Lecture 5   June 10, '24

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 care 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!

$$f^o_{\epsilon\ell} = (kr_o]^{-\ell - 1/2} f_{\epsilon\ell}$$

$$g^o_{\epsilon\ell} = (kr_o)^{\ell + 1/2} g_{\epsilon\ell}$$

$\uparrow$ a characteristic length scale $\sim$ arbitrary-ish.

Not only does this cure the nonanalytic
behavior as $hr \to 0$, 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
→ $(f^o_{\varepsilon\ell}, g^o_{\varepsilon\ell})$ → 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 $(f^o_{\varepsilon\ell}, g^o_{\varepsilon\ell})$

This defines an analytic solution

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

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

(note: $\delta^o_{E\ell}$ is not measurable like $\delta_{E\ell}$ could!) he!)

$\delta^o_{E\ell}$ 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:

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

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

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

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

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

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

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

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

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

must vanish this term!!!

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

This gives us the crucial quantity, the s-wave scattering length

$$a_{\ell=0} = \lim_{E \to 0} \left(-r_0 \tan \delta_{E\ell}^0 \right)$$

$$= \lim_{E \to 0} \frac{-\tan \delta_{E\,\ell=0}}{k}.$$

And the quantization condition reads

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

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

Thus: 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

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

$$\to \quad E = \frac{-\hbar^2}{2m\,a(E)^2}$$
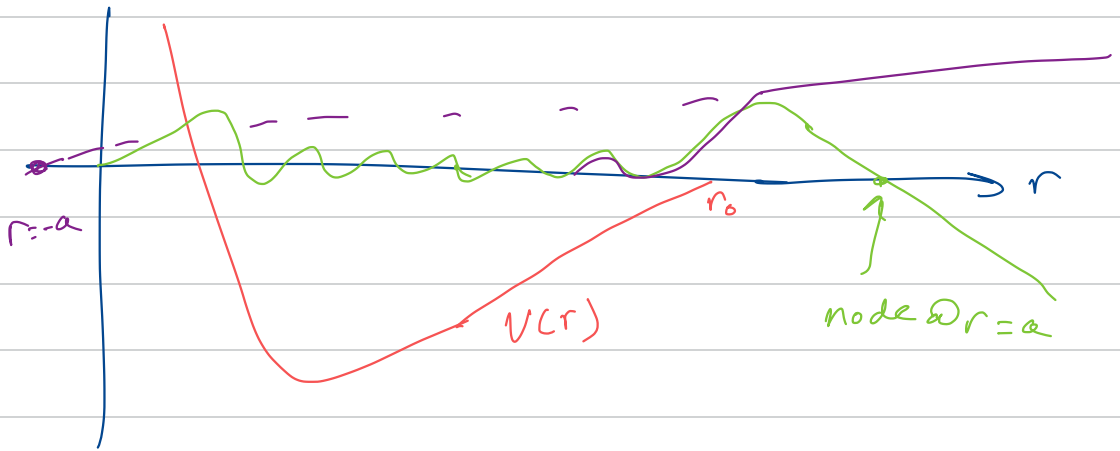
where $\quad a(E) = -r_0 \tan \delta^0_{E,0}$

a has a natural connection to the zero-energy wave function.

At large r, we had $\quad u(r) \to C\dfrac{\sin(kr+\delta)}{k}$

From Wigner: $\quad \delta \to (k r_0)\, \delta^0 \to -k\, a(0)$
$\qquad$ at very small k.

$\to \quad u(r) \to \dfrac{C}{k} \sin(kr - ka) \xrightarrow[k \to 0]{} C(r - a)$

r=-a

r_0

V(r)

node @ r=a

Note what this means: a positive
scattering length means that the
zero-energy scattering wave func
has a __node__ at r=a. For r>a, the
wave function is identical to one where
we had instead on infinitely hard wall
at r=a!

SO: When a>0, the interaction between
the colliding particles is repulsive!
EVEN THOUGH the potential is
actually attractive...

This concept, along with the existence of
tools (Feshbach resonances) to __tune__ a, is
at the heart of ultracold atoms.

