LECTURE 1:

9 Oct '23

Useful stuff:

- meiles@pks.mpg.de
- Office: 2B8 → open door = stop by
- WEBPAGE!

  www.pks.mpg.de/correlations-and-transport-in-rydberg-matter/teaching (or, just find it thru the homepage)

I will post notes, ideas, references, and other important course announcements there - check it Monday AM in case of sickness/emergency!

And of course....

we meet Mondays from 11:10-12:40 in MPI-PKS 1D1.

In addition to other papers/reviews/textbooks I will reference, you will benefit a lot from reading:

- Harald Friedrich: Theoretical Atomic Physics
- " ": Scattering Theory
- Thomas Gallagher: Rydberg Atoms
- Ugo Fano + A.R.P. Rau: Collisions + Spectra
- A good QM book or two -
  - Cohen-Tannoudji
  - Sakurai
  - Griffiths

These books can often be obtained with a little effort online.

Another very good reference when we start QDT/scattering theory is:

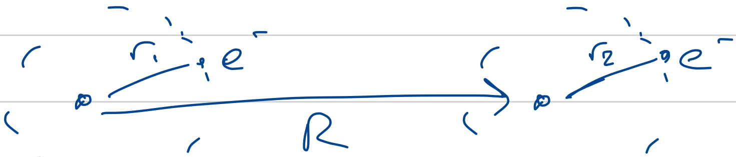
M. Aymar, C.H. Greene, and E. Luc-Koenig
Rev. Mod. Phys. **68** 1015 (1996)

So - what is the point of this course?

① To understand how Rydberg systems
- atoms, molecules, arrays -
<u>really work</u>

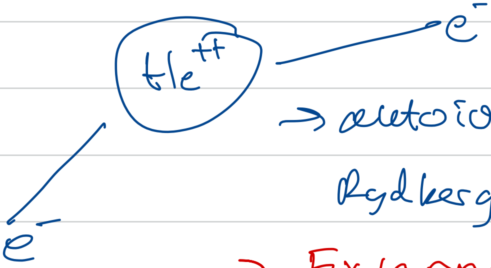
e.g.

→ Ryd-Ryd 'pair' interactions



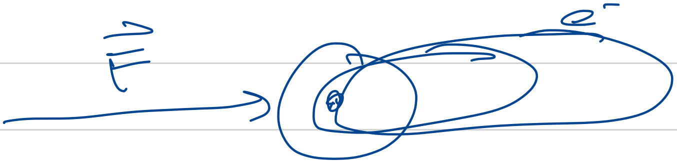
What is $V(R)$?

→ <u>M</u>ultichannel <u>Q</u>uantum <u>D</u>efect <u>T</u>heory: 2-electron systems.



→ autoionizing states, perturbed Rydberg levels, etc.

→ External Field Control



(Stark map
quantum
chaos)

. . . But wait, there's more!

② To use Rydberg systems as examples / models to introduce more general topics in AMO.

e.g.

→ Multichannel scattering theory / methods for solving nonseperable problems

→ Born - Oppenheimer Approx. and beyond Born - Opp. physics

→ SUSY QM

→ Pseudopotentials, ultracold atoms.

→ BEC physics.

We will start the course off with a couple of concepts to illustrate this approach. It gets at some of the main reasons why I enjoy doing Rydberg physics:

→ Describing highly excited states is sometimes easier than you would think, and sometimes much harder, but it is always interesting!

→ Rydberg systems give you a good motivation / excuse to pick up new ideas - and often they upend your intuition due to their exaggerated properties.

Without further ado, let's see what a Rydberg atom actually is!!

Here we'll follow Gallagher closely, but also

Introduction to Atomic Spectra,
H.E. White 1934!!

This textbook gives a very lucid account of the historical development that led to the Rydberg formula + Quantum mechanics itself!

1868: Ångstrom: sun's spectrum
→ precision of $10/10^6$ of a mm!

