# Lecture 4

30 Oct, '23

Last time, we learned:

- How to <u>factorize</u> a Hamiltonian

$$H = A^{+}A$$

so that its susy-partner

$$\tilde{H} = AA^{+}$$

could be found

- That $H$ and $\tilde{H}$ have degenerate spectra except for the ground state.
- How to use this to:
  - relate one $H$ w/ another to solve 2 problems for the price of 1.
  - Build up the solution of the Coulomb problem directly.

We won't do much more with SUSY-QM in the future, but it will pop up in surprising places on occasion. → so stay tuned!

Actually, we can use SUSY to introduce a <u>major topic</u> - quantum defect theory!

the next few weeks in fact.

This comes from:

V. Kostelecky + M. M. Nieto,
"Evidence for a Phenomenological Supersymmetry in Atomic Physics"
<u>PRL</u> <u>53</u> 2285 (1984)

These authors start from the SUSY partner potentials that we used,

$$V^{(1)} = -\frac{1}{r} + \frac{\ell(\ell+1)}{2r^2} + \frac{1}{2(\ell+1)^2}$$

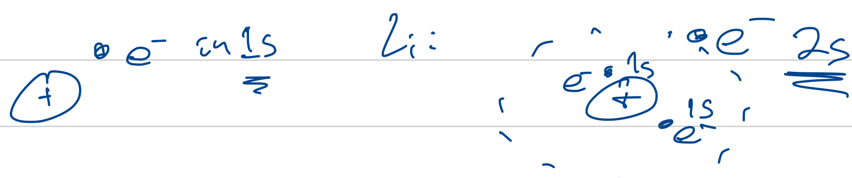
$$V^{(2)} = -\frac{1}{r} + \frac{(\ell+1)(\ell+2)}{2r^2} + \frac{1}{2(\ell+1)^2},$$

and then claim: since $H^{(2)} = -\frac{1}{2}\frac{d^2}{dr^2} + V^{(2)}$ has the same spectrum as $H^{(1)} = -\frac{1}{2}\frac{d^2}{dr^2} + V^{(1)}$ but with the ground state removed, then $H^{(2)}$ describes a system with the 1s orbital removed.

So: in the absence of electron-electron interactions, $H^{(2)}$ is the Hamiltonian of Li!

H:

Li:



The authors then go on to claim that this means that atomic spectra contain evidence for supersymmetry! (And that this supersymmetry is broken by e-e interactions.)

How do they justify this claim? With experiment, of course!

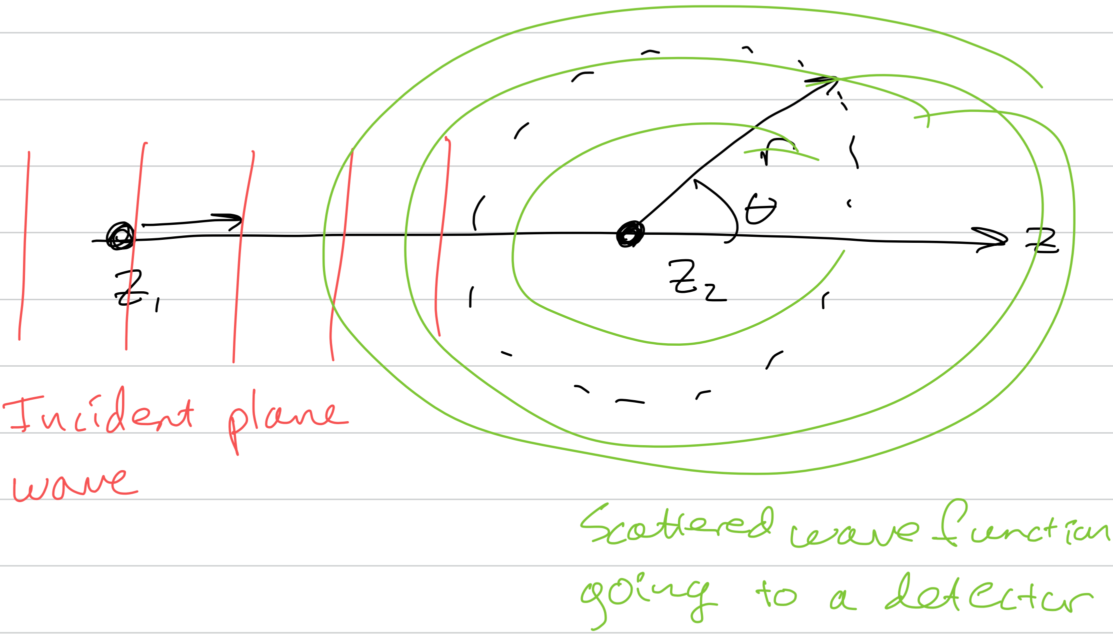
TABLE I. Energy differences (in units of $10^4$ cm$^{-1}$) between selected levels of the alkali-metal atoms (Ref. 6). The best agreements with the H levels are underlined and are those that one would expect from the discussion in the text. → those where e-e int is weak.

