll 1$, $|E_n| = \alpha m_e c^2/2 \ll m_e c^2$

→ electron motion is (very) non-relativistic: approx justified!

→ expect relativistic corrections to be small

Full relativity: Dirac equation

Hamiltonian includes spins of electron and proton

new interactions are $\propto \beta$ or $\beta^2$ → small corrections

→ lifts degeneracy of levels at same $n$

# Multi-Electron Atoms

in first (i.e., non-relativistic) approximation

- principal quantum number $n$ still appears
- spins do not appear in Hamiltonian → atom state only depends on total orbital angular momentum quantum number $L$
- due to Pauli → atom state still does depends on total electron spin quantum number $S$
- states with same $n$, $L$ and $S$ are degenerate

for realistic *multi-electron atoms*
spin interactions are relativistic perturbations
break (“lift”) degeneracy at same $n$, $L$, $S$

To a good first approximation:

- wavefunction (state) of each electron is *independent* of other electrons
- except that Pauli principle is crucial *Q: how?*

# Building Atoms

Pauli: no two (or more) fermions
can occupy the same quantum state

electrons are fermions, each with $s = 1/2$
$\rightarrow$ projection $s_z = \pm 1/2$ adds one last quantum number

"assembly" of multi-electron atoms, to first approximation,

- state of *each* electron has fixed $n$ and $\ell$
  with $\ell = 0, 1, \ldots, n - 1$ (like H-atom)
- but order of state energies *not* always like H-atom
- states "filled" from lowest energy up, according to Pauli
- fill by "subshells" = states with same $(n, \ell)$
  while "shells" are *all* states at fixed $n$
- atom ground state: electrons in lowest possible states

**electron configuration**: distribution of states in atom

- notation: $(n, \ell)$ electron state ("subshell") is $n\Upsilon$
  with $\Upsilon = s, p, d, f, \ldots$ for $\ell = 0, 1, 2, 3, \ldots$
- multiplicity: if $k$ electrons in subshell: $n\Upsilon^k$

for example:

- lowest shell is $(n, \ell) = (1, 0)$
  $\ell = 0$ has only $m = 0$; so filled shell is $1s^2$
- next subshell is $(n, \ell) = (2, 0)$; filled is $2s^2$
- then $(n, \ell) = (2, 1)$: $\ell = 1$, $p$ state
  $m = -1, 0, 1$ allowed, so filled subshell is $2p^6$

`www:  sketches of` $\ell$ `states in 3D`

*Q: how do we know the order of filling states?*
*that is: what determines the ranking of energy levels?*

# Energy Level Rankings

*electron configuration* = set of single-electron states
for atom ground state is the set that places electrons
in the lowest possible energies consistent with Pauli
each subshell filled before beginning next shell

empirical rules of thumb: good for atoms of low $Z$
most of interest to astrophysics

"*Aufbau principle*" – $(n, \ell)$ ordering

▷ states filled in order of increasing $n + \ell$

▷ when two states have same $n + \ell$
filled in order of increasing $n$

*Q: Li states ($Z = 3$)? C ($Z = 6$?) Si ($Z = 14$)?*

- states filled in order of increasing $n + \ell$
- when two states have same $n + \ell$
  filled in order of increasing $n$

lithium: $Z = 3$
filled $1s^2$ = 2 states, $2s^1$ half-filled: $\boxed{1s^2 2s}$

carbon: $Z = 6$
filled: $1s^2 2s^2$ = 4 states, $2p^2$ partial = 2 states
$\boxed{1s^2 2s}$

silicon: $Z = 14$
filled: $1s^2 2s^2 2p^6 3s^2$ = 12 states, $3p^2$ partial = 2 states
$\boxed{1s^2 2s^2 2p^6 3s^2 3p^2}$

`www:  online data`

Aufbau principle gives ordering of $(n, \ell)$ subshells
further splitting at fixed $(n, \ell)$ depending on electron spins

recall: total atomic angular momentum $\vec{J} = \vec{L} + \vec{S}$ sums

- total $e$ orbital angular momenta $\vec{L}$, eigenstates $\hbar L$
  total $e$ spins $\vec{S}$, eigenstates $\hbar S$
- filled subshells have $L_{\text{shell}} = 0 = S_{\text{shell}}$
  so $L$ and $S$ set only by *unfilled subshells*

# Hund's Rule

Hund's rule: energy level orderings in $(n, \ell)$ subshell
for a fixed electron configuration $=$ fixed unfilled $(n, \ell)$ subshell
then the *lowest energy* state(s) are the one(s) with

- ▷ the *largest possible* total spin $S$
- ▷ the *largest possible* total $L$ for this maximal $S$
- ▷ for subshells half-filled our less: pick lowest $J$
  otherwise pick highest $J$

*Q: for $np^2$, which $L, S$ has lowest energy? what $J$ does this have?*

for $np^2$: 2 electrons, each with $\ell = 1$
possible states: $m = -1, 0, +1$, $s_z = \pm 1/2$

lowest energy is
▷ the *largest possible* total spin $S$
this is $S = 1$, gotten for $s_{z1} = s_{z1}$ and so $S_z = \pm 1$

▷ the *largest possible* total $L$
Pauli: cannot both be $m = \pm 1$, not same $m, s_z$: can't have $L = 2$
maximal $L$ when $m_1 = 1$ and $m_2 = 0$ (or $m_1 = -1$ and $m_2 = 0$)
$\rightarrow L = 1$

▷ for subshells half-filled our less: pick lowest $J$
since $J \in (|L - S|, L + S)$, here min at $J = 0$

**Spectroscopic Notation** for $(L, S, J)$ states or "terms"
${}^{2S+1}\mathcal{L}_J$, with $\mathcal{L} = S, P, D, \ldots$ for $L = 0, 1, 2, \ldots$
here: $np^2$ lowest-energy state has $(L, S, J) = (1, 1, 0) = {}^3P_0$
`www: online data`

# Hund's Rules: Physical Origin

then the *lowest energy* state(s) are the one(s) with

▷ the *largest possible* total spin $S$

largest $S \rightarrow$ preference for spins aligned

but then Pauli demands different $m$

$\rightarrow$ fill $m$ states with one $e$ each before "doubling up"

$\rightarrow$ "*bus seat rule*"

▷ the *largest possible* total $L$ for this maximal $S$

largest $L \rightarrow$ preference for orbit planes aligned

orbit in "same direction" and not opposite

$\rightarrow$ $e$ avoid each other, have nucleus in between

$\rightarrow$ decrease $e$ screening of nuclear charge, and $e$ repulsion

# Atomic Fingerprints

atomic wavefunctions, states are complex function of nuclear charge and number of electrons
→ resulting energy levels *unique* to each atom
and to each ionization state, e.g., $C^{3+} \equiv$ C iv

lesson: atomic spectra are "fingerprints"
observed lines can pin down identity and ionization state of emitting atom

sometimes even the mere existence of an element tells an important story
1950's: technetium (Tc) detected in some AGB stars
*Q: what's an AGB star?*
*Q: why is it s Big Deal to find Tc in them?*