1882: Rowland manufacturing grating

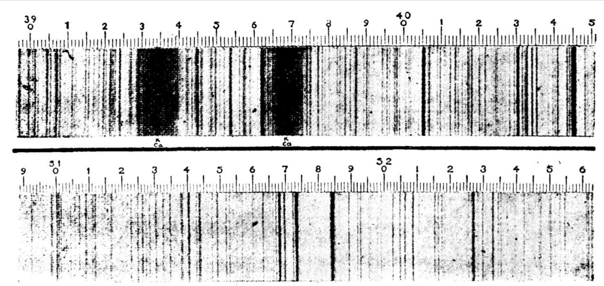


FIG. 1.2.—Sections of Rowland's solar map.

← 50 feet long!

Basic question emerges: why does each element have a characteristic spectrum?

→ And moreover: what determines the distribution + placement of spectral lines?

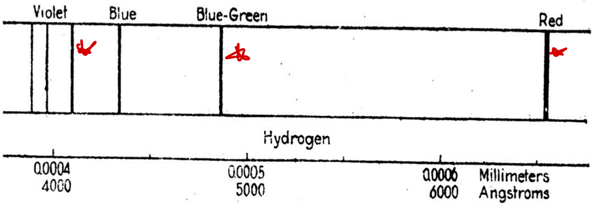


FIG. 1.3.—The Balmer series of hydrogen.

e.g.: Stoney (1871) found that * are 20th, 27th, + 32nd harmonics of 131274.14 Å.

→ but this is random chance!

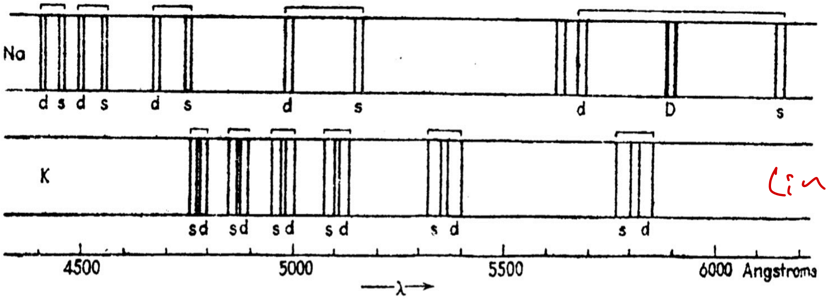


FIG. 1.4.—Schematic representation of the sodium and potassium series. (*After Liveing and Dewar.*)

(1879)

(in K: s, d labels rather than characteristic..)

more clues: s + d lines

sharp diffuse

We will revisit the appearance of s, d lines later - with full QM!

1885: Balmer makes a "theoretical breakthrough"! $\lambda = 3645.6 \cdot \frac{n_2^2}{n_2^2 - n_1^2}$

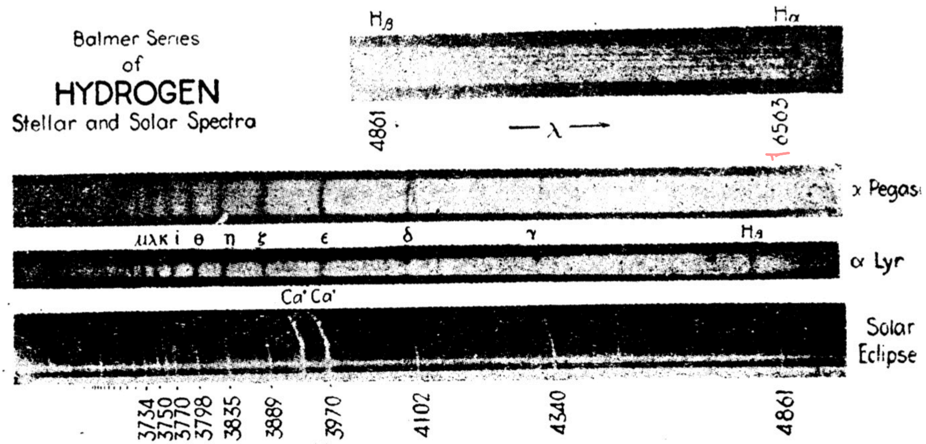
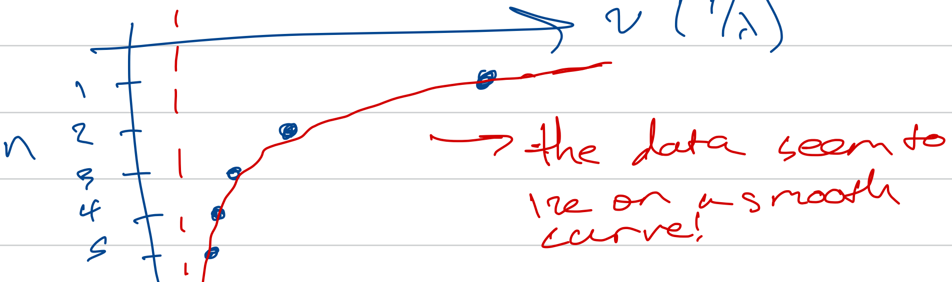


