Lecture 1:   8 Apr '24

Useful stuff:
→ meiles @ pks.mpg.de
→ MPI-PKS 2B8
→ WWW: www.pks.mpg.de/correlations-
                  and-transport-in-rydberg-matter/
                  teaching
Or just find it through google.

→ Lecture notes, ideas, references,
    and announcements — all can be found
    there!
→ And of course: Mondays from
    11:10 - 12:40 in MPI-PKS, 1D1.

Tentative table of topics:
• Interactions in ultracold gases / • Bose-Einstein
  Condensates / • Multichannel scattering theory
  / • Quantum defect theory / • Adiabatic methods
  / • Supersymmetric QM / • Atoms in external
  fields / • Pressure broadening / • Impurities / Polarons

I will try to include a lot of enlightening literature in the course, showing how the concepts we learn in class come to play in actual research topics and giving additional context to all these fascinating concepts.
A few texts are very good for general AMO considerations:

- Harald Friedrich: Theoretical Atomic Physics
- " ": Scattering Theory
- Thomas Gallagher: Rydberg Atoms
- Ugo Fano + A.R.P. Rau: Collisions + Spectra

Additionally, a good QM book goes a long way:
 · Cohen-Tannouji, Sakurai, Griffiths

These books can typically be found online with a modicum of effort.

This course has two main goals.

1) To understand how Rydberg systems - atoms, molecules, arrays, etc - really work.

This includes topics like:

- How do Rydberg atoms interact?

"pair interactions" → Why is their interaction sometimes $\sim R^{-3}$ and other times $\sim R^{-6}$?

- How can we describe the complex Rydberg spectra of atoms with more than a single active electron?

"Multichannel Quantum Defect Theory (MQDT)" → In general, how do we deal with inelastic collisions and high-dimensional quantum systems?

etc etc.

Part of the motivation for this goal is that the vast majority of "modern" Rydberg papers - Rydberg quantum simulation, polaritons, computing, ... - use very simplified descriptions of Rydberg atoms and their interactions. It's vital to know when these simplifications

are valid, how to improve upon them when they break down, and how to dream up more possibilities.

2) To use Rydberg systems to illustrate and encounter more general physical concepts.

For example:

- We can learn about SuperSymmetric quantum mechanics in order to obtain the Rydberg formula!
- We can learn the Born Oppenheimer approximation (and more powerful adiabatic methods) in order to study Rydberg-Rydberg interactions.
- We can study contact potentials/pseudopotentials by considering a Rydberg atom excited in a dense gas.

This works well because the study of Rydberg atoms and molecules is, of course,

just the study of atoms and molecules. All the fundamental concepts and techniques of AMO physics apply here too! The main difference is the scale - Rydberg systems have such exaggerated properties that we can test our new ideas and old intuition in a really different regime.

So, without further ado... <u>what</u> exactly is a Rydberg??

The answer actually lies way back in the very, <u>very</u> early days of atomic physics, and even earlier, in fact. As we'll see, the study of physics then was, in several key ways, motivated by and accelerated through the investigation of Rydberg atoms (even though the scientists in question didn't realize that then). And that fits perfectly with the themes of this course!

An excellent reference for this topic is "Introduction to Atomic Spectra" by H. E. White, published in ¡¡ 1934 !!

Ch 1. of this book gives a very lucid account of the historical development that led to the Rydberg formula + Quantum mechanics itself! Some important years in the early development of spectroscopy are:

1817 : Fraunhofer first mapped the solar spectrum.
→ rather than just seeing how the light refracted into a rainbow (a la Newton), he discovered certain dark spots – some wavelengths were absent!

1860: Foucalt shines light through a sodium flame and sees black lines at the exact positions as some of the sun's lines!
→ Kirchhoff proposes that the sun is

is surrounded by many hot gases, which
are absorbing light just like this Na
flame!

1868: Angstrom measured the sun's spectrum
to a precision of $10/10^6$ mm! That's
where we got the unit...

1882: Rowland manufactured a very precise
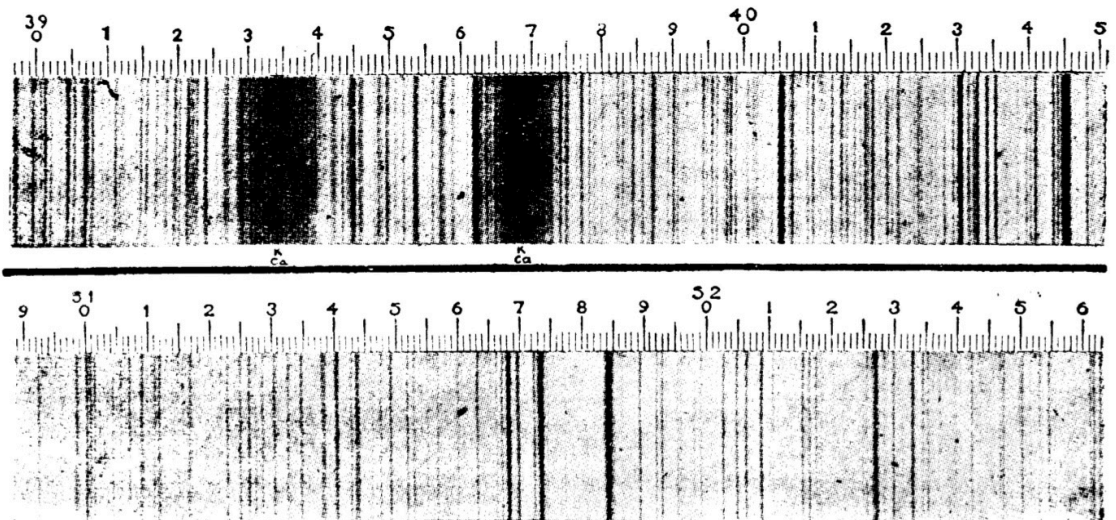grating and produced a map of the
solar spectrum that was 50 ft long!!
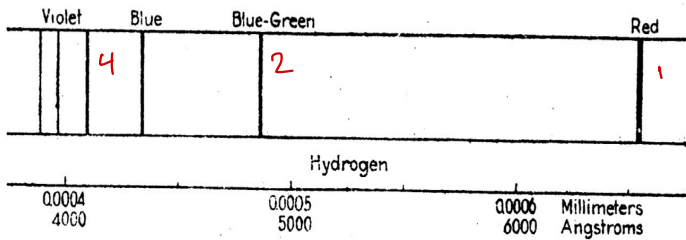

FIG. 1.2.—Sections of Rowland's solar map.