| | H | Li | | | Na | | |
|---|---|---|---|---|---|---|---|
| $n$ | $s/p/d$ | $s$ | $p$ | $d$ | $s$ | $p$ | $d$ |
| 8-9 | 0.0360 | 0.0416 | 0.0366 | 0.0360 | 0.0607 | 0.0496 | 0.0362 |
| 6-7 | 0.0808 | 0.0980 | 0.0826 | 0.0810 | 0.164 | 0.124 | 0.0814 |
| 4-5 | 0.245 | 0.329 | 0.255 | 0.247 | 0.746 | 0.477 | 0.249 |
| 3-4 | 0.533 | 0.781 | 0.555 | 0.534 | 2.57 | 1.33 | 0.538 |
| 2-3 | 1.52 | 2.72 | 1.60 | . . . | . . . | . . . | . . . |

Although agreement between the underlined transitions seems pretty good, you might find this line of argument a bit fishy...

We are going to compute the spectrum of a Ryd atom in a rather roundabout way, for reasons that will become clear later. So let's just get started with...

## TWO-BODY COULOMB SCATTERING




Asymptotic wave function describing this scenario:

$$\psi(\vec{r})_{r\to\infty} = e^{ikz} + f(\theta,\phi)\frac{e^{ikr}}{r}$$

We want to obtain a solution of the Schrödinger equation,

$$\left(\frac{\vec{p}^2}{2m} + \frac{Z_1 Z_2}{r} - \frac{k^2}{2}\right)\psi = 0,$$

satisfying the boundary conditions implied by that scattering solution.

This problem is conveniently solved in parabolic coordinates, defined:

$$\left.\begin{aligned} \xi &= r + z = r(1+\cos\theta) \\ \eta &= r - z = r(1-\cos\theta) \end{aligned}\right\} \text{ both go from } 0 \to \infty.$$

$$\varphi = \varphi.$$

$$\to z = \frac{\xi - \eta}{2}$$
$$r = \frac{\xi + \eta}{2}.$$

With:

$$\nabla^2\psi = \frac{4}{\xi+\eta}\left[\frac{\partial}{\partial\xi}\left(\xi\frac{\partial\psi}{\partial\xi}\right) + \frac{\partial}{\partial\eta}\left(\eta\frac{\partial\psi}{\partial\eta}\right) + \frac{1}{4}\left(\frac{1}{\xi}+\frac{1}{\eta}\right)\frac{\partial^2\psi}{\partial\varphi^2}\right]$$

and

$$dV = \frac{1}{4}(\xi+\eta)\, d\xi\, d\eta\, d\varphi.$$

Thus: $$V = \frac{Z_1 Z_2}{r} \equiv Q/r = \frac{2Q}{\xi+\eta}.$$

The SE is therefore

$$-\frac{1}{2}\nabla^2 \psi + \frac{2Q}{\xi+\eta}\psi = E\psi$$

$$\rightarrow \frac{(\xi+\eta)}{4}\nabla^2\psi - Q\psi = -E\frac{(\xi+\eta)}{2}\psi.$$

Usual trick: assume a separable sol'n:

$$\psi = u(\xi)V(\eta)e^{im\varphi}$$

And then plug in / divide...