We will see how this comes about by deriving the <u>Fermi pseudopotential</u> — which can be applied to problems like the following example:

→ 2 Rb atoms in a BEC approach eachother. In the relative internuclear coordinate, the Born-Oppenheimer potential + scattering wave function near E=0 looks something like:

rapid oscillations due to V(r)

V(r)

r = a
the

long wave length b/c low T.
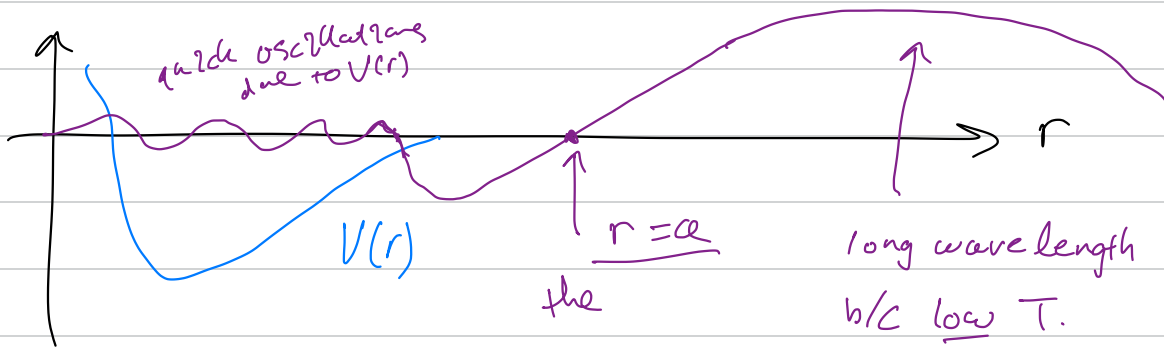
For just 2 atoms, we can solve (numerically at least) this problem with the <u>real</u> V(r) without too much difficulty. But what if we want to add even a 3rd Rb? Or 4 or 5 or 1000s? Now dealing with many $V_{ij}(r)$ interactions gets <u>very</u> hard — especially since all that work goes into what

is essentially just a phase shift for the scattering solutions. Moreover, we can see that some of the key properties of this collision are not really obvious from this picture! We know that the fact that $a > 0$ here means that our particles effectively repel one another despite the $U(r)$ being attractive. But if we make $U(r)$ just a bit shallower, so that this high-lying bound state (recall $a > 0$ $\Rightarrow E_b \sim -\frac{\hbar^2}{2ma^2}$) is no longer their, then $a < 0$ and the wave function is sucked in - the potential feels attractive!

$a < 0$

rapid oscillations due to $V(r)$

$V(r)$

Fig A
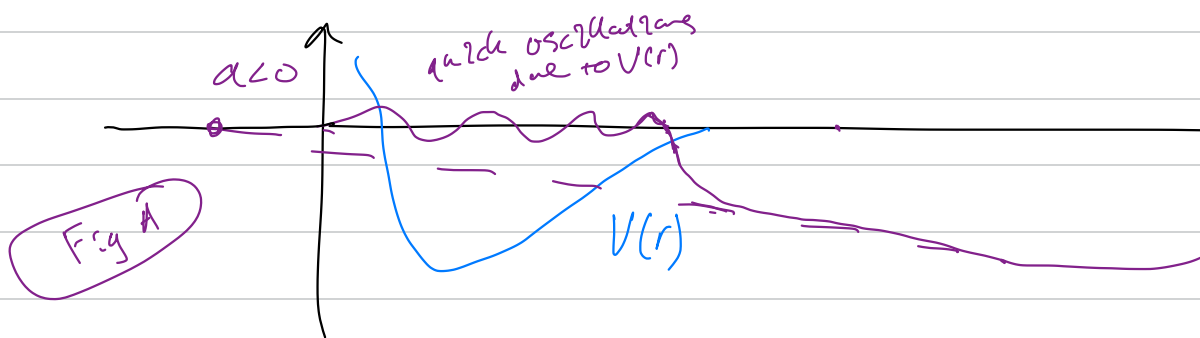
Clearly it would be nice to summarize the actual interaction $V(r)$ with something easier to compute and more intuitive,

which doesn't need to tell us the complex
physics at $r < r_0$ but just needs to get
the wave function outside of this zone right.

