Lecture 4

27 May, '24

In Lecture 3 we focussed a lot on obtaining appropriate solutions to the Coulomb problem which were "smooth" functions of energy. This is vital if we want to see how to connect scattering physics to spectroscopy. The beautiful result at the end of this process was that we obtained the Rydberg formula,

$$E_{n\ell} = -\frac{1}{2(n-\mu_\ell)^2}$$

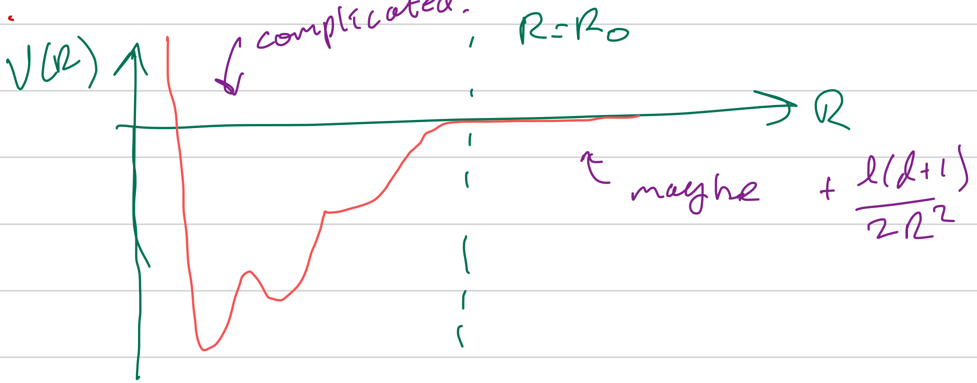
directly from this approach, where $\mu_\ell = \delta_\ell/\pi$ is the quantum defect. This formula is so incredible because it:

1) Connects a scattering quantity (the phase shift δ_ℓ) with the bound state energies.
2) Shows how the effect of short-range interactions in a non-hydrogenic Rydberg atom can be collapsed into a small set of parameters, μ_ℓ.

However, some of the key physical aspects of this formula and its derivation may have been obscured by the mathematical complexity of the Coulomb problem.

So, let's review the whole concept and approach, but for a simpler system with <u>only</u> short-ranged interactions. In addition to being mathematically simpler, this also gives the key formalism for treating a vast number of problems in ultracold physics.

So here is the problem: what are the scattering + bound states of a potential like...



Keep in mind that this very simple spherical square well problem is a stand-in for the following type of single channel problem:

- Spherically symmetric $\Rightarrow$ only solve radial equation for each l.
- Bound + continuum states considered together - and linked when possible.
- Known + "simple" long-range potential
  $\Rightarrow$ typically of the form
  $$V_{LR}(r) = \frac{l(l+1)}{2mr^2} + C_N/r^N.$$
  → Here we have $N=0$ so the longest-range interaction is the centrifugal potential.
  → We already studied $N=1$ case.
- Complicated short-range behavior.
  → goal: formulate the theory so that this is, at most, a numerical annoyance.

Since we have $V(r) = \frac{\ell(\ell+1)}{2r^2}$ at large r outside the range of the potential, we need a different set of solutions than in the Coulomb problem, namely:

"regular at $r=0$": $f_{k\ell}(r) = \sqrt{\frac{2}{\pi k}}\; kr\, j_\ell(kr)$

$kr \ll \ell$: $\longrightarrow \sqrt{\frac{2}{\pi k}} \frac{(kr)^{\ell+1}}{(2\ell+1)!!}$

$kr \gg \ell$: $\longrightarrow \sqrt{\frac{2}{\pi k}} \sin(kr - \ell\pi/2)$

"irregular at $r=0$": $g_{k\ell}(r) = \sqrt{\frac{2}{\pi k}}\; kr\, n_\ell(kr)$

$kr \ll \ell$: $\longrightarrow \sqrt{\frac{2}{\pi k}}\, -(kr)^{-\ell}(2\ell-1)!!$

$kr \gg \ell$: $\longrightarrow \sqrt{\frac{2}{\pi k}}\, -\cos(kr - \ell\pi/2)$

Coulomb compare + contrast:

low-r behavior: <u>same</u>: $f \sim r^{\ell+1}$, $g \sim r^{-\ell}$

large-r behavior:

Same func: sin, −cos

diff phase: 0 vs. $\sigma_\ell + \frac{1}{k}\ln 2kr$

all-r behavior:

Bessels vs. Conf Hyp Geo!

