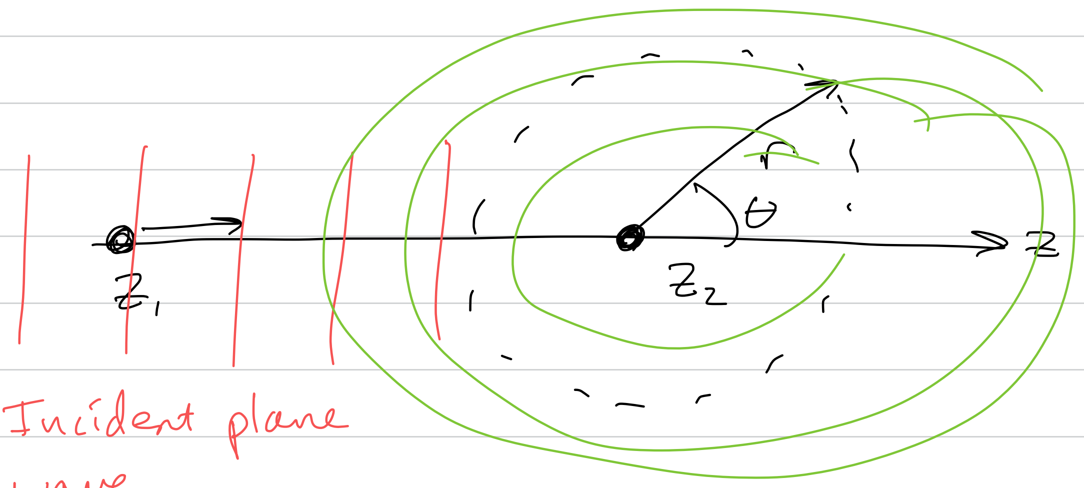
Lecture 3

22 Apr. '24

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



Incident plane wave

Scattered wave function going to a detector

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...

$$\underbrace{\frac{1}{u(\xi)}(\xi u'(\xi))' + \left(\frac{-m^2}{4\xi} + \frac{E\xi}{2}\right)}_{\leftarrow Q_1} + \underbrace{\frac{1}{v(\eta)}[\eta v'(\eta)]' + \left(\frac{-m^2}{4\eta} + \frac{E\eta}{2}\right)}_{\leftarrow Q_2} = Q$$

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

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

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

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

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

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

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

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

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

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

These are known diffy-Q's!

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

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

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

$\to$ we get

$$yf_1''(y) + (1-y)f_1'(y) - \left(\frac{1}{2} - \frac{Q_1}{ik}\right)f_1(y) = 0$$

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

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

You can easily check that:

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

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

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 Γ-func identities...

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

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

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

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

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 $F(a;b;x)$!!!

Lecture 4 starts here! Apr 2 1, '24

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:

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

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

This only has outgoing waves in ξ!

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 Γ-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 ξ-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 ξ 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,

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

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

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!

We will often see how scattering physics, such as phase shifts, connect to bound state physics, such as their energy levels. Learning how to extract these links will be key!

In the present case, we will observe that poles of the scattering amplitude (or S-matrix) determine the bound state energies!

To see why, let's analytically continue to $E<0$ by setting $k \to iK \quad (K>0)$

$$\to E = -K^2/2.$$

Doing this in our scattering solution gives

$$\psi \longrightarrow N\left(e^{-Kz} + f(iK,\theta)\frac{e^{-Kr}}{r} \right)$$

this diverges when $z \to -\infty$, which is simply <u>not</u> acceptable!

To fix this, we need $f(iK,\theta)$ to diverge even better! $\to \Gamma\left(1+\frac{iQ}{iK}\right) \to \infty$.

Recall:

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

This implies that $1 + Q/k$ is a negative int. or zero

$$\rightarrow \quad 1 + \frac{Z_1 Z_2}{k_n} = -(n-1), \quad n = 1, 2, \ldots$$

$$\rightarrow \quad k_n = \frac{Z_1 Z_2}{n}$$

$$\rightarrow \quad E_n = -\frac{Z^2}{2n}, \quad \text{where } -Z = Z_1 Z_2$$

What a coincidence! It's the Rydberg formula yet again!