$$\frac{1}{u(\xi)}(\xi u'(\xi))' + \left(\frac{-m^2}{4\xi} + \frac{E\xi}{2}\right) \leftarrow Q_1$$

$$+\frac{1}{V(\eta)}(\eta V'(\eta))' + \left(\frac{-m^2}{4\eta} + \frac{E\eta}{2}\right) \leftarrow Q_2$$

$$= Q$$

Thus: $Q_1 + Q_2 = Q$ (all constant!)

$$\rightarrow (\xi u'(\xi))' + \left(\frac{-m^2}{4\xi} - Q_1 + \frac{E}{2}\xi\right)u(\xi) = 0 \quad (1)$$

$$\text{and } (\eta V'(\eta))' + \left(\frac{-m^2}{4\eta} - Q_2 + \frac{E}{2}\eta\right)V(\eta) = 0$$

Once we solve these two equations, we'll have our solution. But let's consider again the scattering B.C.'s, namely

$$\psi_{r\to\infty} \rightarrow \text{scattered stuff} + \underbrace{e^{ikz}}_{} \nearrow = e^{\frac{ik}{2}(\xi-\eta)}$$

Since we have azimuthal symmetry, let's also select just $m=0$ to solve.

By defining $\psi = e^{ikz}\,\Phi(\xi,\eta)$, we see that our sep. sol'n looks like

$$\psi = \underbrace{e^{\frac{ik\xi}{2}} f_1(\xi)}_{u(\xi)}\,\underbrace{e^{\frac{-ik\eta}{2}} f_2(\eta)}_{v(\eta)}$$

So rewriting the DEs in ① in terms of these new solutions gives:

scratch work

$$\left(\xi\left[\frac{ik}{2} e^{-} f_1 + e^{-} f_1'\right]\right)' + \left(\frac{E}{2}\xi - Q_1\right)e^{-} f_1 = 0$$

$$\rightarrow \frac{ik}{2} f_1 + f_1' + \xi\cancel{\left(\frac{-k^2}{4}\right)} f_1 + \frac{ik\xi}{2} f_1'$$

$$+ \xi\frac{ik}{2} f_1' \; \xi f_1'' + \left(\cancel{\frac{k^2}{4}\xi} - Q_1\right) f_1 = 0$$

$$\rightarrow \xi f_1'' + (1 + ik\xi) f_1' + \left(\frac{ik}{2} - Q_1\right) f_1 = 0$$

$$\longrightarrow \xi f_1''(\xi) + (1 + ik\xi) f_1'(\xi) + \left(\frac{ik}{2} - Q_1\right) f_1(\xi) = 0$$

and $\eta f_2''(\eta) + (1 - ik\eta) f_2'(\eta) + \left(-\frac{ik}{2} - Q_2\right) f_2(\eta) = 0.$

These are <u>known</u> diffy-Q's!

$$y = -ik\xi \rightarrow \xi = y/-ik$$

$$f''(\xi) = f''(y)\cdot\frac{d^2y}{d\xi^2}$$

$$= f''(y)\cdot(-ik)^2$$

→ we get

$$y f_1''(y) + (1-y) f_1'(y) - \left(\frac{1}{2} - \frac{Q_1}{ik}\right) f_1(y) = 0$$

This eqn, and the similar one for $f_2$, is the diffy-Q defining the CONFLUENT HYPERGEOMETRIC FUNCTION

$$\rightarrow f_1 = F(\underbrace{1/2 - \tfrac{Q_1}{ik}}_{a};\ \underbrace{1}_{b};\ \underbrace{-ik\xi}_{x})$$

This is a very useful special function in Rydberg physics (and elsewhere), so it deserves some special attention.

To get the notation straight, $F(a;b;x)$ obeys the DE

$$x F''(a,b,x) + (b-x) F'(a,b,x) - a F(a,b,x) = 0.$$

You can easily check that:

$$F(a;b;x) = 1 + \frac{a}{b}\frac{x}{1!} + \frac{a(a+1)}{b(b+1)}\frac{x^2}{2!} + \dots$$

$$= \frac{\Gamma(b)}{\Gamma(a)\Gamma(b-a)} \sum_{k=0}^{\infty} \frac{\Gamma(b-a)\Gamma(a+k)}{\Gamma(b+k)} \frac{x^k}{k!}$$

satisfies the DE (at least the constant part is easy to check).