From all of this data, a picture began to become clear - the massive number of lines in the sun's spectrum could all, through careful measurement, classification, and comparison, be matched up with lines seen in the spectrum of gases. So, it seemed to be the case that every element possessed a characteristic set of lines - each blocked (or absorbed?) light of very specific wavelengths. (It also was noticed that gases emitted light at these exact same wavelengths!)

This raised two obvious questions:
1) Why do gases absorb only some light (and why do some elements have so many more lines than others?)
2) What determines the distribution and placement of these lines?

Many empirical or phenomenological attempts were made to answer this second question.

Some efforts now seem a bit silly.
For example, Stoney (1871) found that
the 1st, 2nd, and 4th lines of H are the
20th, 27th, and 32nd harmonics of 131274.14 Å.

FIG. 1.3.—The Balmer series of hydrogen.

Such a finding could make sense - discrete
lines "feel" like harmonics of some more
fundamental property, right? - and besides,
such an agreement seemed too good to be
blind chance!

→ But Schuster (1881) showed that
this is, indeed, a statistical
inevitability and should not be taken
seriously. Back to square one!

Now our hero enters the scene! Johannes
Rydberg, in 1879, distinguished sharp, from
diffuse spectral lines - first in sodium,
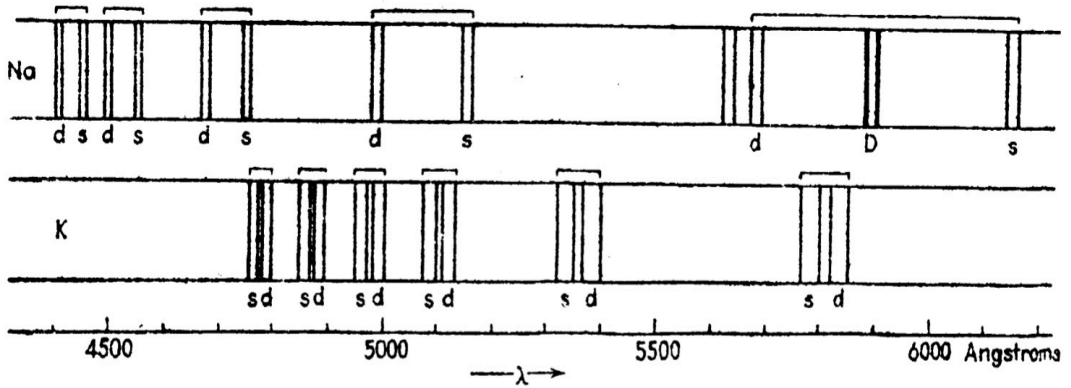(d)   (s)

FIG. 1.4.—Schematic representation of the sodium and potassium series. (*After Liveing and Dewar.*)

This was an important classification because it showed that the spectrum of a given element could be split up into multiple, likely independent, series!

We will revisit these s and d (and eventually p and f!) lines later, using quantum theory to explain their existence.

Around this time, Balmer (1885) made a "theoretical breakthrough" of sorts - he guessed the formula

$$\lambda = \left(3645.6\ \text{Å}\right) \times \frac{n_2^2}{n_2^2 - n_1^2}$$
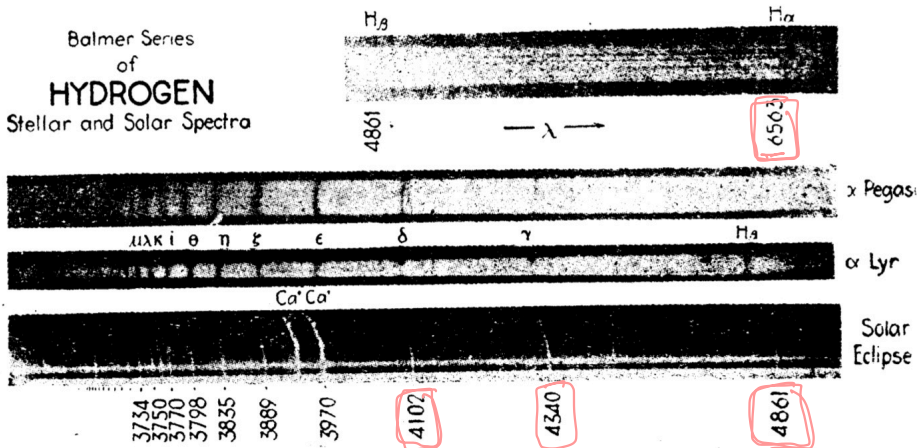

FIG. 1.5.—Stellar and solar spectrograms showing the Balmer series of hydrogen.

This formula "predicts" these 4 lines to ± 0.1 Å if $n_2 = 2$ and $n_3 = 3, 4, \ldots$

But is this just another coincidence, like Stoney's harmonics? It certainly agrees even better with the known data, but without any mechanism — can we trust it?