Coulomb Scattering in spherical coords

Motivation: parabolic coords were very convenient to describe scattering, but atoms are still spherically symmetric! So when we really want to solve more complicated problems, especially for non-hydrogenic atoms, we will need to do this in sph. coords.

The radial sol'ns obey

$$-\frac{1}{2}u_\ell''(r) + \left(\frac{\ell(\ell+1)}{2r^2} - \frac{Z}{r} - \frac{k^2}{2}\right)u_\ell(r) = 0 \qquad (1)$$

A good way to solve equations such as this one is to factor out the <u>long</u> and <u>short</u> range behavior we expect the sol'n to have:

$$u_\ell(r) \sim r^{\ell+1}, \quad r \to 0$$

$$u_\ell(r) \sim e^{ikr}, \quad r \to \infty$$

$$\to \underline{u_\ell(r) = r^{\ell+1} e^{ikr} F_\ell(r)}$$

Putting this into (1) gives, after some algebra,

$$x F_\ell''(x) + (2\ell+2-x)F_\ell(x) - (\ell+1-iZ/k)F_\ell(x) = 0,$$

where $x = -2ikr$. ASTOUNDINGLY, this is just the equation for our old friend, the Conf-Hypo-Geo-Func again! So we already know the radial solution:

$$u_\ell(r) = r^{\ell+1} e^{ikr} F\left(\ell+1-\frac{iZ}{k}; 2\ell+2; -2ikr\right).$$

Recall the asymptotic form we derived:

$$e^{-x/2}F(a,b,x) \to \frac{\Gamma(b)}{\Gamma(b-a)}(-x)^{-a}e^{-x/2} + \frac{\Gamma(b)}{\Gamma(a)}x^{a-b}e^{x/2}.$$

$$\to u_\ell(r) \xrightarrow[r\to\infty]{} \Gamma(2\ell+2)\, r^{\ell+1}\left[\frac{(2ikr)^{+\frac{iZ}{k}-\ell-1}e^{ikr}}{\Gamma(\ell+1-iZ/k)} + \frac{(-2ikr)^{-\frac{iZ}{k}-\ell-1}e^{-ikr}}{\Gamma(\ell+1-iZ/k)}\right]$$

for reasons, we call this the energy-analytic solution $f^0_{E\ell}(r)$.

we are writing $\Gamma \to |\Gamma| e^{i\arg(\Gamma)}$ here

$$\to f^0_{E\ell}(r) \xrightarrow[r\to\infty]{} \frac{\Gamma(2\ell+2)}{(2k)^{\ell+1}\left[\Gamma(\ell+1-iZ/k)\Gamma(\ell+1+iZ/k)\right]^{1/2}}$$

$$\cdot\left(e^{ikr+\frac{iZ}{k}\ln 2kr}\, i^{-\ell-1} e^{i\sigma_\ell} e^{-\pi Z/2k} + e^{-ikr-iZ/k\ln 2kr}(-i)^{-\ell-1}e^{-i\sigma_\ell}e^{-\pi Z/2k}\right)$$

$$(i)^{-\ell-1} = \left(e^{i\pi/2}\right)^{-\ell-1} = e^{i\ell\pi/2}e^{-i\pi/2} = e^{i\ell\pi/2}/i$$

$$(-i)^{-\ell-1} = \left(e^{-i\pi/2}\right)^{-\ell-1} = e^{-i\ell\pi/2}e^{i\pi/2} = -e^{i\ell\pi/2}/i$$

So
$$f^0_{E\ell}(r) = \frac{2e^{-\pi Z/2k}\,\Gamma(2\ell+2)}{(2k)^{\ell+1}\left|\Gamma(\ell+1+iZ/k)\right|} \cdot \sin\left[kr + \frac{Z}{k}\ln 2kr - \frac{\ell\pi}{2} + \sigma_\ell\right]$$

Later on we will want the so-called "energy-normalized" form of this solution, which has to look like $\sqrt{\frac{2}{\pi k}}\sin(\text{stuff})$ as $r\to\infty$.

