

Astronomy 501: Radiative Processes

Lecture 21

Oct 12, 2022

Announcements:

Problem Set 6 due Friday

- Problem 1: updated to have useable data
- Part 1 (e) hint: for optical depth, pick 1-2 observed energies where you expect the *highest* effect
- Problem 2(b): only 40 lowest energy states
2(c): can plot instead of sketch!

- Office hours today after class
- Grading Elf (=BDF) at work on exam

⌊

Last time: began atomic structure

Hydrogen Atom: Honest Non-Relativistic Results

non-relativistic Schrödinger ignores relativistic effects

- electron (and proton) spins absent from Hamiltonian
→ 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!

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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 $n = 1, 2, 3, \dots$

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

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 $n \rightarrow \infty$: bigger radius, slower, more weakly bound

hydrogen wavefunction: 3-D system \rightarrow need 3 quantum numbers

ω Q: *what are the other two?*

Non-relativistic hydrogen wavefunction: states specified by

- *principal* quantum number $n = 1, 2, \dots$
controls wavefunction dependence on r
- *orbital angular momentum* $\ell = 0, 1, \dots, n - 1$
 $\hat{L}^2\psi = \ell(\ell + 1)\hbar^2\psi$
controls wavefunction dependence on θ
- *z-projection* $\hat{L}_z\psi = m\hbar\psi$ with $m = -\ell, \dots, +\ell$
controls wavefunction dependence on ϕ

in non-relativistic case: energy only depends on n

all states with fixed n are *degenerate* (same energy)

- at each ℓ 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

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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 $\propto \beta = v/c$ or $\beta^2 \rightarrow$ small corrections

→ lifts degeneracy of levels at same n

www: visualization of H atom wavefunctions

Building Multi-Electron Atoms

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

- principal quantum number n still appears
- spins do not appear in Hamiltonian \rightarrow atom state only depends on total orbital angular momentum quantum number L
- due to Pauli \rightarrow 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 $s = 1/2$

→ 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 ℓ
with $\ell = 0, 1, \dots, n - 1$ (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, ℓ)
- ↘ while “shells” are *all* states at fixed n
- atom ground state: electrons in lowest possible states

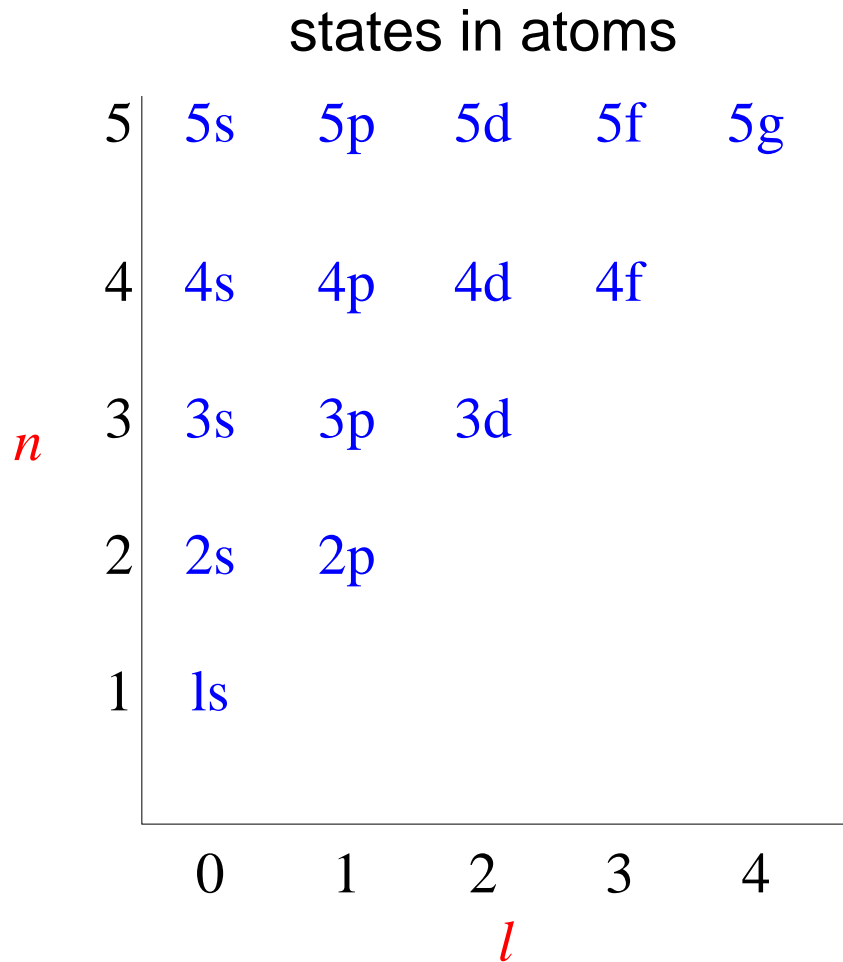
electron configuration: distribution of states in atom