(Note: this is the regular sol'n as $x \to 0$, and b cannot be a negative integer).

To check if our solutions obey the asymptotic boundary conditions, we will need the asymptotic behavior of this!

Let's use some $\Gamma$-func identities...

$$\Gamma(z+1) = z\,\Gamma(z) \qquad \text{and}$$

$$\underbrace{\frac{\Gamma(b-a)\Gamma(a+k)}{\Gamma(b+k)}}_{\text{"}A\text{"}} = \int_0^1 t^{a-1+k}(1-t)^{b-a-1}\,dt$$

So: $$\sum_k A\frac{x^k}{k!} = \int_0^1 t^{a-1}(1-t)^{b-a-1}\underbrace{\sum_k \frac{(tx)^k}{k!}}_{\text{this is } e^{xt}!}\,dt$$

$$\rightarrow F(a;b;x) = \frac{\Gamma(b)}{\underbrace{\Gamma(a)\Gamma(b-a)}_{=\text{"}\lambda\text{"}}}\int_0^1 e^{xt}t^{a-1}(1-t)^{b-a-1}\,dt$$

We want the $x\to\infty$ asymptotic form. To get this, let's split up the integral into two parts:

$$F = \lambda\int_0^{-\infty} e^{xt}t^{a-1}(1-t)^{b-a-1}\,dt$$
$$+\lambda\int_{-\infty}^{1} e^{xt}t^{a-1}(1-t)^{b-a-1}\,dt$$

In green: let $t \equiv -w/x$.

In blue: let $t \equiv 1-u/x$

$$\rightarrow F = \lambda(-x)^{-a}\int_0^\infty e^{-w}\, w^{a-1}\left(1+\frac{w}{x}\right)^{b-a-1} dw$$
$$+\lambda x^{a-b} e^{x}\int_0^\infty e^{-u}\, u^{b-a-1}\left(1-u/x\right)^{a-1} du$$

Woohoo! We now have an asymptotically small parameter, $w/x$ and $u/x$, in both integrals!

$\rightarrow$ insert the binomial expansion

$$\left(1-\frac{u}{x}\right)^{a-1} \rightarrow \underline{1} - (a-1)\,u/x + \ldots$$

We actually only need the leading order term $\underline{1}$ because this gives us some very friendly integrals:

$$\int_0^\infty e^{-u} u^{p-1}\, du = \Gamma(p)$$

Thus: as $x \rightarrow \infty$,

$$F \rightarrow \lambda(-x)^{-a}\,\Gamma(a) + \lambda x^{+a-b} e^{x}\,\Gamma(b-a)$$
$$= \underbrace{\frac{\Gamma(b)}{\Gamma(b-a)}(-x)^{-a} + \frac{\Gamma(b)}{\Gamma(a)} x^{a-b} e^{x}}$$

This is a very important property of $F(a;b;x)$ !!!

Let's return to $f_1$, $f_2$, which are:

$$f_1(\xi) = F(1/2 - Q_1/ik \,;\, 1 \,;\, -ik\xi)$$
$$f_2(\eta) = F(1/2 + Q_2/ik \,;\, 1 \,;\, ik\eta)$$

As $\xi, \eta \to \infty$ we can inspect our solution to see if it obeys BC's!

$$u(\xi)v(\eta) \longrightarrow \frac{\Gamma(1)}{\Gamma(1/2 + \frac{iQ_1}{k})\Gamma(1/2 - iQ_1/k)} \cdot \frac{\Gamma(1)}{\Gamma(1/2 - \frac{iQ_2}{k})\Gamma(1/2 + \frac{iQ_2}{k})}$$
$$\cdot \left[\Gamma\left(\tfrac{1}{2} + \tfrac{iQ_1}{k}\right)(ik\xi)^{-1/2 - iQ_1/k} e^{\frac{ik\xi}{2}} + \Gamma\left(1/2 - \tfrac{iQ_1}{k}\right)(-ik\xi)^{-1/2 + \frac{iQ_1}{k}} e^{-ik\xi/2}\right]$$
$$\cdot \left[\Gamma\left(\tfrac{1}{2} - \tfrac{iQ_2}{k}\right)(-ik\eta)^{-1/2 + iQ_2/k} e^{-\frac{ik\eta}{2}} + \Gamma\left(1/2 + \tfrac{iQ_2}{k}\right)(ik\eta)^{-1/2 - \frac{iQ_2}{k}} e^{ik\eta/2}\right]$$