Clearly, this is satisfied by

$$f_{\varepsilon\ell}(r) = B_{\varepsilon\ell}^{1/2} f_{\varepsilon\ell}^{0}(r)$$

where

$$B_{\varepsilon\ell}^{1/2} = \left(\frac{2}{\pi k}\right)^{1/2} \Bigg/ \left(\frac{(2k)^{\ell+1}\left|\Gamma(\ell+1+iZ/k)\right|}{2e^{-\pi Z/2k}\,\Gamma(2\ell+2)}\right)$$

Brilliant! While we are here, we will want to extend this solution to negative energies again using analytic continuation...

$$f_\ell^{0}(r) = r^{\ell+1} e^{-kr} F(\ell+1-Z/k,\ 2\ell+2,\ 2kr)$$

$$\rightarrow \Gamma(2\ell+2)\, r^{\ell+1}\left[\frac{(-2kr)^{Z/k-\ell-1}e^{-kr}}{\Gamma(\ell+1+Z/k)} + \frac{(2kr)^{-Z/k-\ell-1}\,e^{kr}}{\Gamma(\ell+1-Z/k)}\right].$$

Ack! $\longrightarrow$

This is again <u>NOT</u> <u>OK</u>!!

So, let's kill it off! First, we define $\frac{Z}{\kappa} = \nu$.
$\underline{\nu}$ is gonna be our "effective quantum number".

We proceed using yet another Γ-func identity,

$$\Gamma(z)\Gamma(1-z) = \frac{\pi}{\sin \pi z} \rightarrow \sin \pi z\, \Gamma(z)\Gamma(1-z) = \pi.$$

This gives:

$$f^{0}_{\varepsilon \ell}(r) \rightarrow \Gamma(2\ell+2)\, r^{\ell+1} \Bigg[\frac{(2k)^{-\ell-1} (2k)^{-\nu} r^{-\nu} r^{-\ell-1} e^{kr} \pi}{\pi\, \Gamma(\ell+1-\nu)} \quad 1-z \Rightarrow z = \nu - \ell$$

$$-e^{i\pi(\nu-\ell)} \quad + \frac{(-1)^{\nu-\ell-1} (2k)^{\nu} (2k)^{-\ell-1} r^{\nu} r^{-\ell-1} e^{-kr} \pi^{1/2}}{\Gamma(\ell+1+\nu)\, \pi^{1/2}} \Bigg]$$

$$= \frac{\Gamma(2\ell+2) \left[(2k)^{-(2\ell+1)}\right]^{1/2} (2k)^{-1/2}}{\pi^{1/2}} \Bigg[\frac{\sin\pi(\nu-\ell)(2k)^{-\nu} r^{-\nu} e^{kr}\, \Gamma(\nu-\ell)}{\pi^{1/2}}$$

$$- \frac{e^{i\pi(\nu-\ell)} (2k)^{\nu} r^{\nu} e^{-kr} \pi^{1/2}}{\Gamma(\ell+1+\nu)^{1/2}\, \Gamma(\ell+1+\nu)^{1/2}} \cdot \left(\frac{\Gamma(\nu-\ell)}{\Gamma(\nu-\ell)} \right)^{1/2} \Bigg]$$

$$= \underbrace{\left[\frac{2(2k)^{+2\ell+1}\, \Gamma(\ell+1+\nu)}{\Gamma(2\ell+2)^2\, \Gamma(\nu-\ell)} \right]^{-1/2}}_{A_{\varepsilon\ell}} (\pi k)^{-1/2} \Bigg[\sin\pi(\nu-\ell)\, e^{kr} r^{-\nu} \cdot \overbrace{\left(\frac{(2k)^{\nu} \pi^{1/2}}{\Gamma(\ell+1+\nu)^{1/2}\, \Gamma(\nu-\ell)^{1/2}} \right)^{-1}}^{D_{\varepsilon\ell}}$$

$$- e^{-i\pi(\nu-\ell)} r^{\nu} e^{-kr} \cdot \underbrace{\left(\frac{(2k)^{\nu} \pi^{1/2}}{\left[\Gamma(\ell+1+\nu)\Gamma(\nu-\ell)\right]^{1/2}} \right)^{+1}}_{D_{\varepsilon\ell}} \Bigg]$$