In 1888, Rydberg made a huge breakthrough. This was thanks to some clever plots — when in search of an explanation for something, this almost always helps! He plotted the spectral frequencies vs whole numbers:

data points

fitted curve

Cool! There appears to be a clear relationship here!
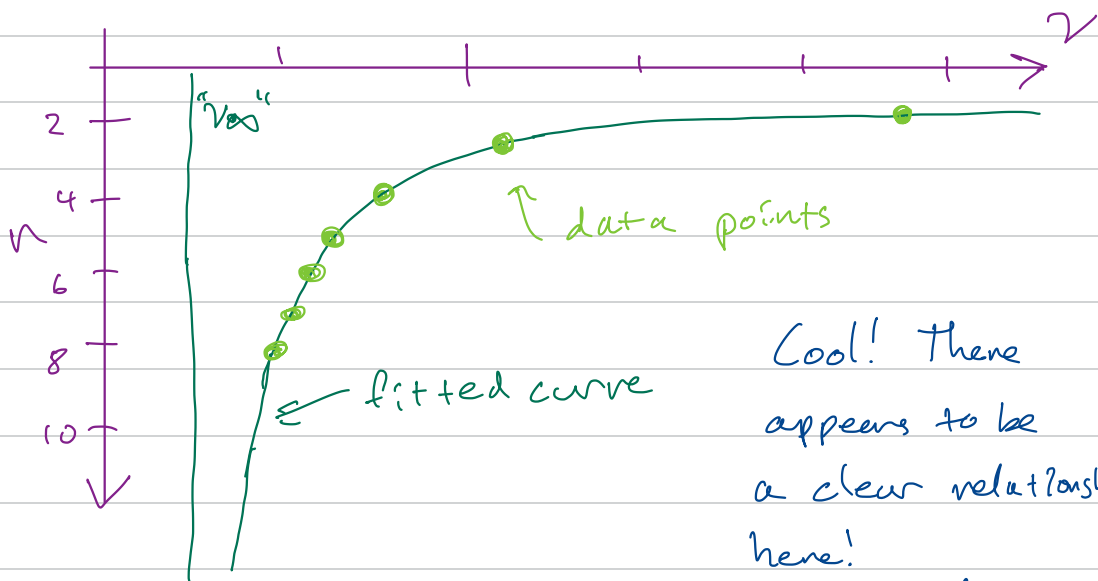
Lesson: plot stuff whenever possible!!

But keep in mind: this jump required good classification of good data to work at all! Without separation into s, p, d, f series and complementary data from multiple elements, this would not have been successful.

Rydberg's next step was to fit this data.

Guess #1: $\nu_n = \nu_\infty - \dfrac{C}{n + \mu}$, $n = 2, 3, \ldots$

Sadly, this did not work. But Rydberg was not beaten, and he tried again!

Guess #2: Try a different exponent:

$$\nu_n = \nu_\infty - \frac{N}{(n+\mu)^2} \quad , \quad n = 2, 3, \ldots \infty$$

This is (an early version of) the famous

RYDBERG FORMULA!!!

Don't let your familiarity with this equation lessen its impact! This is a beautiful success of physics! → And one obtained purely from careful study of experimental data, with no theoretical input!

Why is it so beautiful?

First, Rydberg noticed that N (now called R_∞, the Rydberg constant) was the same for all series and for all elements. This level of universality really helps this formula to seem legit!

Second, Rydberg noticed that differences in the fit parameters ν_∞ and μ could be used to learn some hints about what physics is really happening here!

Here is what I mean. For Li, Mr. Rydberg fit three curves to the s, p, and d data available (all units in wavenumbers, cm^{-1}):

$$\nu_n^s = 28601.6 - \frac{109721.6}{(n + 0.5951)^2} \qquad n = 2, 3, \ldots$$

$$\nu_n^p = 43487.7 - \frac{109721.6}{(n + 0.9596)^2} \qquad n = 2, 2, \ldots$$

$$\nu_n^d = 28598.5 - \frac{109721.6}{(n + 0.9974)^2} \qquad n = 2, 3, \ldots$$

R_∞ is the same!

These are different! or?

μ is different!

Rydberg assumed that $28601.6 = 28598.5$,

within expt. error. So why is 43487.7 so different?

Notice that the frequency predicted for $\nu^s_{n=1}$ is negative, and thus $n=1$ was excluded. But, just the second term with $n=1$ has the value

$$\frac{109721.6}{(1+0.5951)^2} = 43123.7$$

And this is basically equal to 43487.7!

Furthermore, if we take the second term of ν^p_n, and put $n=1$, we get:

$$\frac{109721.6}{(1+0.9596)^2} = 28573.1$$

And this basically equals 28601.6!

Rydberg concluded: the series limits $\nu^{s,p,etc}_{\infty}$ are actually related to components of other series!

Therefore, Rydberg's formulas can be written:

$$\nu_n^S = \frac{R_\infty}{(1+\mu_p)^2} - \frac{R_\infty}{(n+\mu_s)^2}$$

$$\nu_n^P = \frac{R_\infty}{(1+\mu_s)^2} - \frac{R_\infty}{(n+\mu_p)^2}$$

$$\nu_n^d = \frac{R_\infty}{(1+\mu_p)^2} - \frac{R_\infty}{(n+\mu_d)^2}$$

Conclusions: each of these spectral lines can be interpreted as frequency differences between the first member of one series and members of a different series!

So, 30 years before the Schrödinger Eq., Rydberg had guessed (correctly) a formula describing transitions between discrete energy levels

$$E_{n\ell} = - \frac{R}{(n-\mu_\ell)^2} ,$$

which even incorporates dipole selection rules! And note that the only "non-universal" piece here is the "QUANTUM DEFECT," μ_ℓ,