Yikes, what a mess! But recall: the soln should look like:

$$\psi \to e^{ikz} + f(\theta)\frac{e^{ikr}}{r}$$

$$\to e^{\frac{ik(\xi - \eta)}{2}} + f(\theta)\frac{e^{\frac{ik}{2}(\xi + \eta)}}{\frac{1}{2}(\xi + \eta)}$$

This only has outgoing waves in $\xi$!

So everything in the mess above which has $e^{-\xi}$ in it MUST GO!

$$\boxed{\to \Gamma\left(1/2 + \frac{iQ_1}{k}\right) \to \infty}$$

Thus we know what $Q_1$ must be:

$$Q_1 = \frac{ik}{2} + nik, \quad n = 0, 1, 2 \ldots$$

(keep in mind: what we are really doing is making sure that $\frac{\Gamma(1/2 - iQ_1/k)}{\Gamma(1/2 + 2Q_1/k)} \to 0$. But since $\Gamma$-funcs only have poles, no zeros, the denom must blow the func up! And this happens when $1/2 + \frac{2Q_1}{k} = -n$

$$\to Q_1 = +nik + \frac{ki}{2}.)$$

When we impose this condition, we get the surviving $\xi$-dependent term to be:

$$\sim (-ik\xi)^n e^{ik\xi/2}.$$

But once again our BCs say: no! There are no "extra powers" of $\xi$ at $\xi \to \infty$!

So $\underline{\underline{n = 0}}$.

Thus $Q_1 = \frac{ik}{2}$ and $Q_2$ must then be

$$Q_2 = Q - ik/2.$$

After all that pain we finally obtain:

$$\psi = u(\xi)v(\eta) \xrightarrow[\xi,\eta\to\infty]{} \frac{e^{\frac{ik}{2}(\xi-\eta)}(-ik\eta)^{iQ/k}}{\Gamma(1+iQ/k)} + \frac{e^{\frac{ik}{2}(\xi+\eta)}(ik\eta)^{-1-iQ/k}}{\Gamma(-iQ/k)}.$$

or, in a more familiar form,

$$\longrightarrow e^{ikz}(\eta)^{iQ/k} + \frac{e^{ikr}}{ik\eta}(\eta)^{-iQ/k}(ik)^{-iQ/k}(-ik)^{-iQ/k}$$

$$\text{or: } e^{ikz + \frac{iQ\ln\eta}{k}} + \frac{e^{ikr - \frac{2Q}{k}\ln\eta}}{ik\eta}\frac{\Gamma(1+\frac{iQ}{k})}{\Gamma(-iQ/k)}(k^2)^{-iQ/k} \quad \text{✫}$$

Notice these r-dependent phases - a distinctive (and often annoying) feature of the Coulomb potential, but one which is ultimately irrelevant for most results as it is "just" a phase.

From ✫ we can read off the scatt. amplitude.

$$f(\theta) = \frac{1}{ik(1-\cos\theta)}(k^2)^{-iQ/k}\frac{\Gamma(1+\frac{iQ}{k})}{\Gamma(-\frac{iQ}{k})}e^{-\frac{2iQ}{k}\ln(1-\cos\theta)}$$

And with this, the differential cross section

$$\frac{d\sigma}{d\Omega} = |f(\theta)|^2 = \frac{Q^2}{4k^4 \sin^4(\theta/2)},$$

which is exactly the classical Rutherford formula!

So, that was a lot of work to solve the problem of 2-body Coulomb scattering for positive collision energies $E = \frac{k^2}{2}$. What could this possibly have to do with Rydberg spectra?

One consistent theme I want to develop in this course, and which will be both illustrated by and a key tool in developing our Rydberg theory, is that

collisions

and

spectroscopy

are very related, even unified, concepts!