And so, finally:

$$f^0_{\varepsilon\ell}(r) \xrightarrow[r\to\infty]{} A_{\varepsilon\ell}^{-1/2}(\pi K)^{-1/2}\Big[\sin\pi(\nu-\ell)\, e^{Kr} r^{-\nu} D_{\varepsilon\ell}^{-1} - e^{2\pi(\nu-\ell)} e^{-Kr} r^{\nu} D_{\varepsilon\ell}\Big]$$

with

$$A_{\varepsilon\ell} = \frac{2\Gamma(\ell+1+\nu)}{\Gamma(2\ell+2)\,\Gamma(\nu-\ell)}(2K)^{2\ell+1}$$

$$D_{\varepsilon\ell} = \frac{(2K)^{\nu}\pi^{1/2}}{[\Gamma(\ell+1+\nu)\Gamma(\nu-\ell)]^{1/2}}\,.$$

Ok! Now we see how to remove these pesky divergences:

$\sin\pi(\nu-\ell)=0 \rightarrow \nu-\ell = \text{integer}$

$\rightarrow \underline{\nu = n_r+\ell+1}$

recall: $Z/K = \nu$

$\rightarrow K = \frac{Z}{n} \rightarrow \varepsilon = -\frac{K^2}{2} = -\frac{Z^2}{2n^2}\,.$

$\nu > l$ is important to remove the chance of $\Gamma(\nu - l)$ blowing up, leaving us with no solution. Going back to the def'n of K, ν, etc, we see that we have once again obtained

$$E = \frac{-K^2}{2} = \frac{-Z^2}{2n^2} = \frac{-Z^2}{2(n_r + l + 1)^2}$$

Notice a weird feature of this asymptotic form: everything was real until the end, when suddenly we got an $e^{i\pi(\nu - l)}$!

The reason for this is rather messy... involving branch cuts and other annoying things... So we argue as physicists that our real solution to a real DE should indeed be real, and take $e^{i\pi(\nu - l)} \to \cos \pi(\nu - l)$.

To treat scattering from modified Coulomb potentials, we need the 2^{nd} solution to this 2^{nd}-order DE! → importantly, this must be linearly independent to f to be any good!

remember: while $f \to r^{\ell+1}$ as $r \to 0$,

the other sol'n goes like $g \to r^{-\ell}$.

One thing we could try, to define g, would be to define $\underline{\ell \to -\ell - 1}$.

Note that this maps $\underline{f \to g}$ as $r \to 0$ and also leaves the SE unchanged, as

$$\ell(\ell+1) \to (-\ell-1)(-\ell-1+1) \to (\ell+1)(\ell).$$

But, the power series solution that we used for $F(a;b;x)$ was proportional to

$$\Gamma(b) = \Gamma(2\ell+2) \xrightarrow[\ell \to -\ell-1]{} \Gamma(-2\ell)$$

This blows up for integer ℓ, which is unfortunately the type of ℓ we are interested in. Ack!

It's rather tedious to derive this 2^{nd} Solution. WKB (to be covered later, maybe) yields a cute solution rather easily.

In the classically allowed region, $r_1 < r < r_2$, we have

$$f_{\varepsilon\ell}^{WKB}(r) = \left(\frac{2}{\pi k(r)}\right)^{1/2} \sin\left(\int_{r_1}^{r} k(r')\,dr' + \underbrace{\pi/4}_{\text{from connection formula}}\right).$$

This sol'n is regular at $r=0$ and is a smooth function of ε at small r.

At $\varepsilon < 0$ (a.k.a. larger!) this becomes (using more WKB formulas)

$$f_{\varepsilon\ell}^{WKB}(r) \underset{r\to\infty}{=} \frac{1}{\sqrt{\pi k(r)}}\left[\sin\beta \frac{e^{kr} r^{-\nu}}{D^{WKB}} - \cos\beta\, r^{\nu} e^{-kr} D^{WKB}\right]$$

$$\beta^{WKB} = \int_{r_1}^{r_2} k(r')\,dr' + \pi/2 = \pi(\nu - \ell).$$

Hmm... compare with the exact $f_{\varepsilon\ell}$ behavior we obtained earlier... this has the same structure!