For all problems ⇒ LR potential determines f, g!

Check: this (f,g) "base pair" is the energy-normalized one:

$$\int_0^\infty f_{E\ell}\, f_{E'\ell}\, dr = \delta(E-E').$$

The introduction of phase shifts is the same as in the Coulomb case: for $r > r_0$ the sol'n is

$$u_{E\ell}(r) = A_\ell \left[f_{E\ell}(r)\cos\delta_\ell - g_{E\ell}(r)\sin\delta_\ell \right]$$

$$\to A_\ell \sqrt{\frac{2}{\pi k}}\, \sin(kr - \ell\pi/2 + \delta_\ell).$$

Similarly, we match this outer solution to the inner one, $F_{E\ell}(r)$ (for $r \leq r_0$), to obtain the phase shift:

$$-b_E = \left.\frac{F'_{E\ell}(r)}{F_{E\ell}(r)}\right|_{r=r_0} = \left.\frac{f'_{E\ell}(r)\cos\delta_\ell - g'_{E\ell}(r)\sin\delta_\ell}{f_{E\ell}(r)\cos\delta_\ell - g_{E\ell}(r)\sin\delta_\ell}\right|_{r=r_0}$$

$$\to \tan\delta_\ell = \left.\frac{W[f_{E\ell}, F_{E\ell}]}{W[g_{E\ell}, F_{E\ell}]}\right|_{r=r_0}$$

$$= \left.\frac{f'_{E\ell} + b_{E\ell}\, f_{E\ell}}{g'_{E\ell} + b_{E\ell}\, g_{E\ell}}\right|_{r=r_0}.$$

We have introduced a special quantity here, the logarithmic derivative - b_{El}. Wigner proved that this is a meromorphic function of energy - analytic in E except for simple poles. That means that we could easily interpolate its energy dependence, or even do crazy things like analytic continuation to obtain b_E, $E<0$ from b_E, $E>0$! But for now, note that f_{El}, g_{El} are not energy-analytic, so by extension neither is the phase shift, as can be seen at low positive energy:

$$\tan\delta_l(E) \sim \frac{(l+1)/(2l+1)!!\,(kr)^{l+1}/r + b_{El}\,(kr)^{l+1}/(2l+1)!!}{+(2l-1)!!/(kr)^l \cdot l/r - b_{El}\,(2l-1)!!/(kr)^l}$$

$$\sim \frac{\frac{k^{l+1}}{(2l+1)!!}\cdot\left[(l+1)r^l + b\,r^{l+1}\right]}{\frac{k^{-l}}{(2l-1)!!}\left[l/r - b/r^l\right]}$$

$$\sim k^{2l+1} a_l \left\{1 + C_1 E + C_2 E^2, \ldots\right\}$$

this is the Wigner Threshold Law!

and it is very useful!

→ Take care: this is only valid for short-range potentials. It definitely does not apply to the Coulomb potential.

To test out when it's applicable, we can use the Born Approx:

$-C_N/r^N$

$$\tan\delta_{E\ell} = -\pi\int_0^\infty \underline{f_{E\ell}(r)}\, V(r)\, \underline{f_{E\ell}(r)}\, dr$$

regular sol'ns for free particle

$$f = \sqrt{\frac{2m}{k}}\, kr\, j_\ell(kr)$$

$$= k^{N-1} C_N \pi \sqrt{\frac{2m}{\pi k}}^2 \int_0^\infty (kr)^2 j_\ell^2(kr)\, \frac{dr}{r^N}\cdot\frac{k}{k^N}$$