Such a potential wight look something like:

$$U(r) = 2\pi a \, \delta^3(r)$$

+ when +,
− when −.
→ (pointing to a)

simple, no $U(r)$ details
↑ (pointing to $\delta^3(r)$)

...and this is exactly the Fermi pseudopot.

And the great thing for us is: Fermi derived
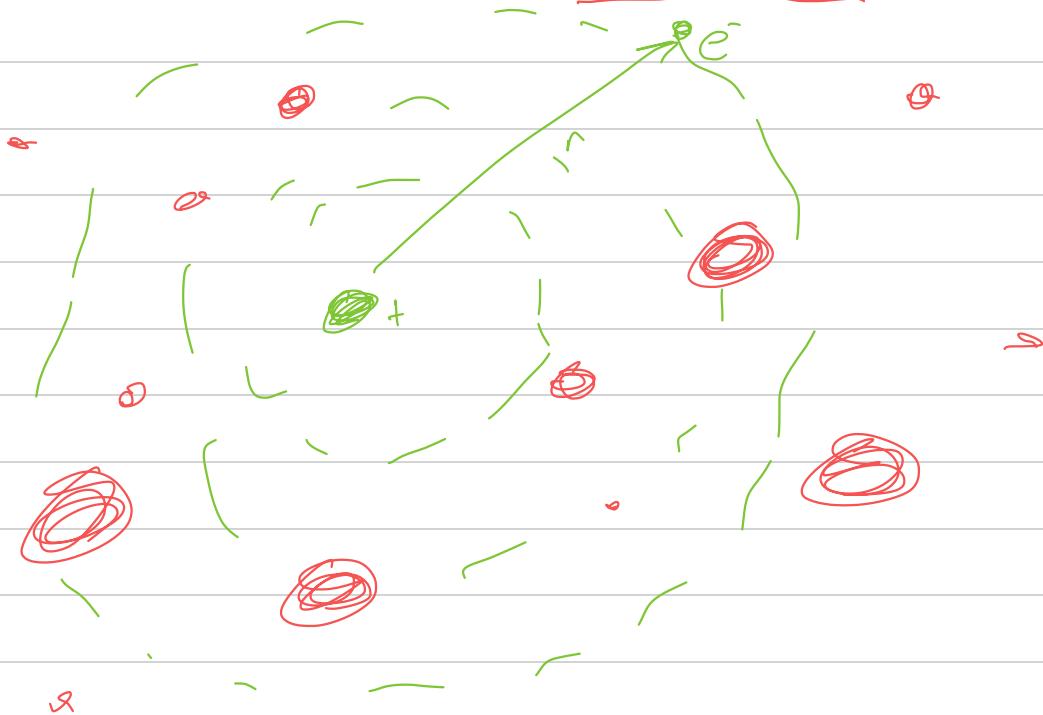this to solve a problem in Rydberg Physics
→ so we can too!

Back in 1934, no less!

A nice history / review article is:
   "Fermi's Favorite Figure...", Gould +
   Sharapov EPJ H 47, 10 (2022).

(shows also Fermi's much better sketch of "Fig A")

This was the system: A Rydberg atom
excited inside of a dense gas

This was actually an experiment done by
Amaldi and Segre - who, along with Fermi,
Majorana, and others were members of the
"Via Panisperna Boys" - in Rome in the
early 30s. The background density was
so large that ~1000s of atoms were
within the Rydberg orbit!

Amaldi and Segre anticipated that they
would no longer be able to observe any
Rydberg spectra, since collisions with the background
atoms must surely destroy the ability to
excite such weakly bound states!

But to their surprise, they did observe Rydberg
series - just at slightly different transition
frequencies...