At large r, our 2^{nd} linearly indep. sol'n should have the <u>same amplitude</u> as $f_{\varepsilon\ell}(r)$ but with a <u>90° phase lag</u> – think of an $\ell=0$ zero potential case where the two sol'ns are sin, −cos. Here,

$$g_{\varepsilon\ell}^{WKB}(r) \xrightarrow[r\to\infty]{} -\frac{1}{\sqrt{\pi k(r)}}\left[\frac{\cos\beta\, e^{kr} r^{-\nu}}{D^{WKB}} + \sin\beta\, e^{-kr} r^{+\nu} D^{WKB}\right]$$

And as it turns out, this matches the exact result very well (in all the ways that matter, as we'll see)

For completeness:

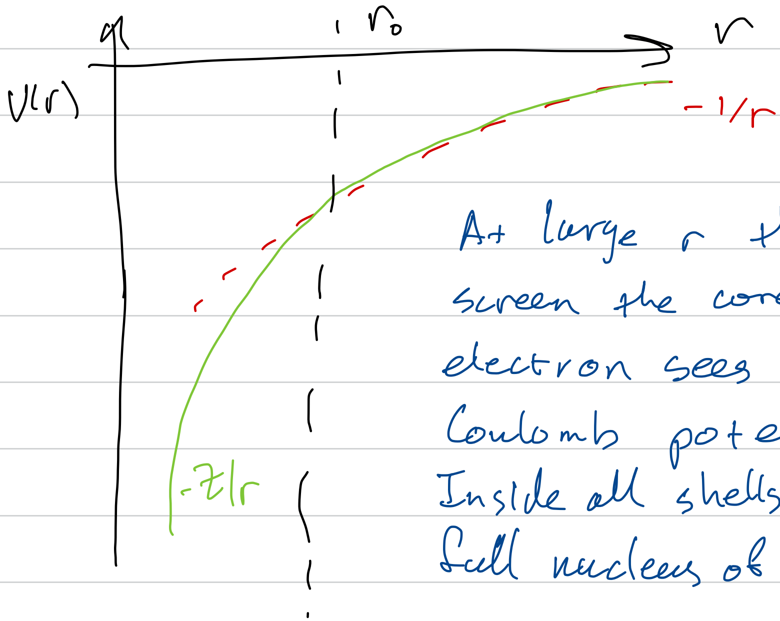
remember:

$$e^{2i\sigma_\ell} = \frac{\Gamma(\ell+1-i/k)}{\Gamma(\ell+1+i/k)}$$

$$g_{\varepsilon\ell}(r) \longrightarrow \begin{cases} -\left(\frac{2}{\pi k}\right)^{1/2}\cos\left[kr + \frac{1}{k}\ln 2kr - \frac{\ell\pi}{2} + \sigma_\ell\right] & \text{for } \varepsilon>0 \\ -(\pi k)^{-1/2}\left[\cos\pi(\nu-\ell)\, e^{kr} r^{-\nu} D_{\varepsilon\ell}^{-1} - \sin\pi(\nu-\ell)\, e^{-kr} r^{\nu} D_{\varepsilon\ell}\right] & \text{for } \varepsilon<0. \end{cases}$$

We now have all the preliminaries out of the way. It's time to treat a non-hydrogen atom, i.e. solve the MODIFIED Coulomb potential to obtain energy levels of, say, Rb.

The idea is: within the independent electron model, an electron in a multi-electron atom sees the potential:



At large r the other e^-'s screen the core and our electron sees a pure $1/r$ Coulomb potential.
Inside all shells it sees the full nucleus of Z protons.

Everywhere in between, the potential is complicated!

Aside: one can fit model potentials very accurately to exp. energy levels in order to describe this complicated physics, see Marinescu, Sadeghpour, Dalgarno PRA 49 982 (1994)

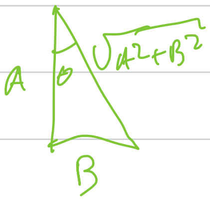
They use:

$$V(r) = -1/r \quad \text{(long-range Coulomb)}$$
$$- (z-1)e^{-a_1 r}/r \quad \text{(short-range Coulomb)}$$
$$+ (a_3 + a_4 r)e^{-a_2 r} \quad \text{(additional parameters)}$$
$$- \underbrace{\alpha_c}_{\text{core polarizability}}/2r^4 \left(1 - \exp(-r/r_c)^6\right) \quad \text{(polarization potential)}$$

and this works very well if l-dependent a_i are used. But our potential can actually be the much more generic, yet conceptually simpler:

$$V(r) = \begin{cases} \text{complicated}, & r < r_0 \\ -1/r, & r \geq r_0. \end{cases}$$