$x = kr$

$$= \underbrace{2C_N m k^{N-2}}_{k\text{-dependance}} \cdot \underbrace{\int_0^\infty \frac{j_\ell(x)^2}{x^{N-2}}\, dx}_{\text{constant} = A}$$

From this we might think that the Wigner threshold law should be replaced by

$$\tan\delta_{E\ell} \sim k^{N-2},$$

removing all ℓ-dependence. But this isn't quite true since the integral A diverges as $r \to 0$:

$$\frac{j_\ell(x)^2}{x^{N-2}} \sim x^{2\ell-N+2}$$

So: $2\ell - N + 2$ $\underline{\text{must be}}$ > -1

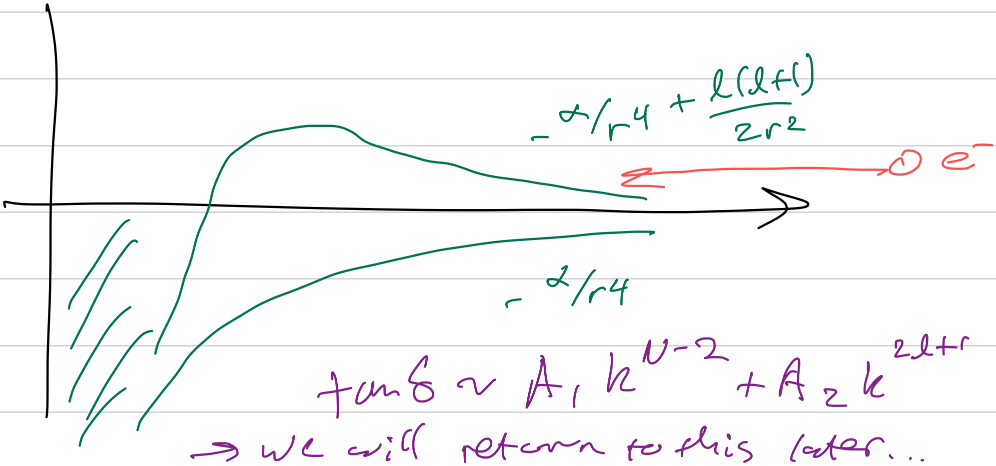
This implies that this threshold law is only valid if

$$\boxed{l_{min} = N-2.}$$

So we would expect the threshold law to be different than Wigner's in some situations. For example, the polarization potential for e-atom interactions is

$$V_{pol} = \frac{\alpha}{2r^4}.$$

For d partial waves or higher we expect deviations from the Wigner threshold law there!



$$\tan\delta \sim A_1 k^{N-2} + A_2 k^{2l+1}$$

→ we will return to this later...

These threshold laws are highly useful - just a couple of my favorite examples are:

1) The effect of short-ranged potentials in a collision are suppressed at small k → low-energy physics/ultracold physics is dominated by s-wave collisions!

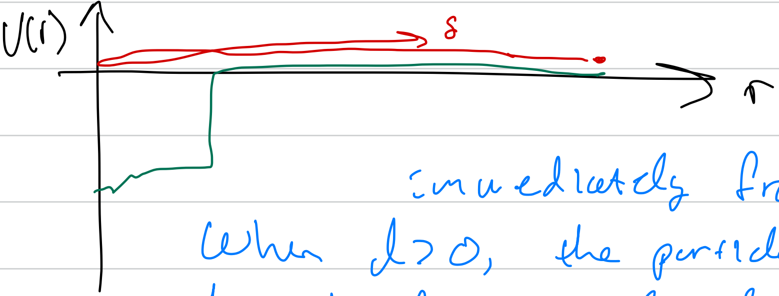
2) Behavior of cross-sections near thresholds say a lot about the details of that process - especially due to the rapid and even "cuspy" nature of the threshold behavior.

Here's a few points to keep in mind as we think about threshold behavior over the next week or two.