which tells us how much these energies
differ from those of hydrogen! (Note that
Balmer's formula is recovered from Rydberg's
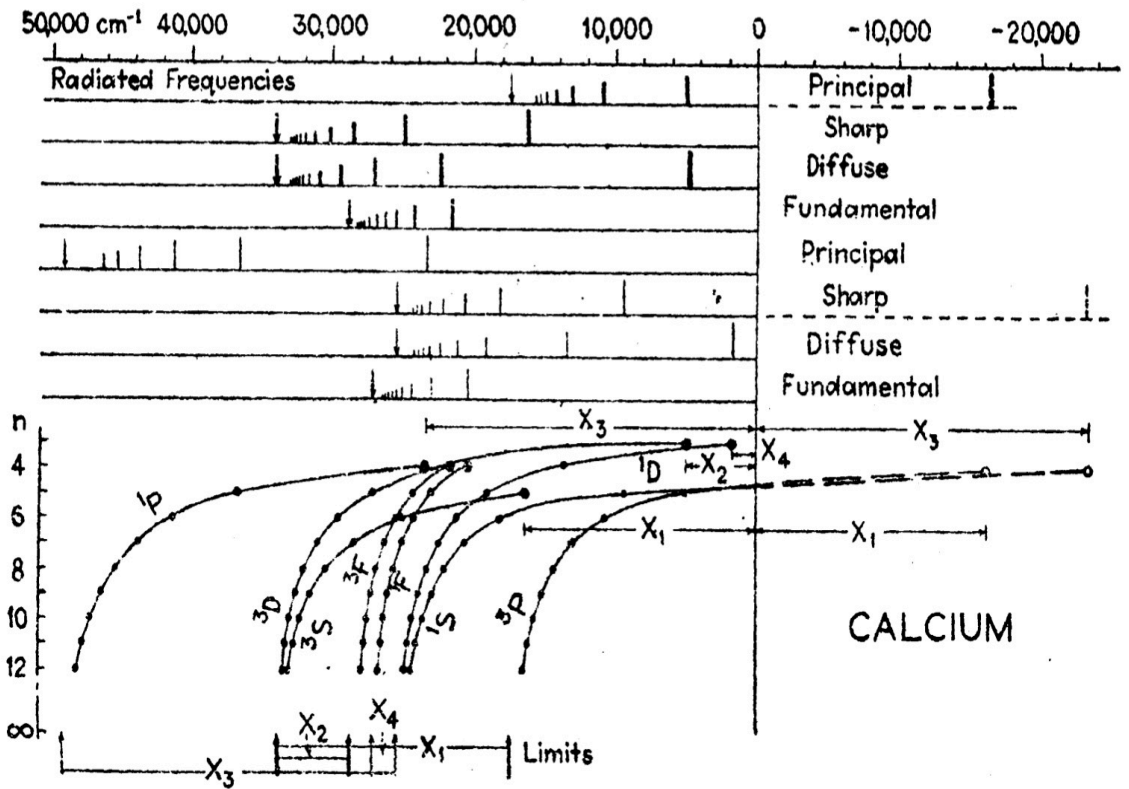by setting $\mu_e = 0$).

FIG. 1.8.—Schematic plot of the chief triplet and singlet series of calcium showing the Rydberg-Schuster and Runge laws.

Even for much more complicated spectra,
this approach holds and relates absorption
lines to energy levels!

There's also a nice 'cautionary tale' here.
   The PICKERING Series:

These were spectral lines observed in the
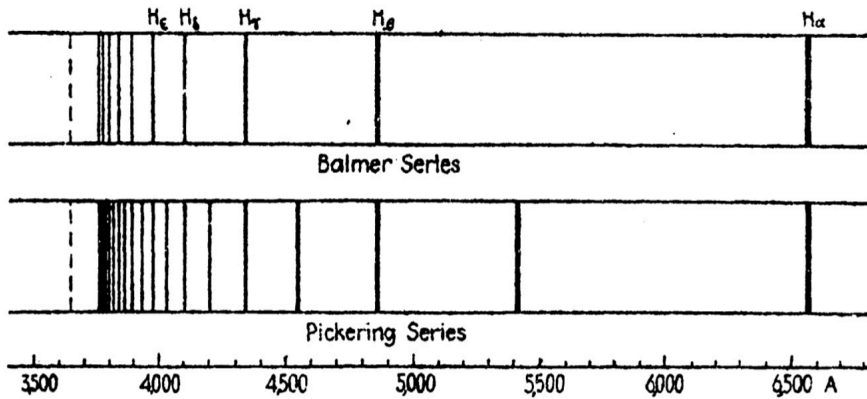spectrum of the star ζ - Puppis:

FIG. 1.14.—Comparison of the Balmer series of hydrogen and the Pickering series.

The spectrum of this star consisted of lines
found in the Balmer series, confirming the
presence of H, but additionally it contained
lines in between those of Balmer!
Rydberg once again made a bold leap-
in some sense anticipating the future jump
of allowing half-integer angular momentum in
dealing with spin- and wrote down a modified

Balmer formula using both integer and half-
integer principal quantum numbers:

$$\nu_n = R_\infty \left(\frac{1}{2^2} - \frac{1}{n_2^2} \right), \quad n_2 = \frac{5}{2}, 3, \frac{7}{2}, 4 \ldots$$

This worked beautifully!

Feeling confident, Rydberg thought that
restricting $n_1 = 2$ was too much — half-integers
should be OK there too! And indeed, lines at

$$\nu_n = R_\infty \left(\frac{1}{1.5^2} - \frac{1}{n_2^2} \right), \quad n_2 = 2, \frac{5}{2}, \ldots$$

were observed!

This looks like yet another smashing success
for Rydberg: make a bold generalization to
form a theory accounting for new experimental
data, trust that generalization a step further
to make a prediction, and verify that with
additional experiment!

Rydberg and Pickering therefore thought they had observed a new type of hydrogen, found only in distant stars!

Weirdly, these same lines were eventually detected from a helium source, even though they have nothing to do with the 'chief' series of He!

This puzzle requires us to find a theoretical footing for the Rydberg formula!

Aside: there is a super interesting article on this Pickering series, stellar spectroscopy, history of physics, and most importantly, the often thankless and un-appreciated role of women in physics/astronomy that just recently came out on the arXiv: 2402.14734.
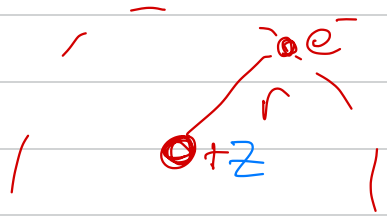   Check it out!!

BOHR'S MODEL OF THE ATOM

Mr. Bohr made two 'ad hoc' assumptions:

1) Angular momentum is quantized, $L = n\hbar$

2) Electrons do not radiate continuously.

technically: this is demanded by experiment!

Bohr also assumed this new model of an atom!

Kindergarten Physics : Newton's law for uniform circular motion gives

(centripetal acceleration) $\dfrac{mv^2}{r} = \dfrac{1}{4\pi\varepsilon_0} \dfrac{Ze^2}{r^2}$ (Coulomb force)

And from (1): $\quad mvr = n\hbar \quad$ (quantized ang-mo)

$\rightarrow \quad (mvr)^2 = \dfrac{1}{4\pi\varepsilon_0} Ze^2 mr$

$\rightarrow \quad r = \dfrac{\hbar^2 n^2}{Z}\left(\dfrac{4\pi\varepsilon_0}{e^2 m}\right)$

Message 1: $r \sim n^2$.