We have already solved the SE, at any energy but before applying any BCs, for the pure Coulomb part:



$$u^{out}_{\varepsilon\ell}(r) = A_{\varepsilon\ell}\, f_{\varepsilon\ell}(r) - B_{\varepsilon\ell}\, g_{\varepsilon\ell}(r)$$
$$= \sqrt{A^2+B^2}\left[\frac{A}{\sqrt{A^2+B^2}} f_{\varepsilon\ell}(r) - \frac{B}{\sqrt{A^2+B^2}} g_{\varepsilon\ell}(r)\right]$$
$$= N_{\varepsilon\ell}\left[f_{\varepsilon\ell}(r)\cos\delta_{\varepsilon\ell} - g_{\varepsilon\ell}(r)\sin\delta_{\varepsilon\ell}\right].$$

Inside, the solution w/ $U(r)$ = complicated is something complicated, but in principle solvable:

$$u^{in}_{\varepsilon\ell}(r) = u^{in}_{\varepsilon\ell}(r).$$

A continuous wf exists when we match logarithmic derivatives at r_0:

$$\frac{d}{dr}\ln\left(u^{in}_{\varepsilon\ell}(r)\right)\Big|_{r=r_0} = \frac{u^{in\,\prime}_{\varepsilon\ell}(r)}{u^{in}_{\varepsilon\ell}(r)} = \frac{f'_{\varepsilon\ell}(r)\cos\delta_{\varepsilon\ell} - g'_{\varepsilon\ell}(r)\sin\delta_{\varepsilon\ell}}{f_{\varepsilon\ell}(r)\cos\delta_{\varepsilon\ell} - g_{\varepsilon\ell}(r)\sin\delta_{\varepsilon\ell}},$$

all at $r=r_0$.

After some rearrangement,

$$\tan \delta_{\epsilon \ell} = \left. \frac{W(f_{\epsilon\ell}, u^{in}_{\epsilon\ell})}{W(g_{\epsilon\ell}, u^{in}_{\epsilon\ell})} \right|_{r=r_0}.$$

Since $f \xrightarrow[r\to\infty]{} \sin(\ \ )$ and $g \xrightarrow[r\to\infty]{} -\cos(\ \ )$,

Coulomb phase shift

modified Coulomb phase shift.

$$u_{\epsilon\ell} \to \sqrt{\frac{2}{\pi k}} \left[\sin(\ \ )\cos\delta + \cos(\ \ )\sin\delta \right]$$