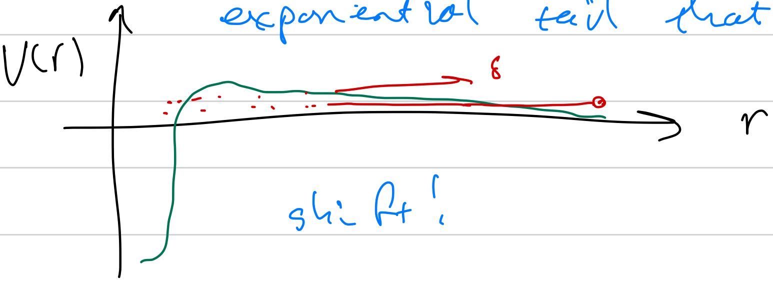
1) Just because the WTL predicts $\underline{\sigma \to 0 \text{ @ } k \to 0}$, this does not

mean that the scattering potential is invisible or has no effect at zero energy. We'll see this shortly when we consider the zero-energy wavefunction.

2) A lot of the physics of the WTL is just a statement about the centrifugal barrier. A particle with zero angular momentum can "see" the short range potential starting immediately from threshold.



When $l > 0$, the particle has to tunnel through the centrifugal barrier at arbitrarily small energy. Only the exponential tail that penetrates can be responsible for the phase shift!



3) The WTL is strongly connected to normalization → recall that these powers of k come from our explicit choice of (f,g) → and in the next section we will even change this to remove this non-analytic behavior.

Basically, since we demand

① $f \sim k^{-1/2}\sin(kr+\delta)$, $r\to\infty$

$g \sim k^{-1/2}\cos(kr+\delta)$,

this fixes a normalization for our exact base pair, $f \sim k^{-1/2}\, kr\, j_\ell(kr)$

$g \sim k^{-1/2}\, kr\, n_\ell(kr)$.

And this, in turn, fixes their low-ℓ behavior.

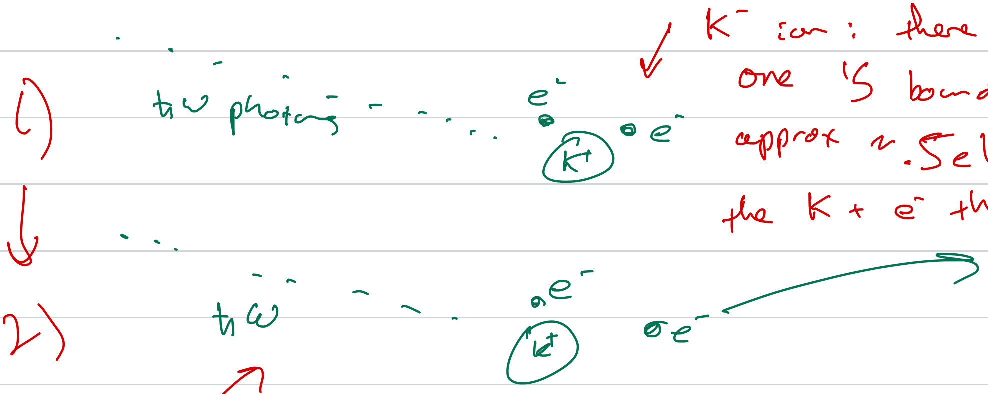
If we abandon ①, like in the analytic (f^0, g^0) pair we define next, then we can redefine everything to not have this threshold behavior.

Point is: be careful not to confuse physically relevant things (like δ_ℓ) w/ theoretically useful concepts (like δ_ℓ^0).