Na 35-8P
Hg 2537

Na + H perturbers
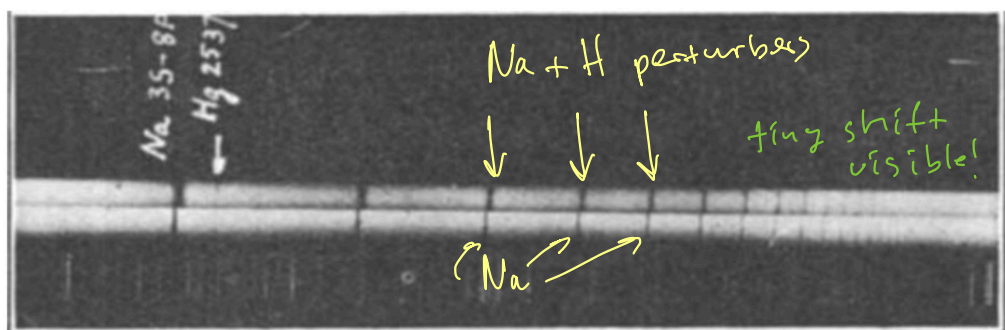tiny shift visible!
(Na)

FIG. 1. Absorption spectra of sodium-hydrogen mixtures at
higher pressures (above) and at lower pressures (below) of
hydrogen. Note the unshifted mercury line 2537, which lies
in the background.

(Amaldi & Segré
Nature 133, 141 (1934))

Depending on the background gas, this shift
in the lines was at times towards higher
energies (blue) lower energies (red) and

sometimes none at all!

This was also observed basically contemporaneously by Füchtbauer + coworkers in Rostock!

blue

nothing!

red

Fig. 4. Gesamtverlauf der Verschiebung bei 0° und 1 Atm. für die Cäsiumhauptserie.

Fermi quickly realized that this was a hint that more was going on in the "Atomic Gonfs" than anticipated.

Why? His first calculation assumed that the residual ion would polarize and attract the neutral gas atoms through the interaction potential

$$V(R_i) = -\frac{\alpha}{2R_i^4} .$$

(we will derive this formula soon).
He then calculated the energy shift resulting from the polarization of the medium by the ion.

The basic idea is simple:

Wigner
Seitz
sphere

Ryd
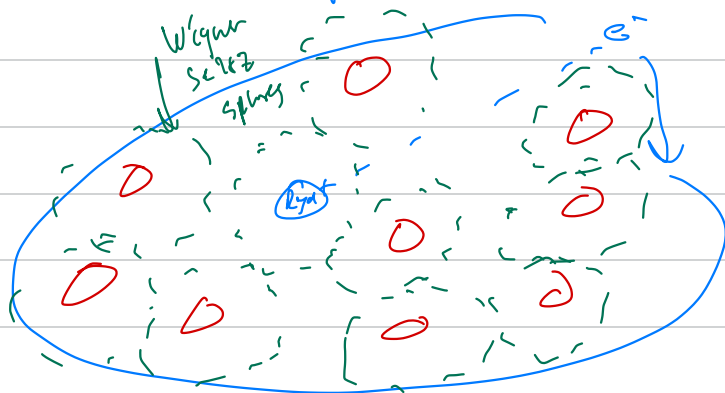
$$\Delta E = \sum_i \frac{\alpha}{2R_i^4}$$

just have
to add
up all possible
configurations
$\{R_i\}$!

Assume a uniform distribution → every atom
occupies a "Wigner Seitz" sphere of volume
$1/\rho$, where ρ is the density. Thus, we can
go from $\sum_i$ to $\int dR$, where the lower limit
is not zero (causing a divergence!) but instead

$$\frac{4\pi}{3} R_{ws}^3 = 1/\rho \quad \rightarrow \quad R_{ws} = \left(\frac{4\pi\rho}{3}\right)^{-1/3}$$

$$\rightarrow \sum_i \frac{1}{R_i^4} = \int_{R_{ws}}^{\infty} \frac{\rho}{R^4} \cdot R^2 dR \int d\Omega = -4\pi \frac{\rho}{R}\bigg|_{R_{ws}}^{\infty}$$

$$= 4\pi\left(\frac{4\pi}{3}\right)^{1/3} \rho^{4/3}$$

$$\sim 20\rho^{4/3}.$$

The R^{-4} dependence means: we can just sum
over all space since contributions outside the
Ryd orbit are negligible.