Fig. 1.5.—Stellar and solar spectrograms showing the Balmer series of hydrogen.

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

1888: Rydberg makes a major breakthrough. To do so, he realized that a convenient way to visualize all of these lines was to plot:



→ the data seem to lie on a smooth curve!

To do this requires *good classification*: separation of *all* spectral lines into *series*
s, p, d, f, ...

It also requires *good data*: Rydberg saw that this plot gives similar curves for many species!

Natural next step: fit a curve to these data!

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

This did not work.

Guess #2: try a different exponent

→ *Rydberg's Formula* ←

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

Don't let your familiarity with this formula lessen its impact! This is a beautiful success of physics.

Why? Two reasons:

1) The constant N (now called R_∞, the Rydberg constant) is the same for all atoms.

(1a): since this formula matches Balmer's for $\mu=0$, we can calculate R_∞ for H...

2) The series limits ν_∞ are the same for all series in an atom.

i.e. for Na:

$$\nu_s(n) = \nu_\infty - \frac{R_\infty}{(n+\mu_s)^2}$$

$$\nu_p(n) = \nu_\infty - \frac{R_\infty}{(n+\mu_p)^2}$$

$$\nu_d(n) = \nu_\infty - \frac{R_\infty}{(n+\mu_d)^2}$$

$$\vdots$$

Side note: it actually wasn't so easy. Recall that Rydberg was fitting (as we now know - he had no idea!) transitions between energy levels.

Actually, Rydberg first came up with:

$$\nu_n^s = \underline{28601.6} - \frac{\underline{R}}{(n+0.5951)^2}, \quad n=2,\dots$$

$$\nu_n^p = \underline{43487.7} - \frac{\underline{R}}{(n+0.9596)^2}, \quad n=1,\dots$$

$$\nu_n^d = \underline{28598.5} - \frac{\underline{R}}{(n+0.9974)^2}, \quad n=1,\dots$$

$R = 109721.6$ is the same for all, but the series limits are not!

But if we take $n=1$:

from $\underline{s}$: $\frac{R}{(n+0.5951)^2} \approx 43123.7 \approx \nu_n^p$

from $\underline{p}$: $\frac{R}{(n+0.5951)^2} \approx 28573.1 \approx \nu_n^s$ or ν_n^d

Rydberg assumed these are the same, up to experimental error, and thus:

$$\nu_n^s = \frac{R}{(1+\mu_p)^2} - \frac{R}{(n+\mu_s)^2}$$ (D same as S)

$$\nu_n^p = \frac{R}{(1+\mu_s)^2} - \frac{R}{(n+\mu_p)^2}$$

Thus, the lines observed all look like differences between a 'ground state' frequency and an 'excited' frequency. We of course know now how to interpret all of this - frequency differences, the connection b/w s,p; p,d; etc, and the Rydberg constant, but it is amazing to see that all of this was basically figured out for 30 years before QM!