Total energy:
$$E = \frac{1}{2}mv^2 - \frac{1}{4\pi\varepsilon_0}\frac{Ze^2}{r}$$
$$= \frac{1}{2}\frac{(n\hbar)^2}{mr^2} - \frac{1}{4\pi\varepsilon_0}\frac{Ze^2}{r}$$
$$= \frac{1}{2}\frac{n^2\hbar^2}{m}\cdot\frac{Z^2}{(\hbar^2n^2)^2}\left(\frac{e^2m}{4\pi\varepsilon_0}\right)^2$$

$$- \frac{1}{4\pi\varepsilon_0}Ze^2 \cdot \frac{e^2m}{4\pi\varepsilon_0}\cdot\frac{Z}{\hbar^2n^2}$$

$$= \frac{1}{2}\frac{Z^2e^4m}{(4\pi\varepsilon_0)^2}\frac{(-1)}{\hbar^2n^2}$$

$$= \frac{-R_y}{n^2} \quad,\quad R_y = \frac{Z^2e^4m}{2(4\pi\varepsilon_0)^2\hbar^2}$$

Message 2: microscopic definition of the Rydberg constant and the Rydberg formula!

Message 3: $E_n \sim n^{-2}$.

Aside: Bohr's model does not predict those pesky "quantum defects" μ:
$$E_n = -\frac{R}{(n+\mu)^2}$$
So it is quantitatively useless for all other atoms!

For some fun reading on other semiclassical
attempts to improve on the Bohr model, see
   Tanner, Richter, and JM Rost
      RMP 72 497 (2000), → try to quantize
                                      He yourself!
But the Bohr model <u>does</u> explain the
Pickering series!
Rydberg's matching of the spectrum to
half-integer n values was an unlucky
match to what Bohr's formula predicts: these
are transitions in an 'atom' with $Z = 2$,
a.k.a. He^+!
<u>End Aside!</u>

At the end of all this talk about
atomic spectra, Rydberg's work + the Bohr
model give us a formula generally applicable
to the energy levels of atoms:

$$E_n = - \frac{1}{2(n-\mu)^2},$$

where I now use atomic units $\hbar = e = m_e = \frac{1}{4\pi\varepsilon_0} = 1$

Since we trust this formula, both from the predictive / explanatory power of the Bohr model and the agreement with experiment, let's explore it a bit. What if $n \to \infty$?

→ E_n gets arbitrarily close to threshold (e.g. in H: the ground state is at $-13.6 \, eV$. The $n=10$ state has energy $-13.6/10^2 = -0.136 \, eV$.

$n=100$: $-0.00136 = -1.36 \, meV$!

→ The level spacing also gets very tight:

$$-\frac{1}{2(n+1)^2} - \left(-\frac{1}{2(n)^2}\right) = \frac{-n^2 + (n+1)^2}{2n^2(n+1)^2}$$
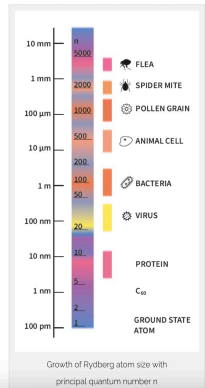
$$\approx n/n^4 \approx \underline{n^{-3}}.$$

⇒ The atom gets very large!

$r \sim n^2 \Rightarrow r_{n=30} \sim \underbrace{5.29 \times 10^{-11} m}_{\text{Bohr radius}} \cdot 30^2$

a_0

(Barry Dunning, Tom Killian)

$\sim 10s \, of \, nm.$

$r_{n=100} \sim 1 \, \mu m.$

Growth of Rydberg atom size with principal quantum number n

These properties, in a nutshell, define what Rydberg atoms are:

Atoms with a very high principal quantum number n, which endows them with many exaggerated properties
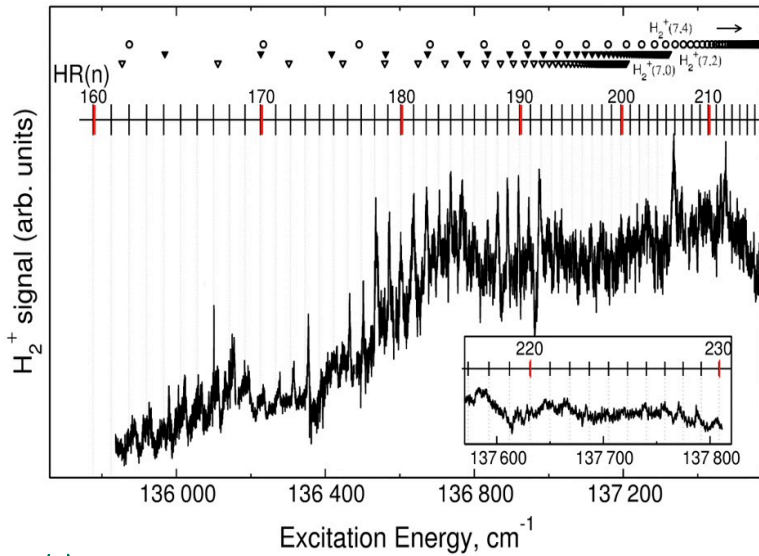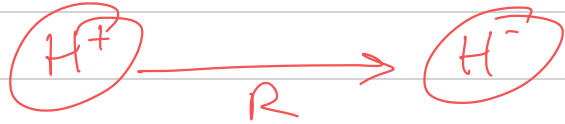
These will be our topic.
But more generally, we can consider 'Rydberg physics' to mean excited electronic states of various objects:

· Molecules

He⁺ labeled, R, He labeled, e^-
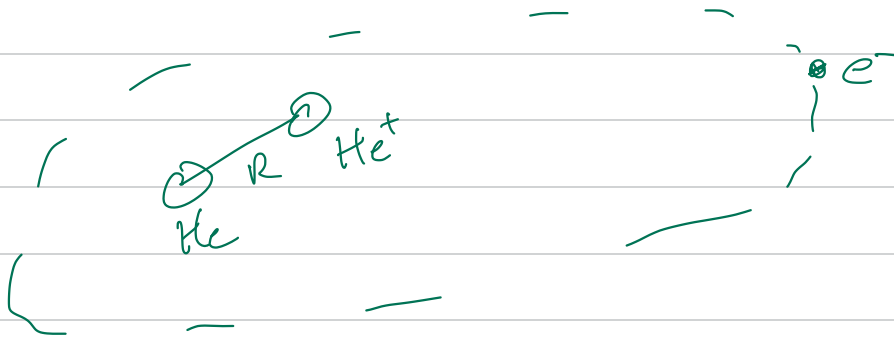
→ Very tough problem!
(likely outside our scope)

But another type of Rydberg molecule is easier to model:

$$H^+ \xrightarrow{\hspace{3cm}} H^-$$

R

(notice —
here it is
the vibrational
excitation that
is "Rydberg")
→ already
my definition
used!