Finally, here are some examples of the utility of the Wigner threshold law, here meant more generally to apply to the behavior of the photo detachment cross section near threshold,

$$\sigma_\ell(k) \sim k^{2\ell+1}$$
$$\sim E^{\ell+1/2}.$$

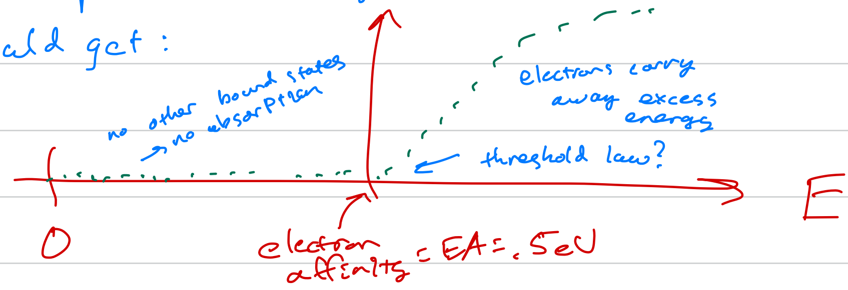
Picture the photodetachment experiment:



K⁻ ion: there is one ¹S bound state approx ~.5eV below the K + e⁻ threshold

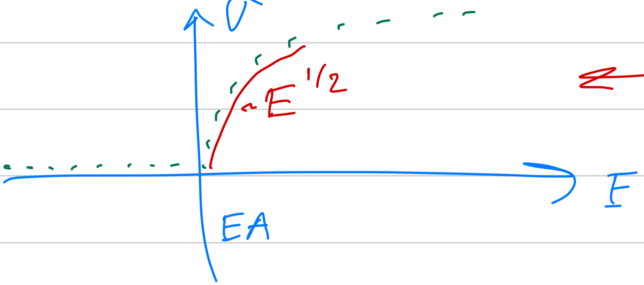
in a photodetachment expt: if ħω > .5eV, an electron pops out!

So if you plot something like e⁻ counts vs. ħω you would get:



The EA is a nice property to know: but not so easy to measure. How do you precisely measure when you go from 0 counts to >0 counts? → Threshold laws!

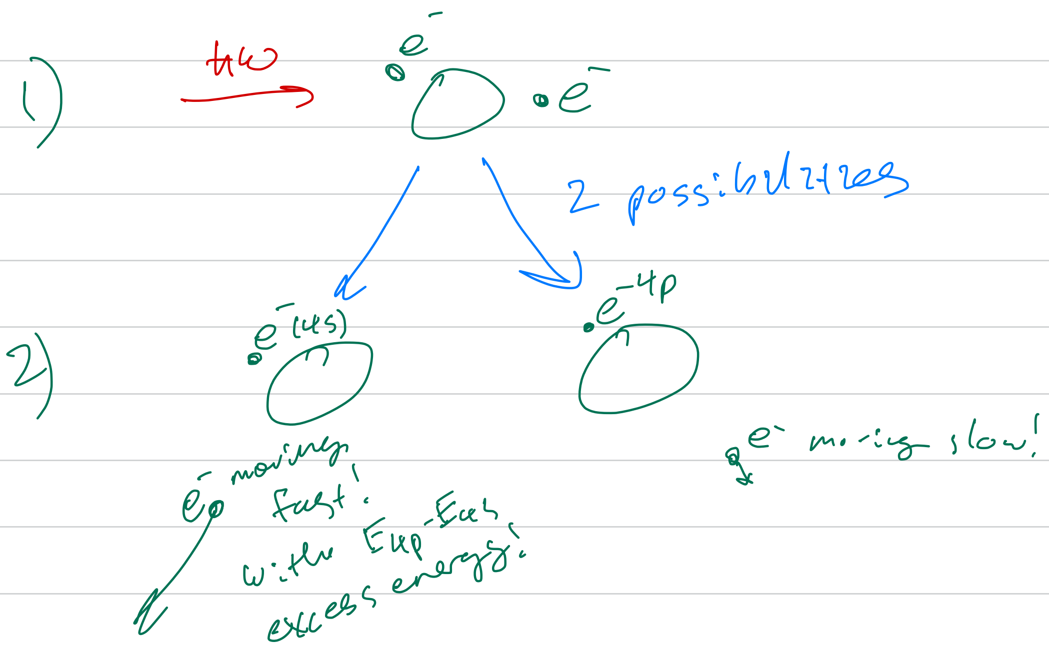
Note that, when the electron has $l=1$, the WTL predicts a cusp at threshold!