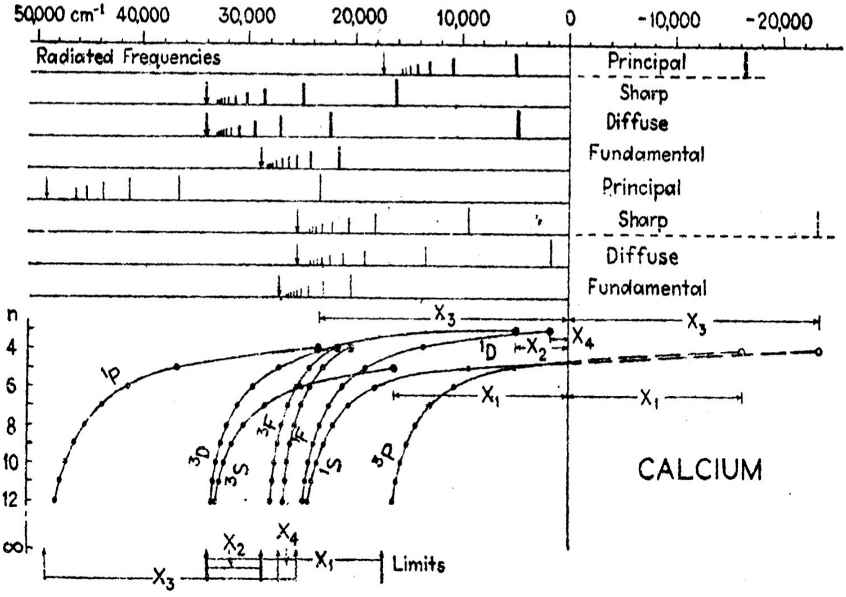


FIG. 1.8.—Schematic plot of the chief triplet and singlet series of calcium showing the Rydberg-Schuster and Runge laws.

There's also a nice 'cautionary tale' here in addition to this success story!

Pickering Series:

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

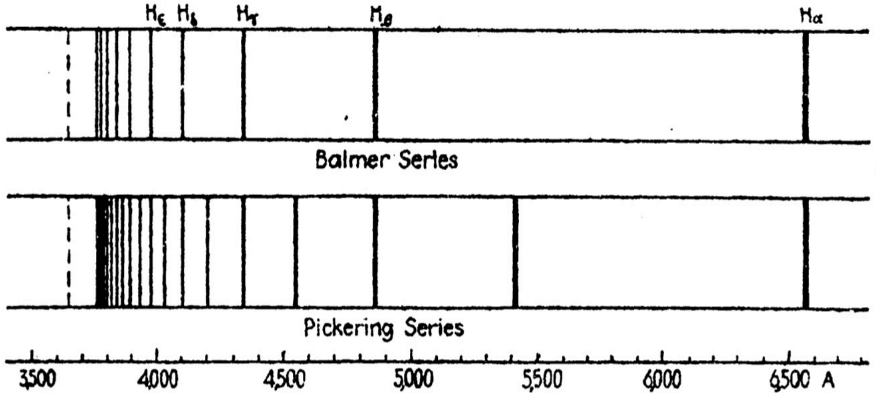


FIG. 1.14.—Comparison of the Balmer series of hydrogen and the Pickering series.

The Pickering series included lines overlapping the Balmer series, i.e. like H, but also lines well-described by half-integer n in the Rydberg formula!

$$\nu_n = R\left(\frac{1}{2^2} - \frac{1}{n_2^2}\right), \quad n_2 = 2.5, 3, 3.5, \dots$$

Feeling confident, Rydberg thought that restricting $n_1 = 2$ was too much if n_2

could also be half-integer. So he predicted lines also at

$$\nu_n = R\left(\frac{1}{1.5^2} - \frac{1}{n_2^2}\right), \quad n_2 = 2, 2.5, \ldots$$

AND they were observed!!

→ Rydberg predicted a new type of hydrogen, found only in stars, and it was experimentally confirmed!