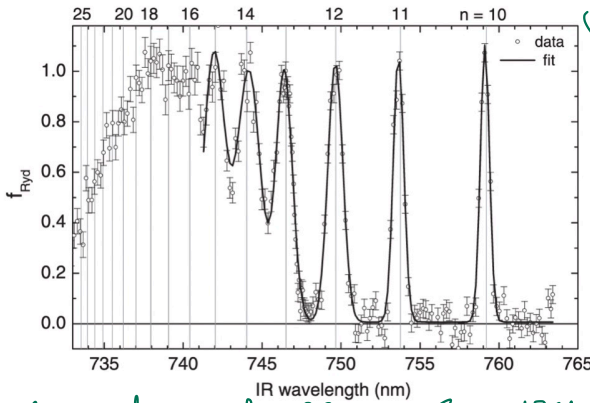Vleitez et al PRL [10] 163001 (2008)

Recall: $R_y \sim m_e$ in the Bohr model.
Actually, that is only for an infinitely heavy atom. It should depend on $\dfrac{M_1 M_2}{M_1 + M_2}$,
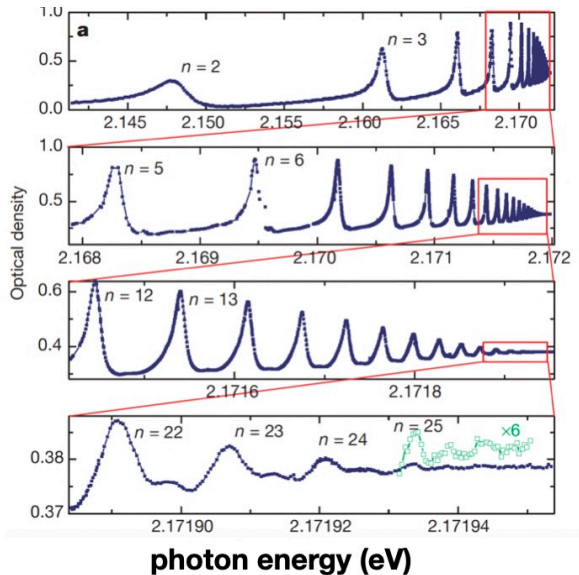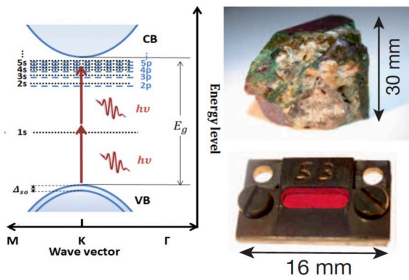
the reduced mass, μ.

Remember also: $r \sim n^2/\mu$, so these molecules are much smaller than the analogous atom!

We can also Rydberg excite more exotic
things - Ps for example

e^-

e^+

Cassidy et al PRL 108 043401 (2012)

← Perfect fit to
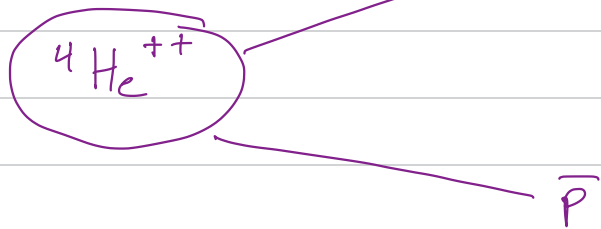Rydberg formula,
but again without
the R∞!

Rydberg excitons -
hole + electron pairs -
have been excited ad
are a vibrant area
of study!

Kazimierczuk et al
Nature 514 343 (2014)

And my current favourite, from Sótér et al
Nature 603 411 (2022) involves
superfluid ^{4}He and antiprotons!

He^{++} + $\bar{p}$ is hydrogen-like, with Z=2 and
a reduced mass ~ 1000x heavier
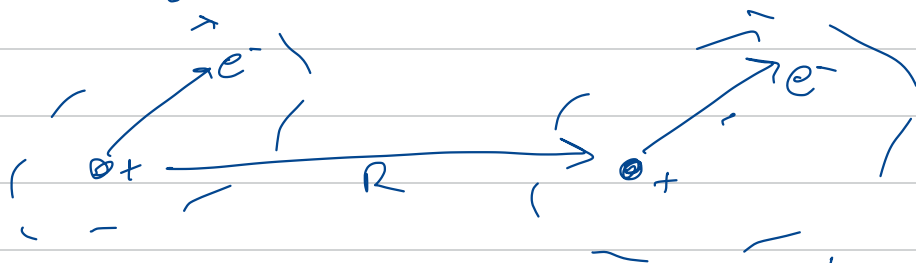thanks to e$^-$ → $\bar{p}$ replacement

^{4}He^{++}

e

$\bar{p}$

In the experiment, they measure transitions
between Rydberg states of He^{++}+$\bar{p}$ (37→38
to be precise) which, due to the large μ,
are smaller in size than the electronic ground
state!

A quick teaser: why are Rydberg atoms so popular?

→ CONTROLLABLE INTERACTIONS
OVER **12** ORDERS OF
MAGNITUDE!!!

Rough idea (we'll figure this out more rigorously later):

each atom can be polarized so that it has a dipole moment, d. A dipole creates a field $F \sim d/R^3$, which can polarize the other atom to have a dipole moment d, which then gives a potential $U_{int} \sim d^2/R^3$.