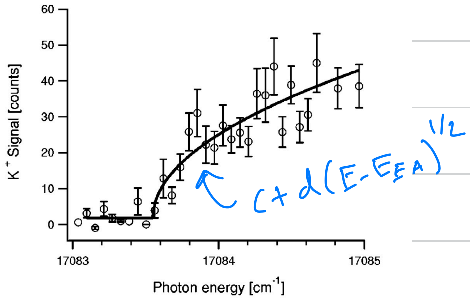
A Fit of $\sigma(E)$ to the WTL will be very accurate!

Specifically, $\sigma = (E - E_{EA})^{1/2}$.

In the experiment, this is done by using enough photon energy to kick off one electron and excite the other!

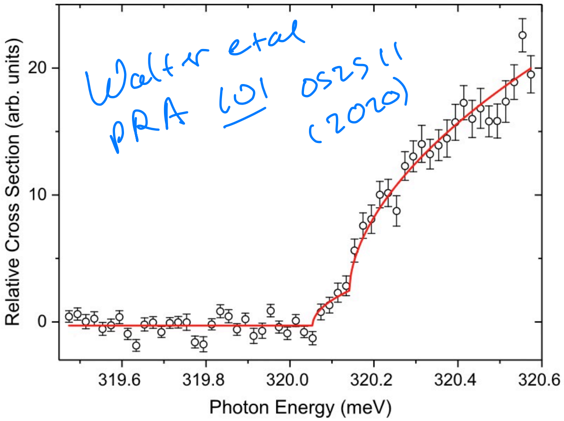


So: if photodetachment is done, and the partial cross sections reported by detecting also the state of the residual atom (often by exciting it yet again to a Rydberg state!), then the cross section looks like:



From Andersson et al PR A 62 022503 (2000)

FIG. 4. A typical scan showing the variation of the cross section for photodetachment K⁻ in the vicinity of the opening of the K($4p_{3/2}$)+e^-(ks) channel. The solid line through the data points represents the weighted best fit of the data to the form shown in Eq. (7). The fit yielded a value for the threshold wave number. Twenty



Walter et al
PRA 101 052511
(2020)

This can and has been done in many species! Even exotic ones with multiple negative ion bound states like thallium!

FIG. 3. Narrow scan near the threshold for the Tl$^-$ ($^3P_0$) to Tl ($^2P_{1/2}$) ground-state to ground-state transition using the seeded laser; the bin width of 0.02 meV chosen for processing the measured data (circles) in this figure is approximately twice the bandwidth of the laser (~0.01 meV). The solid line is a fit of the pure *s*-wave Wigner law [Eq. (1)] with two nested detachment thresholds to the $F = 0$ and 1 levels of Tl ($^2P_{1/2}$) separated by the hyperfine splitting of 0.088 134 53(2) meV [14]. The lower-energy

Or indium!
Walter et al
PRA 82
032507
(2010)

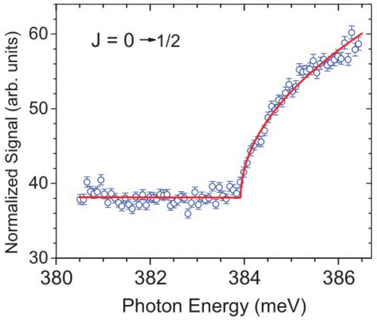


FIG. 2. (Color online) A fit of the *s*-wave Wigner law [Eq. (3)] (solid line) to the measured relative photodetachment cross-section data (circles) near the threshold for the In$^-$ ($^3P_0$)–to–In ($^2P_{1/2}$) ground-state-to-ground-state transition. The energy at the threshold corresponds to the electron affinity of In.