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!

BOHR'S MODEL OF THE ATOM

2 'ad hoc' assumptions:

1) Angular momentum is quantized, $L = n\hbar$
2) Electrons ~~do~~ not radiate continuously.

technically: this is demanded by experiment!

technically: this picture is a big approx too!

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

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

And from (1): $mvr = n\hbar$

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

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

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

Total energy: $$E = \frac{1}{2}mv^2 - \frac{1}{4\pi\varepsilon_0}\frac{Ze^2}{r}$$

$$= \frac{1}{2}\frac{(n\hbar)^2}{mr^2} - \frac{1}{4\pi\varepsilon_0}\frac{Ze^2}{r}$$

$$= \frac{1}{2}\frac{\cancel{n^2\hbar^2}}{m}\cdot\frac{Z^2}{(\hbar^2 n^2)^{\cancel{2}}}\left(\frac{e^2 m}{4\pi\varepsilon_0}\right)^2$$

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

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

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

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

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

Aside: Bohr's model does not predict those pesky "quantum defects"

$$\nu_s = -\frac{R}{(n+\underline{\mu})^2}$$

So it is quantitatively useless for anything but H!

For some fun reading on other semiclassical attempts to improve on the Bohr model, see

Tanner, Richter, and JM Rost

RMP 72 497 (2000).

But the Bohr model does 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^+!

End Aside!

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:

$$-\frac{1}{2(n+1)^2} - \left(-\frac{1}{2(n)^2}\right) = \frac{-n^2+(n+1)^2}{2n^2(n+1)^2}$$

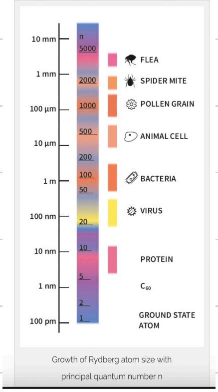
$$\approx n/n^4 \sim \underline{n^{-3}}.$$

→ The atom gets very large!

$$r \sim n^2 \Rightarrow r_{n=30} \sim \underbrace{5.29\times10^{-11}\,\text{m}}_{\text{Bohr radius } a_0} \cdot 30^2$$

$\sim$ 10s of nm.

$r_{n=100} \sim 1$ μm.



Growth of Rydberg atom size with principal quantum number n

←

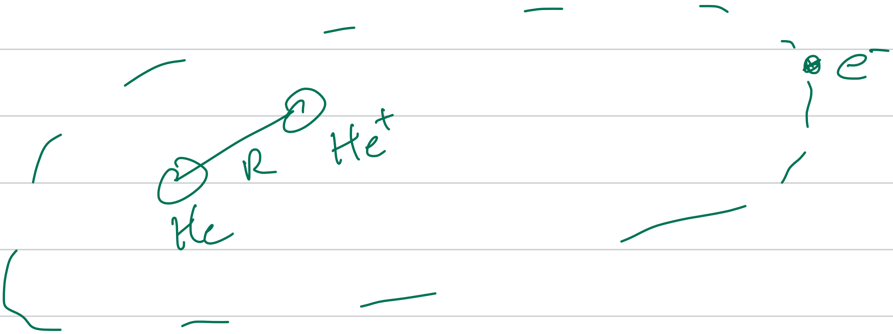
(Berg, Dunning, Tom Killian)

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

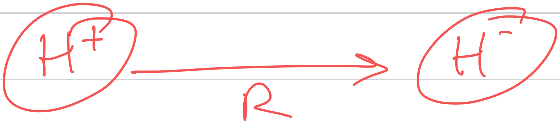
These will be our topic.
But more generally, we can consider 'Rydberg physics' to mean excited electronic states of various objects:

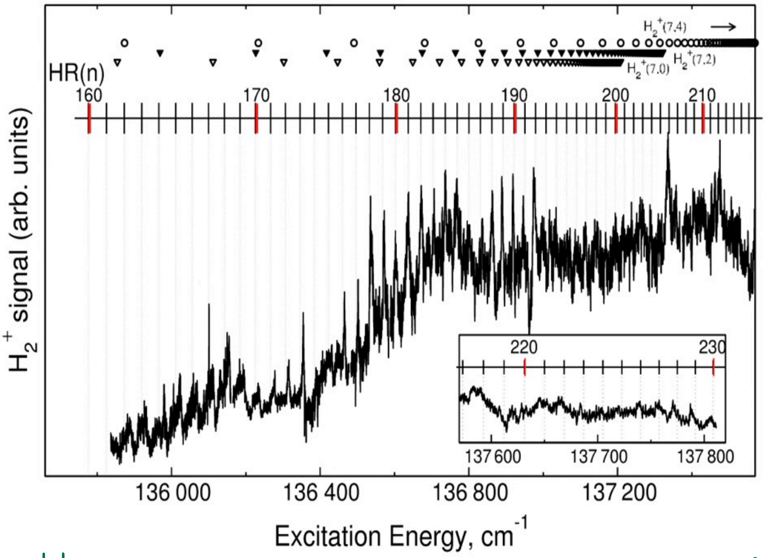
- Molecules



→ Very tough problem!
(likely outside our scope)

But another type of Rydberg molecule is easier to model:





Vieitez et al PRL 101 163001 (2008)

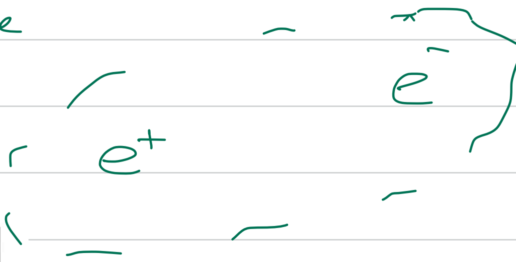
(notice - here it is the vibrational excitation that is 'Rydberg') → already my definition used!

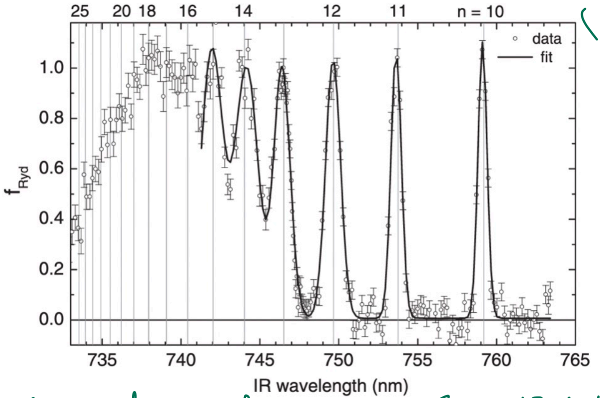
Recall: $R_y \sim m_e$ in the Bohr model.

Actually, that is only for an infinitely heavy atom. It should depend on $\frac{m_1 m_2}{m_1 + m_2}$, the reduced mass, μ.

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

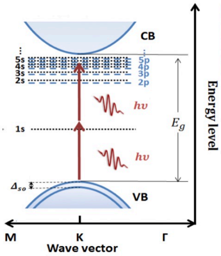
We can also Rydberg excite more exotic things - Ps for example



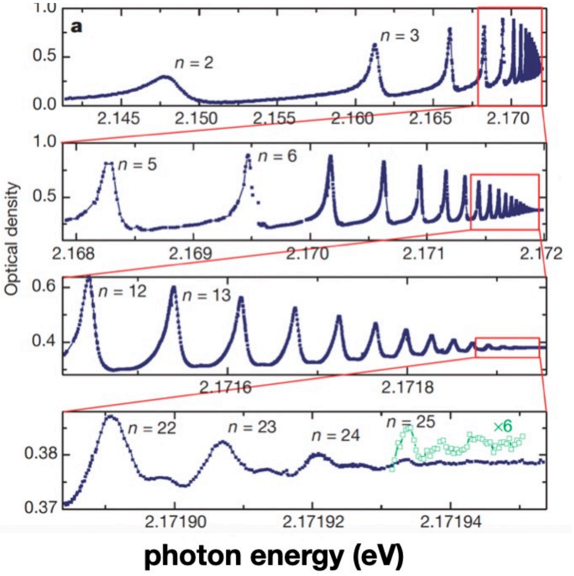


← Perfect fit to Rydberg formula, but again without the R_∞!