- notation: (n, ℓ) electron state (“subshell”) is $n\Upsilon$
with $\Upsilon = s, p, d, f, \dots$ for $\ell = 0, 1, 2, 3, \dots$
- 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 ℓ 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

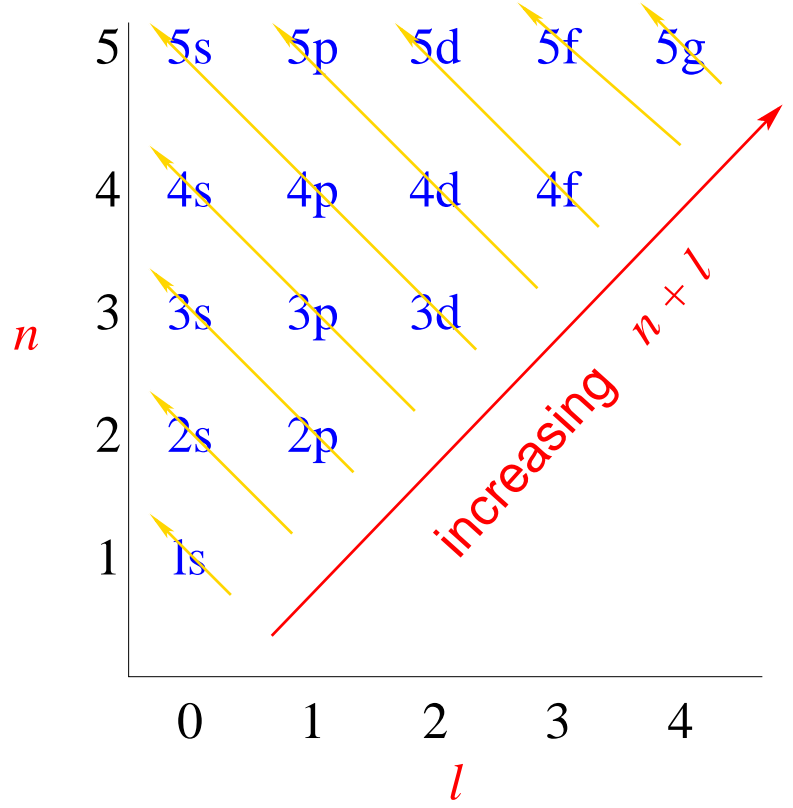
“*Aufbau principle*” – (n, ℓ) ordering

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

▷ when two states have same $n + \ell$

filled in order of increasing n , i.e., lowest n first

aufbau principle



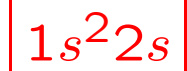
- ▷ filled in order of increasing $n + l$
- ▷ for same $n + l$: lowest n first