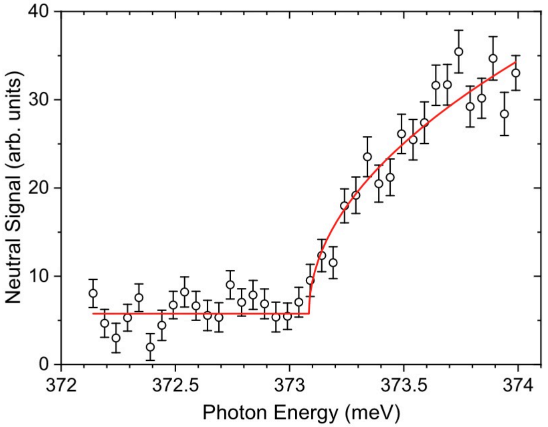


FIG. 2. Measured photodetachment threshold from the $\mathrm{Bi}^{-}\ {}^{3}P_{0}$ excited state to the $\mathrm{Bi}\ {}^{4}S_{3/2}$ ground state: circles, data; line, *s*-wave Wigner law fit.

Bismuth even?!

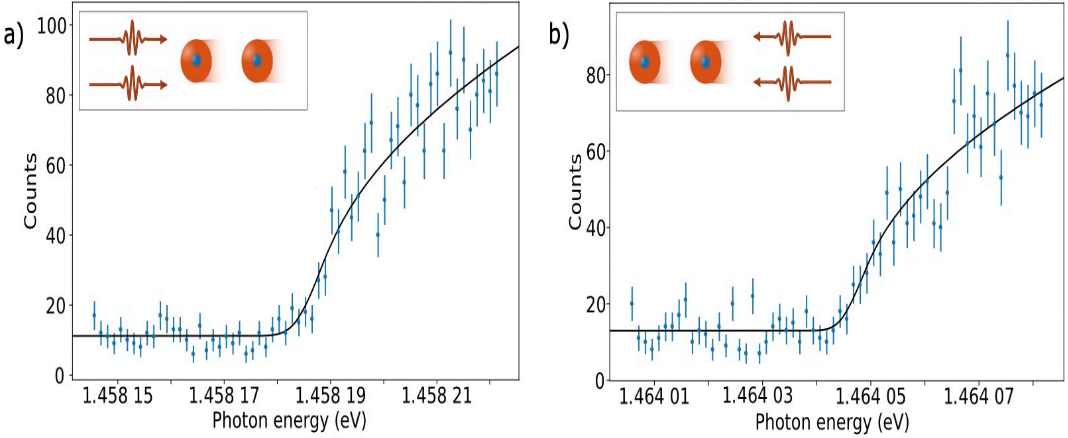
Walter et al PRL 126 083001 (2021)

Compare w/ Fig 5 of Branscomb et al PR 111 504 (1958) and EA = 1.465 ± 0.005

And very high precision on O^-:

EA = 1.461112972(87) eV

¡WOW!



Kristiansson et al Nat. Comm. 13 5906 (2022)

We want to understand the energy dependence of our scattering problem near zero energy in a systematic way.

First, we notice that our f, g solns that we wanted to use are not analytic at small k.

$$f_{\epsilon\ell} \sim k^{\ell+1/2}$$
$$g_{\epsilon\ell} \sim k^{-\ell-1/2}$$

This sucks for the ANALYTIC CONTINUATION that we love to do! But, if we just pick two different, but still valid, solutions, everything is nice and analytic!

$$f^{0}_{\epsilon\ell} = (kr_0)^{-\ell-1/2} f_{\epsilon\ell}$$
$$g^{0}_{\epsilon\ell} = (kr_0)^{\ell+1/2} g_{\epsilon\ell}$$

↑ a characteristic length scale ~ arbitrary-ish.

Not only does this cure the nonanalytic behavior as $kr \to 0$, but one can prove that they are analytic and entire functions of energy for all r.

→ $(f_{\varepsilon\ell}, g_{\varepsilon\ell})$ → energy normalized base pair

→ $(f^0_{\varepsilon\ell}, g^0_{\varepsilon\ell})$ → analytic base pair.