Obviously, this is a 2nd order effect. The
field of one (induced) dipole is required to
induce the other, and vice versa! So let's
turn to 2nd order perturbation theory:

$$U(R) \sim \frac{V_{int}^2}{\Delta E}.$$

Rydberg ingredients:

- $d \sim$ size of the atom $\sim n^2$
- $\Delta E \sim$ change b/w Rydberg energy
  levels $\sim n^{-3}$

$$\Rightarrow U(R) \sim \frac{\left(n^2 \cdot n^2 / R^3\right)^2}{n^{-3}} \sim \frac{n^{11}}{R^6}.$$

This __enormous__ power law is what makes
Rydberg atoms so useful.

They have appreciable interactions at
a > μm. range.
   __AND__, this interaction can be toggled
      on/off! (compare w/ trapped ions)

Interlude: Rydberg's Research Lessons:

1) Always plot things you are confused about!

2) Look for patterns and classify!

3) Don't be afraid to guess, and guess again!

4) Have an open mind when deciding — are two data points with experimental uncertainty the same or different? Sometimes theoretical breakthroughs take place when you realize a theory predicts differences not yet seen in expt — and sometimes universal properties are obscured by apparent expt differences!

End Interlude.

Earlier, we 'derived' the Rydberg formula using the Bohr model. This approach manages to get the right energy levels, and had some useful explanatory power (recall the Pickering series), but it can't do much else. In particular, it was clear soon after the Bohr model was developed that it can't handle even the helium atom — but lots of clever generalizations were attempted (see RMP 2000)

So, now, let's solve it the correct way, using the Schrödinger equation. We'll stick with hydrogen for now, as it is still the only atom with an analytical solution.

But, even though we're just solving (again) the hydrogen atom, we'll do so in a way that nicely illustrates how Rydberg physics is a fun 'playground' in which we can explore the wide world of AMO / Quantum physics.

So, to start with, we have the Hamiltonian:

$$H = -\frac{\nabla_1^2}{2m_1} - \frac{\nabla_2^2}{2m_2} + V(\vec{r}_2 - \vec{r}_1)$$

Where...

- $\nabla^2 = \Delta = $ Laplacian
- $V(\vec{r}_2 - \vec{r}_1) \equiv V(r) = -1/r,$ (Coulomb)

$$\vec{r} = \vec{r}_2 - \vec{r}_1$$

Note: we are using atomic units!

Evidently, this is a **6D** equation, but the interaction only depends on a single distance! This encourages us to try a change of coordinate system...

$$\vec{R} = \underbrace{\frac{m_1\vec{r}_1 + m_2\vec{r}_2}{m_1 + m_2}}_{M}, \quad \vec{r} = \vec{r}_1 - \vec{r}_2.$$

follow this on your own! It's a very helpful exercise to so on occasion.

So:
$$\partial_{r_1} = \frac{\partial R}{\partial r_1} \cdot \frac{\partial}{\partial R} + \frac{\partial r}{\partial r_1} \cdot \frac{\partial}{\partial r} = \frac{m_1}{m}\partial_R + \partial_r$$

$$\partial_{r_2} = \frac{\partial R}{\partial r_2} \cdot \partial_R + \frac{\partial r}{\partial r_2}\partial_r = \frac{m_2}{m}\partial_R - \partial_r$$

And then:

$$-\frac{\nabla_1^2}{2m_1} - \frac{\nabla_2^2}{2m_2} = -\left[\begin{array}{c} \frac{1}{2}\frac{m_1}{m^2}\partial_R^2 + \frac{\partial_R\partial_r}{m} + \partial_r^2/m_1 \\ + \frac{1}{2}\frac{m_2}{m^2}\partial_R^2 + - \frac{\partial_R\partial_r}{m} + \partial_r^2/m_2 \end{array}\right]$$

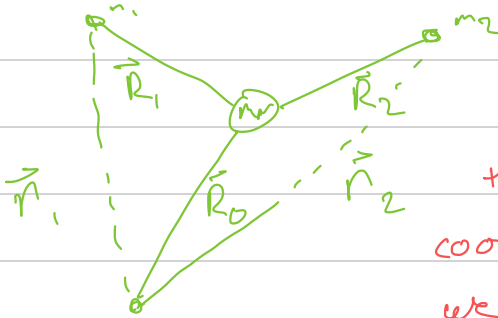$$= -\frac{1}{2}\frac{m_1 + m_2}{m}\partial_R^2 + \frac{m_2\partial_r^2 + m_1\partial_r^2}{m_1 m_2}$$

$$= -\frac{1}{2M}\nabla_R^2 - \frac{1}{2m}\nabla_r^2$$

So in the end our transformed Ham is:

$$H = -\frac{\nabla_R^2}{2M} - \underbrace{\frac{\nabla_r^2}{2\mu} - \frac{1}{r}}_{\text{relative}}$$

$$\underbrace{\phantom{-\frac{\nabla_R^2}{2M}}}_{\text{CoM}}$$

Such transformations should be fairly routine, but it's good to remember how to do it when more complicated situations emerge, for ex:

He: $H = -\frac{\nabla_1^2}{2n_e} - \frac{\nabla_2^2}{2m_e} - \frac{\nabla_0^2}{2M_n} - \frac{1}{|\vec{R}_1 - \vec{R}_0|} - \frac{1}{|\vec{R}_2 - \vec{R}_0|} + \frac{1}{|\vec{R}_1 - \vec{R}_2|}$

After transforming to the obvious relative coordinates (try it @ home), we get...

$$H = -\frac{\nabla_0^2}{2M} - \frac{\nabla_1^2}{2\mu} - \frac{\nabla_2^2}{2\mu} - \frac{1}{r_1} - \frac{1}{r_2} + \frac{1}{|\vec{r}_1 - \vec{r}_2|} - \underbrace{\frac{\nabla_1 \cdot \nabla_2}{M_n}}$$

- $M = M_n + 2m_e$
- $\mu = \frac{m_e M_n}{M_n + m_e}$

this 'mass-polarization' term adds a type of kinetic correlation/interaction b/w the electrons

So, generic many-particle systems will have their overall dimensionality reduced when we choose clever coordinates, but this often comes at a cost via these terms. In atoms it is almost always a perturbation, but similar terms in molecules cannot be ignored.