Cassidy et al PRL 108 043401 (2012)



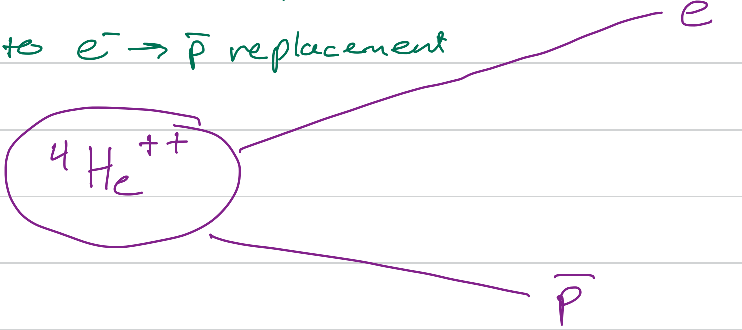
Rydberg excitons - hole + electron pairs - have been excited and are a vibrant area of study!



Kazimierczuk et al Nature 514 343 (2014)

And my current favorite, 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 $e^- \to \bar{p}$ replacement

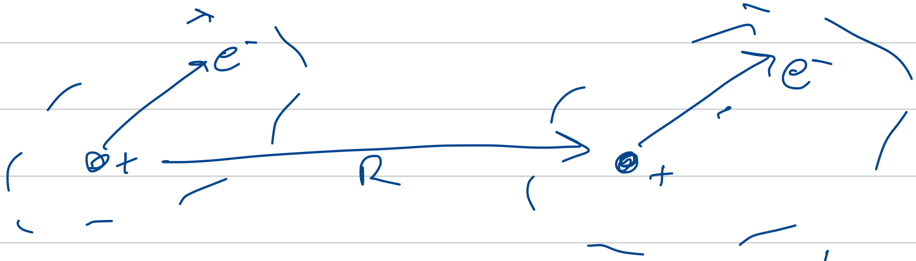


In the experiment, they measure transitions between Rydberg states of $He^{++} + \bar{p}$ (37→38 to be precise) which, due to the large μ, are smaller in size than the electronic ground state!

A quick teaser: why are Rydberg atoms so popular?

→ CONTROLLABLE INTERACTIONS OVER $\underline{\underline{12}}$ 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 $E \sim d/R^3$, 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 $\sim n^{-3}$

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

This <u>enormous</u> power law is what makes Rydberg atoms so useful.

They have appreciable interactions at a > μm. range.

<u>AND</u>, this interaction can be toggled on/off! (compare w/ trapped ions)

Since ~2000-2002, when several seminal papers came out:

- Lukin et al PRL 87 037901 (2001)
  "Dipole Blockade and Quantum Info. Processing..."

- Jaksch et al PRL 85 2208 (2000)
  "Fast Quantum Gates for Neutral Atoms"

- Boisseau et al PRL 88 133004 (2002)
  "Macrodimers: Ultralong Range Ryd. Molecules"

the field has grown tremendously due to those aspects!

Related Topics:

- Electromagnetically Induced Transparency (EIT)
- Rydberg Polaritons
- Quantum Simulation in Ryd. arrays
- Quantum many-body scars / PXP Hamiltonian
- Quantum information / computing

BUT:

I do not plan to cover most, if not all, of these topics in this course!

There isn't enough time and I'm just not sufficiently enthusiastic about them!

But I would like to be.

→ **Project:** prepare a ~20 minute lecture / journal club on one of these topics.

Pick a topic and a date, and confirm with me!