And naturally - since we defined $\tan\delta_{\varepsilon\ell}$ using $(f_{\varepsilon\ell}, g_{\varepsilon\ell})$ - we can define an energy-analytic phaseshift using $(f^0_{\varepsilon\ell}, g^0_{\varepsilon\ell})$

This defines an analytic solution

$$u_{E\ell}(r) = \begin{cases} u^{in}_{E\ell}(r), & r < r_0 \\ f^0_{E\ell}(r)\cos\delta^0_{E\ell} - g^0_{E\ell}(r)\sin\delta^0_{E\ell}, & r > r_0 \end{cases}$$

And clearly $\tan\delta^0_{E\ell} = \dfrac{\tan\delta_{E\ell}}{k^{2\ell+1}}$.

(note: $\delta^0_{E\ell}$ is not measurable like $\delta_{E\ell}$ could be!)

$\delta^0_{E\ell}$ is now also a smooth function of energy → we can analytically continue!

Let's do this! The crucial thing to determine the discrete spectrum is, as always, to construct sol'ns where the exponential growth at $r \to \infty$ is killed off. This dependence is found from:

$$f^{0}_{E\ell}(r) \xrightarrow[kr\to\infty]{} k^{-\ell-1/2}\left(\frac{2m}{\pi\hbar}\right)^{1/2} \sin(kr - \ell\pi/2)$$

$\star$ for $E = \frac{k^2}{2} > 0$

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

$$\xrightarrow[k\to i\kappa]{} \left(\frac{2m}{\pi}\right)^{1/2} \kappa^{-\ell-1}\left(e^{\kappa r} - (-1)^{\ell} e^{-\kappa r}\right)$$

We do the same for $g^{0}_{E\ell}(r)$ to get:

$$g^{0}_{E\ell}(r) \to -\left(\frac{m}{2\pi}\right)^{1/2} \kappa^{\ell}\left((-1)^{\ell} e^{\kappa r} + e^{-\kappa r}\right)$$

So, we have: $\delta^{0}_{E\ell}$, $g^{0}_{E\ell}$, and $f^{0}_{E\ell}$ all as smooth functions of E.

$\Rightarrow$ We have $u^{0}_{E\ell}$!

$$u^{0}_{E\ell}(r) \xrightarrow[r\to\infty]{} \left(\frac{2m}{\pi}\right)^{1/2} \left\{ e^{\kappa r}\left(\cos\delta^{0}_{E\ell}\,\kappa^{-\ell-1} + \sin\delta^{0}_{E\ell}\,(-1)^{\ell}\kappa^{\ell}\right) + e^{-\kappa r}\left(-(-1)^{\ell}\cos\delta^{0}_{E\ell}\,\kappa^{-1-\ell} + \sin\delta^{0}_{E\ell}\,\kappa^{\ell}\right) \right\}$$

must vanish this term!!!

So: $\tan\delta^0_{E\ell} + (-1)^\ell (\kappa r_0)^{-2\ell-1} = 0$

This gives us the crucial quantity, the <u>s-wave scattering length</u>

$$\boxed{\begin{aligned} a_{\ell=0} &= \lim_{E\to 0} \left(-r_0 \tan\delta^0_{E\ell}\right) \\ &= \lim_{E\to 0} \frac{-\tan\delta_{E\ell=0}}{k}. \end{aligned}}$$

And the quantization condition reads

$$a = \frac{1}{\kappa}. \quad \text{(so } a>0 \text{ naturally!)}$$

And this in turn implies that the bound state has energy $\underline{E_b = -\frac{\hbar^2}{2ma^2}}$.

<u>Thus</u>: a scattering parameter, $\underline{a}$, determines a spectroscopy value, E_b!

This is only approximate since a is the $E\to 0$ limit of $-\tan\delta_{E\ell}/k$. But if we make a energy-dependent, then the quantization condition reads

$$a(E) - \frac{1}{k} = 0$$

$$\rightarrow \quad E = \frac{-\hbar^2}{2ma(E)^2}$$

where $a(E) = -r_0 \tan\delta^{0}_{E,0}$