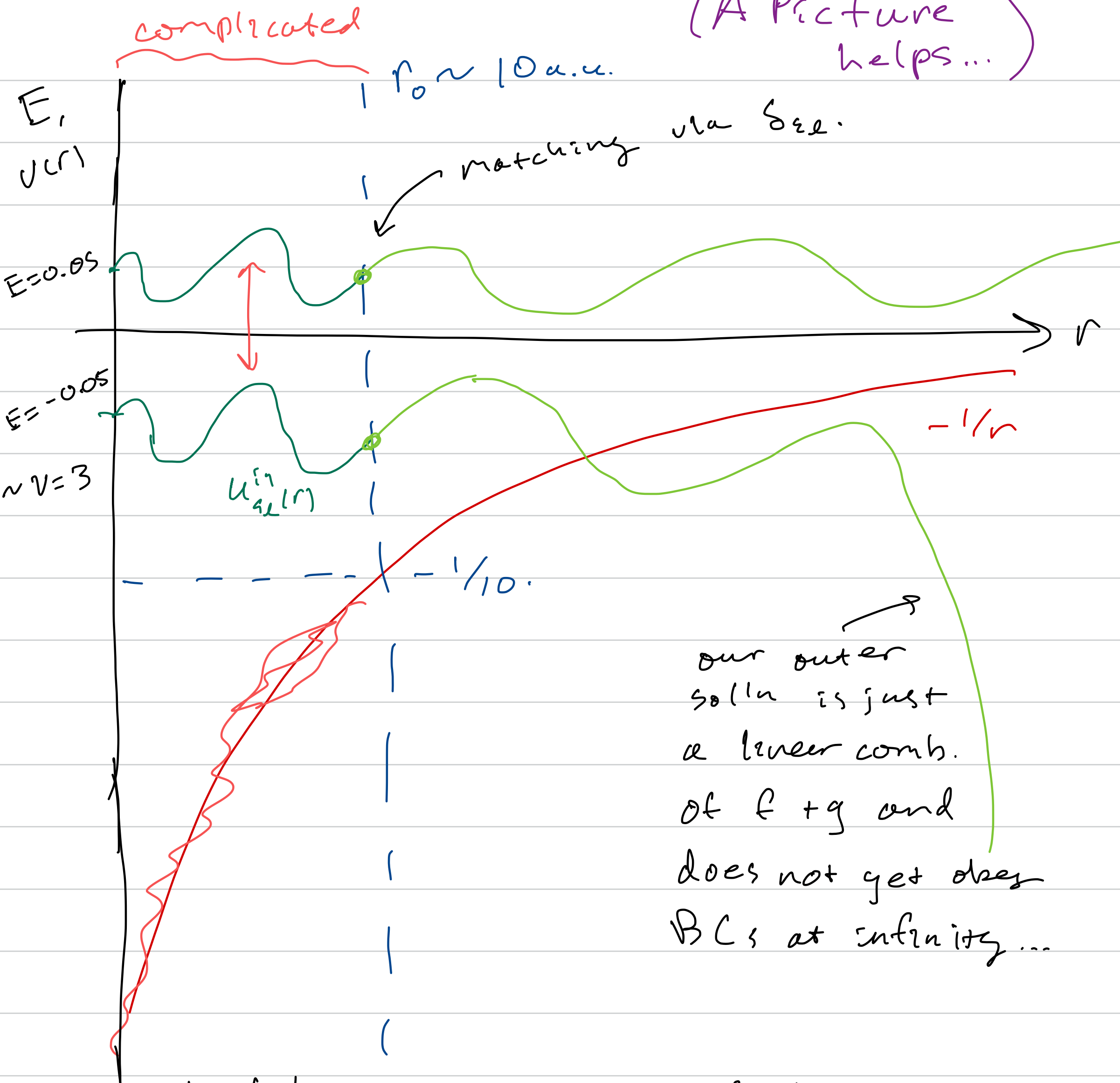
trig identity

$$= \sqrt{\frac{2}{\pi k}} \sin\left(kr + \frac{1}{k}\ln 2kr - \frac{\ell\pi}{2} + \sigma_\ell + \delta_{\epsilon\ell}\right).$$

So: our solution, at very large r, is a phase-shifted sine wave!

A comment: one thing that we have done under the rug in our derivation of f, g is to ensure that they are <u>smooth</u> and <u>almost-analytic</u> functions whenever possible. The mathematical reasons for this can be a bit obscure (see the Seaton paper ref'd previously for more details), but this is crucial for us as we can treat the phase shift also as a very smooth function of E.

(A Picture helps...)



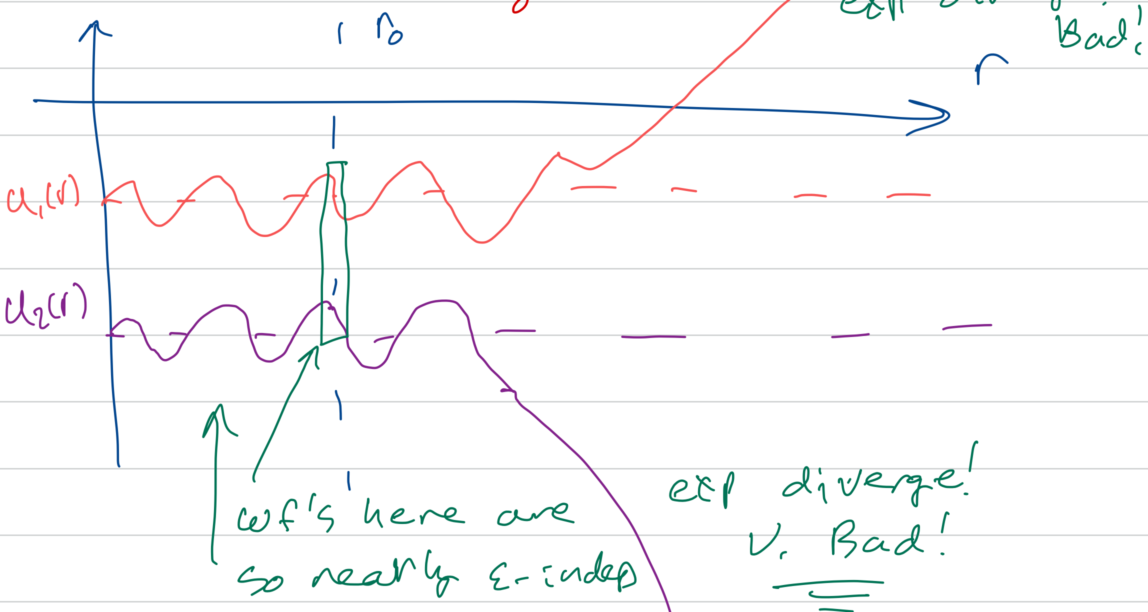
$|V(r)| \gg |E|$ at small r, so $u^{in}_{\ell\ell}(r)$ is nearly energy-independent!

