# **Astronomy 501: Radiative Processes**

Lecture 22

Oct 14, 2022

Announcements:

- **Problem Set 6 due Friday ... formally**
  but Monday is okay if you were expecting more time :)
- **Problem Set 7 due next Friday**
- Exams back on Monday; don't miss that class!

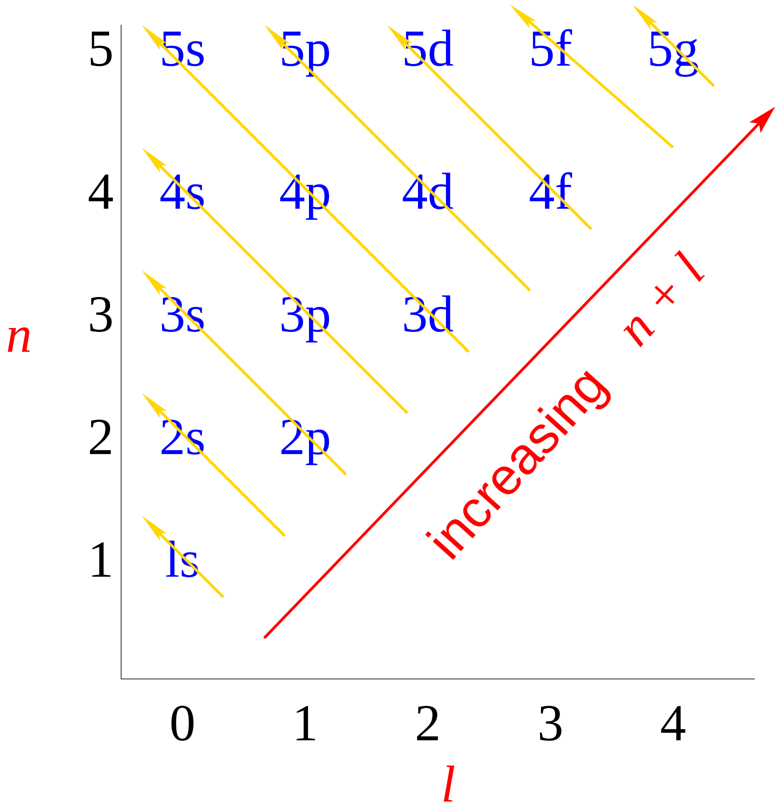
Last time: the structure of atoms

- Aufbau rule for filling states by $n, l$ values
- key feature: filled vs unfilled shells

*Q: total $L$ and $S$ values for filled shell?*

*Q: what determines the $L$ and $S$ values all $e$ in an atom?*

aufbau principle




- filled in order of increasing $n + \ell$
- for same $n + \ell$: lowest $n$ first

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

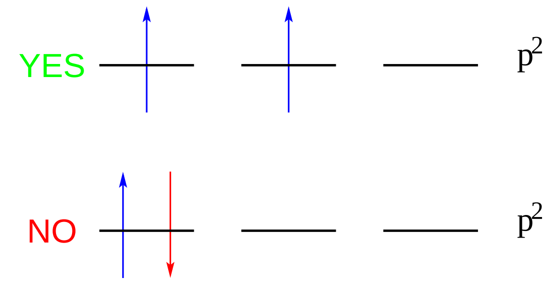
Hund's rule: energy level orderings in $(n, \ell)$ subshell
for a fixed electron configuration = fixed unfilled $(n, \ell)$ subshell
then the *lowest energy* state(s) are the one(s) with

▷ the *largest possible* total spin $S$
▷ the *largest possible* total $L$ for this maximal $S$
▷ for subshells half-filled or 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 $m_2 = 0$)

$\to L = 1$

▷ for subshells half-filled or 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 $L = 0, 1, 2, \ldots$

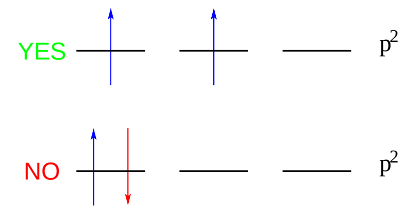
here: $np^2$ lowest-energy state has $(L, S, J) = (1, 1, 0) = {}^3P_0$