Our next move is to solve the relative-motion Ham, $H_e = -\frac{\nabla_r^2}{2} - \frac{1}{r}$. Here we took the sensible limit $m_p \gg m_e$ to write $\mu = 1$ a.u. To solve this 3D PDE, we exploit the spherical symmetry of $1/r$.

We look up ∇^2 in sph. coords, and find:

$$\nabla^2 = \frac{\partial}{\partial r}\left(r \frac{\partial}{\partial r}\right) - \frac{\vec{L}^2}{r^2} \quad ,$$

$$\ell = 0, 1, 2, \ldots$$

where

$$\vec{L}^2 \; Y_{\ell m}(\theta, \varphi) = \ell(\ell+1) \; Y_{\ell m}(\theta, \varphi) \quad ⓵$$

Spherical Harmonics

Our TISE to solve is therefore:

$$\left(-\frac{1}{2r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r} \right) + \frac{\vec{L}^2}{2r^2} - \frac{1}{r} - \varepsilon \right)\Psi(\vec{r}) = 0. \quad ②$$

Let's think about the form $\Psi(\vec{r})$ should take.

The first thing to notice is that the eigenstates $Y_{\ell m}$ of $\vec{L}^2$ define a complete and orthonormal basis in $\Omega = \hat{r} = \theta, \varphi$.

↳ perhaps "transform" is better

So, we can reduce the complexity of this 3D problem into infinitely many coupled 1D problems by expanding Ψ into this basis!

Even though this is a silly example, it illustrates a process that we will repeat many, many times in this course!

So, we write

$$\Psi(\vec{r}) = \sum_{\ell m} \frac{u_{E\ell m}(r)}{r} Y_{\ell m}(\hat{r}) \quad ③$$

↑ maybe a helpful analogy: this is just the same argument as Fourier analysis: here we just get coefficients at each r!

Remember: this is exact!

Note that this form of radial function means
we only have to deal with 1st derivatives:

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 \frac{\partial}{\partial r}\frac{u}{r}\right) = \frac{1}{r^2}\frac{\partial}{\partial r}\left(ru' - u\right) = \frac{1}{r^2}\left(u' + ru'' - u'\right)$$

$$= \frac{1}{r}u''.$$

So everywhere the $1/r$ cancels out and ② , with
our wavefunction ③ , is ...

$$\left(-\frac{1}{2}\frac{d^2}{dr^2} + \frac{l(l+1)}{2r^2} - \frac{1}{r} - E\right)\sum_{em} u_{E\ell m}(r)\, Y_{\ell m}(\hat{r}) = 0.$$

Now we can utilize $\langle lm|l'm'\rangle = \delta_{ee'}\delta_{mm'}$
by projecting (left-multiplying and integrating)
this eq. onto $\langle l'm'|$. This gives an equation for
each l, m :

$$\left(-\frac{1}{2}\frac{d^2}{dr^2} + \frac{l(l+1)}{2r^2} - \frac{1}{r} - E\right)u_{E\ell}(r) = 0$$

→ Our problem of solving the S.E. for
a Rydberg atom boils down to
the solution of a radial S.E. for each l

These equations decoupled because our
potentials are spherically symmetric →
conservation of angular momentum
really saves a _lot_ of time!
This will _not_ generically be the
case, as we will see, and many of
the problems we encounter will require a
lot of clever thinking to avoid solving
infinitely-many coupled equations!

Aside: an electric field $\vec{F}$ gives a
potential $\vec{r} \cdot \vec{F} = rF\cos\theta$.

→ $\langle \ell'm' | rF\cos\theta | \ell m \rangle = \sqrt{\frac{4\pi}{3}} \, rF \, \underline{\langle \ell'm' | Y_{10} | \ell m \rangle}$

• this term couples equations with
ℓ to those with $\ell' = \ell \pm 1$.

For now, though, we will have to
settle for just solving ∞ decoupled 1D
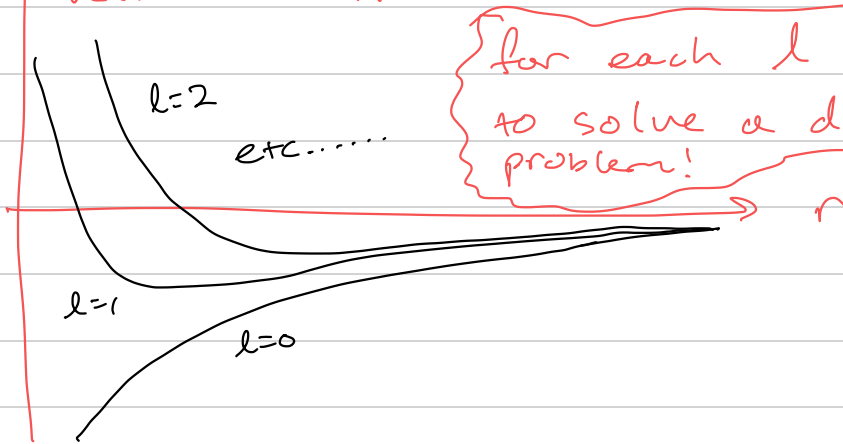equations, $(H_\ell - E) u_{E\ell}(r) = 0$.

where $H_\ell \equiv -\frac{1}{2}\frac{d^2}{dr^2} + \frac{\ell(\ell+1)}{2r^2} - \frac{1}{r}$.

Let's solve this equation,
subject to b.c.'s

$$U_{El}(r=0) \sim r^{l+1} = 0 \qquad (\nabla^2 \text{ behavior})$$

$$U_{El}(r=\infty) = 0 \qquad (\text{finite probability})$$
everywhere

$$V_{eff}(r) = -1/r + l(l+1)/2r^2$$

$l=2$

etc......

$l=1$

$l=0$

for each l we have
to solve a different
problem!

r

But let's not solve them with a garbage
method like power series... let's solve them
(next time) using the power of ...

Super-
Symmetric
Quantum
Mechanics!

woohoo!