And thus: $\delta_{\ell\ell}$ must also be very smooth as a function of energy!

We can go ahead and analytically continue our whole scattering solution from $\varepsilon > 0$ to $\varepsilon < 0$, obtaining

$$u_{\varepsilon \ell}(r) \xrightarrow[r \to \infty]{} \frac{1}{\sqrt{\pi k}} \Big[\sin(\pi(\nu - \ell) + \delta_{\varepsilon \ell}) \, r^{-\nu} e^{kr} D^{-1} - \cos(\pi(\nu - \ell) + \delta_{\varepsilon \ell}) \, r^{\nu} e^{-kr} D \Big]$$

The full solution, at two arbitrary energies $\varepsilon < 0$, must look something like:



wf's here are so nearly ε-indep that $\delta_{\varepsilon \ell}$ hardly changes. And we have no rapid ε-fluctuations because no BCs @ $r \to \infty$!

Looking at our long-range sol'n, we see that exp. growth is proportional to

$$\sin[\pi(\nu - \ell) + \delta_{\varepsilon\ell}]$$

Now, we impose the BC and shut off this unphysical divergence. This will now lead to rapid energy-dependence in some parameters (think - ν is currently a continuous parameter and w/ the energy must become discrete!) but the key physics of the "complicated" part is contained in essentially a few numbers.

$$\rightarrow \pi(\nu - \ell) + \delta_{\varepsilon\ell} = n_r \pi$$

$$\rightarrow \quad n = \ell + n_r = \nu + \delta_{\varepsilon\ell}/\pi$$

or: $$\varepsilon_{n\ell} = -\frac{1}{2(n - \mu_{\varepsilon\ell})^2}.$$

By golly, we did it again! And better!

- Some notes:
  - → $\mu_{\epsilon\ell} = \delta_{\epsilon\ell}/\pi$ is the QUANTUM DEFECT!
  - → For alkali atoms: $\delta_{\epsilon\ell}$ is constant (to ~ 3 sig figs) already from $n=50$ or so...
  - → Infinite numbers of bound states are compactly described by one parameter, which is closely connected to the scattering phase shift!

→ Core of QDT: we try our DARNDEST to put everything in terms of analytical smooth functions of energy, and don't apply all BCs (which give rapid energy dependence) until the bitter end.

→ $\mu_{\epsilon\ell} = 0$ for sufficiently high ℓ (we cover polarization effects later) because $\frac{\ell(\ell+1)}{2r^2}$ shields the e^- from the core.

Now to return to "Phenomenological evidence for SUSY".
In his comment on this PRL (PRL 56 (1986)), Rau points out that comparison of Rydberg series is kind of silly to do via energies; it should really be done using quantum defects.

And here, $\mu_s = 0.4$ for Li and
$\mu_s = 0$ for H.
These are not similar!! Even though the transition energies Kostelecky + Nieto mention seem to get closer, 0.4 <u>never</u> gets close to 0.

Furthermore, the agreement b/w d states is little more than an acknowledgement that $\mu_{\ell>1} \sim 0$.

The authors do reply in that same reference. See what you think!