`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

$\rightarrow$ resulting energy levels *unique* to each atom
and to each ionization state, e.g., $\mathrm{C}^{3+} \equiv \mathrm{C\ IV}$

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?*

# Annie Cannon and the Mystery of Stellar Hydrogen Lines

turn of 20th century: birth of stellar spectroscopy
stellar spectra classified according to spectral lines

master classifier: Annie Jump Cannon

later also determined stellar temperatures

**hydrogen lines** are prominent in some stars
but strange result: `www: data`

- H lines are weak for hottest stars
- H lines are weak for coldest stars
- H lines strongest for middle temperatures

*Myster: why this behavior?*

# Thermal Population of Atomic States

if atoms can interact, $e$ not necessarily all in ground state
in general: a big job to calculate population of atomic states

but as usual: much simplification if *thermodynamic equilibrium*

Boltzmann: consider a single atomic state having energy $E_i$
for an ensemble of $n_{\text{tot}}$ atoms in thermodynamic equilibrium at $T$
the population = numbers $n_i$ of atoms in state $i$ is

$$n_i = \frac{n_{\text{tot}}}{Z} e^{-E_i/kT} \tag{1}$$

interpret $p_i = e^{-E_i/kT}/Z$ as the probability that an atom
is found in state $i$
*Q: how do we find the normalization constant $Z$?*

each state has population $n_i$, and if we sum all states must recover total population $n$, so

$$n_{\text{tot}} = \sum_{\text{states } i} n_i \frac{n_{\text{tot}}}{Z} \sum_{\text{states } i} e^{-E_i/kT} \tag{2}$$

and thus we find the **partition function**

$$Z = \sum_{\text{states } i} e^{-E_i/kT} \tag{3}$$

and thus $p_i = e^{-E_i/kT} / \sum_j e^{-E_j/kT}$ and clearly $\sum_i p_i = 1$

in many cases, more than one atomic state has energy $E_i$
let the number of states with $E_i$ be $g_i$
i.e., $g_i$ counts the "degeneracy" at level $E_i$
then the number of states with energy $E_i$ is

$$n(E_i) = g_i \frac{n}{Z} e^{-E_i/kT} \tag{4}$$

and the partition function can be written

$$Z = \sum_{\text{levels } E_i} g_i e^{-E_i/kT} \tag{5}$$

consider two states of energies $E_1$, $E_2 > E_1$
for an ensemble of atoms in thermodynamic equilibrium at $T$
the populations = numbers $n_1$, $n_2$ of atoms the states
is given by

$$\frac{n_2}{n_1} = \frac{g_2}{g_1} e^{-(E_2-E_1)/kT} \tag{6}$$

note that for a given atomic system and temperature $T$
the partition function $Z = \sum_{\rm states} g_i e^{-E_i/kT}$ is *a number*

*Q: physical dimensions of $Z$?*

*Q: what does this number represent physically? hint: roughly at what levels does the sum effectively terminate?*

*Q: what is $Z$ as $kT \to 0$?*

roughly:
the partition function counts all states with $E_i \lesssim kT$
so $Z \approx$ number of states with $E_i \lesssim kT$
$\rightarrow$ i.e., "partitions" full set of atomic states
into those "accessible" at $T$

as $kT \rightarrow 0$: all states suppressed except ground state $E_1 = 0$
so $Z \rightarrow g_1$, the degeneracy of the ground state

consider the partition function for *atomic hydrogen*
where $E_n = -B/n^2$, with $B = |E_1| = e^4 m_e / 2\hbar^2$, the binding energy
recalling that the shell each $n$ has degeneracy $g_n = 2n^2$:

$$Z(\mathrm{H}) = 2 \sum_{n=1}^{\infty} n^2 e^{\beta B/n^2} \tag{7}$$

where $\beta = 1/kT$

*Q: roughly what is the value of $Z$(H)? why? implications?*

neutral hydrogen partition function, with $\beta = 1/kT$

$$Z(\mathrm{H}) = 2 \sum_{n=1}^{\infty} n^2 e^{\beta B/n^2} \tag{8}$$

$e^{\beta B/n^2} \to 1$ for large $n$, so

$$Z(\mathrm{H}) \approx 2 \sum_{\text{large } n}^{\infty} n^2 \sim n_{\text{max}}^3 \to \infty \tag{9}$$

infinite partition function!