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

lithium: $Z = 3$

$1s^2 = 2$ states, filled

$2s^1 = 1$ state, half-filled,



carbon: $Z = 6$

$1s^2 2s^2 = 4$ states, filled

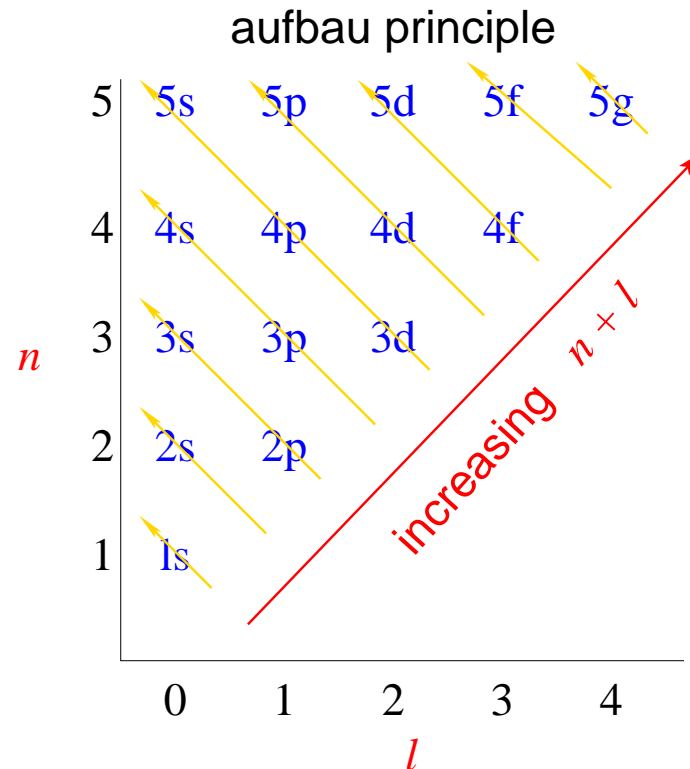
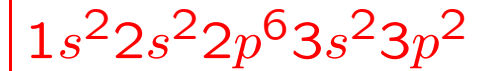
$2p^2 = 2$ states, part filled



silicon: $Z = 14$

$1s^2 2s^2 2p^6 3s^2 = 12$ states, filled

$3p^2 = 2$ states, part filled



www: check vs online data

Aufbau principle gives ordering of (n, ℓ) subshells
further splitting at fixed (n, ℓ) 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

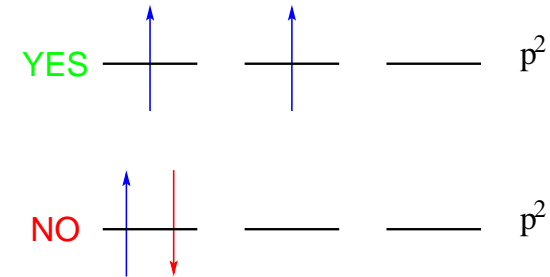
Hund's rule: energy level orderings in (n, ℓ) subshell for a fixed electron configuration = fixed unfilled (n, ℓ) subshell then the *lowest energy* state(s) are the one(s) with

- ▷ 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 $s_{z1} = s_{z2}$ 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 $m_2 = 0$)

→ $L = 1$

▷ 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 $\mathcal{L} = S, P, D, \dots$ for $L = 0, 1, 2, \dots$

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

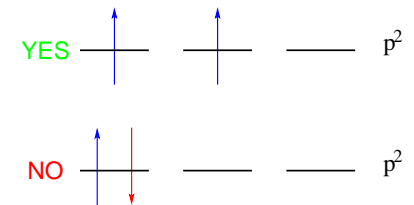
▷ the *largest possible* total spin S

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

17 Q: *what's an AGB star?*

Q: *why is it s Big Deal to find Tc in them?*

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 ensemble of n_{tot} atoms in thermodynamic equilibrium at T
the population = numbers n_i of atoms in state i is

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

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

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

and thus we find the **partition function**

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

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

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

and the partition function can be written

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

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

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

note that for a given atomic system and temperature T the partition function $Z = \sum_{\text{states}} g_i e^{-E_i/kT}$ 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 $kT \rightarrow 0$?

roughly:

the partition function counts all states with $E_i \lesssim kT$

so $Z \approx$ number of states with $E_i \lesssim kT$

→ 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 $g_n = 2n^2$:

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

22 where $\beta = 1/kT$

Q: roughly what is the value of $Z(\text{H})$? why? implications?

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

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

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

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

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 $n \rightarrow$ *ionized!*

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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_{\max} such that $n_H d^3 \sim 1$ or $d_{\max} \sim n_H^{-1/3}$

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

$$n_{\max} \sim \sqrt{d_{\max} a_0} \sim (a_0^3 n_H)^{-1/6} \sim 10^4 \left(\frac{n_H}{1 \text{ atom/cm}^3} \right)^{-1/6} \quad (10)$$

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