but what does this mean?!
strictly: probability to be in state $i$ is $p_i \propto 1/Z = 0$?!
that is: high probability to be at high $n$

physically: if H atoms in equilibrium with a thermal bath at $T$
and all states $n$ are accessible
then eventually all atoms fluctuate to high $n \to$ *ionized!*

this can't be right! atoms do exist! *Q: what's the fix?*

# Partition Function Cutoff

We implicitly assumed that we could carry our sum out to *arbitrarily large $n$*

While it is true that atomic H has such states recall $r_n = n^2 a_0$: high-$n$ states are physically large!

physically, real $e$ orbits in an H atom cannot extend beyond the nearest-neighbor H atom
which typically lies at distance $d_{\rm max}$ such that $n_{\rm H} d^3 \sim 1$
or $d_{\rm max} \sim n_{\rm H}^{-1/3}$

setting $d_{\rm max} = n_{\rm max}^2 a_0$, we estimate

$$n_{\rm max} \sim \sqrt{d_{\rm max} a_0} \sim \left(a_0^3 n_{\rm H}\right)^{-1/6} \sim 10^4 \left(\frac{n_{\rm h}}{1 \ {\rm atom/cm^3}}\right)^{-1/6} \qquad (10)$$

but: a very Wild West estimate! real physics is more complex...

# Thermodynamics of Ionization

consider a hydrogen gas in thermodynamic equilibrium at $T$
ionization and recombination both occur

$$\mathrm{H} + \gamma \leftrightarrow p + e \tag{11}$$

and the number densities $n_e$, $n_p$, and $n_\mathrm{H}$ adjust themselves until the recombination and ionization rates are equal

this equilibrium determines a relationship among the densities which we want to find

Method I (R&L):
starting point–the ratio of free electrons at speed $v$
to neutral hydrogen atoms in the ground state

$$\frac{\delta n_+(v)}{n_\mathrm{H}} = \frac{\delta g(v)}{g_\mathrm{H}} e^{-[E_e(v)-E_1]/kT} = \frac{\delta g(v)}{g_\mathrm{H}} e^{-(B+m_e v^2/2)/kT} \tag{12}$$

where $B = -E_1$ is hydrogen binding energy

Boltzmann gives

$$\frac{\delta n_+(v)}{n_{\mathrm{H}}} = \frac{\delta g(v)}{g_{\mathrm{H}}} e^{-(B+m_e v^2/2)/kT} \tag{13}$$

and with statistical weight

$$g(v) = g_p \; g_e \tag{14}$$

$$= 2 g_p \, \frac{dx\,dy\,dz \;\; dp_x\,dp_y\,dp_z}{h^3} \tag{15}$$

where electron volume element chosen so that number density $n_e = 1/d^3\vec{x} = 1/dxdydz$, and thus

$$\frac{n_p}{n_{\mathrm{H}}} = \frac{4\pi}{h^3 n_e} \frac{g_p}{g_{\mathrm{H}}} \int e^{-(B+p_e^2/2m)/kT} \; p^2 \; dp \tag{16}$$

$$= \frac{4\pi}{n_e} \frac{g_p}{g_{\mathrm{H}}} \left(\frac{2kT}{m_e h^2}\right)^{3/2} e^{-B/kT} \int_0^\infty e^{-x^2} x^2 \; dx \tag{17}$$

and we arrive at the **Saha equation**

$$\frac{n_e n_p}{n_{\mathrm{H}}} = \frac{g_e g_p}{g_{\mathrm{H}}} \left( 2\pi \frac{m_e m_p}{m_{\mathrm{H}}} \frac{kT}{h^2} \right)^{3/2} e^{-B_{\mathrm{H}}/kT} \tag{18}$$

where *hydrogen binding energy*

$B_{\mathrm{H}} = (m_e + m_p - m_{\mathrm{H}})c^2 = 13.6\ \mathrm{eV}$

*Q: behavior at high $T$? low $T$? does this make sense?*

# The Saha Equation

define *ionization fraction*

$$x_e = \frac{n_e}{n_{\text{tot}}} \tag{19}$$

with total electron number density $n_{\text{tot}} = n_e + n_{\text{H}}$
using $n_e = n_p$ (charge neutrality):

$$\frac{x_e^2}{1 - x_e} \approx \frac{2(2\pi m_e kT/h^2)^{3/2}}{n_{\text{tot}}} e^{-B_{\text{H}}/kT} = \frac{n_{\text{Q},e}}{n_{\text{tot}}} e^{-B_{\text{H}}/kT} \tag{20}$$

for $kT \gg B_{\text{H}}$, $x_e \to 1$: (nearly) fully ionized
for $kT \ll B_{\text{H}}$, $x_e \ll 1$: (nearly) fully neutral

but note that, e.g., temperature at which $x_e = 1/2$
also depends on particle density $n_{\text{tot}}$

# Awesome Saha Example: Cosmic Recombination

the early universe: *hot!*
$kT \gg B_{\mathrm{H}} \rightarrow$ totally ionized, $x_e \rightarrow 1$

present-day universe: on average, *cold!*
$T = 2.725$ K $\rightarrow$ if no stars, U would be neutral, $x_e \rightarrow 0$

thus there was a transition: **(re)combination**
our mission: estimate $T_{\mathrm{rec}}$ = when cosmic $x_e = 1/2$

*Q: naïve, zeroth order estimate?*
*Q: how to improve?*

naïvely, expect recombination when $kT_{\mathrm{rec}} \sim B_{\mathrm{H}}$
with $B_{\mathrm{H}} = 13.6$ eV, this gives
$T_{\mathrm{rec,naive}} = B_{\mathrm{H}}/k \sim 120,000$ K

but we can do better using Saha
exponential dependence on $B_{\mathrm{H}}$, but also
dependence on $n_{\mathrm{tot}}$

big-bang nucleosynthesis teaches* us that
the cosmic baryon-to-photon ratio is

$$\eta \equiv \frac{n_{\mathrm{b}}}{n_{\gamma}} = 6 \times 10^{-10} \tag{21}$$

most baryons are hydrogen, so $n_{\mathrm{tot}} \sim n_{\mathrm{b}}$
and thus there are *many photons for each $p$ and $e$*

*Q: anticipated effect on $T_{\mathrm{rec}}$? higher or lower than $T_{\mathrm{rec,naive}}$?*



*How? find out next semester in Physical Cosmology!

many photons per $p$ and $e \rightarrow$ very easy to ionize H

- when $kT < B_{\mathrm{H}}$, there are still many photons in Wien tail with $h\nu > B_{\mathrm{H}}$
- thus expect $T_{\mathrm{rec}} < T_{\mathrm{rec,naive}}$

in detail:
recall that $n_\gamma \sim (kT/hc)^3$, so

$$n_{\mathrm{tot}} \sim \eta n_\gamma \sim \eta (kT/hc)^3 \tag{22}$$

and so Saha becomes

$$\frac{x_e^2}{1 - x_e} \sim \frac{1}{\eta} \left( \frac{m_e c^2}{kT} \right)^{3/2} e^{-B_{\mathrm{H}}/kT} \tag{23}$$

note: $1/\eta \gg 1$ and $m_e c^2/kT \gg 1$

so when $x_e = 1/2$ we have (PS 7)
$T_{\mathrm{rec}} \simeq T_{\mathrm{rec,naive}}/40 \sim 3000$ K
k$T_{\mathrm{rec}} \simeq 0.3$ eV $\ll B_{\mathrm{H}}$
and thus $1 + z_{\mathrm{rec}} = T_{\mathrm{rec}}/T_0 \sim 1000$