In sum, this gives an energy shift of about

$$\Delta \varepsilon = -10 \alpha \beta^4 / 3.$$

This is always negative as α is (in the ground state) always positive $\Rightarrow$ this predicts a <u>RED</u> shift.

So we obviously need to see what the electron is really doing $\rightarrow$ and we have to go beyond the somewhat naive picture of the electron-atom interaction being incapsulated as $U \sim - \frac{\alpha}{2} / |\vec{R} - \vec{r}|^4$. (as usual, more on this point later...)

To start the derivation, notice that the Rydberg electron is very <u>slow</u>:
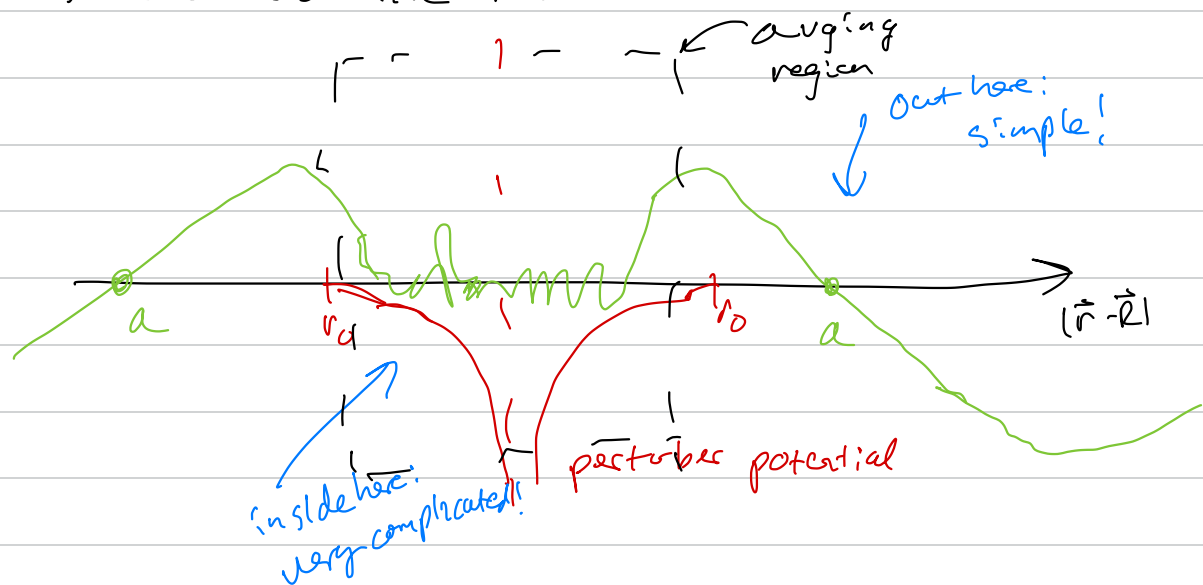
$$v \sim 1/n$$

so it has a very long deBroglie wavelength.

When it encounters a perturber, it does so at nearly zero energy $\Rightarrow$ s-wave is all that matters!

The electronic TISE is:

$$\left[\frac{-\hbar^2}{2m}\nabla^2 + \underbrace{U(r)}_{\substack{\text{elec-ion} \\ (-1/r \text{ in simplest cas})}} + \underbrace{\sum_i U(r, R_\xi)}_{\substack{\text{perturber-elec} \\ (-\frac{\alpha}{2|r-r_q|^4} \text{ in simplest} \\ \text{case})}}\right]\psi = E\psi \qquad \text{①}$$

Now let's think about what the elec w.f.
"should" look like near an atom:

From this picture, we can see that a good idea
might be to consider averaging this WF over
a region approx equal to the size of the
perturber. Outside, such a procedure just

gives the same WF back (maybe a bit
"pixellated' since it is so slowly verging over
R_{ws}.

That means: take ① and integrate it over a
small volume $d\vec{x}_i$ around the perturbers:

$$\rightarrow 0 = \nabla^2 \overline{\Psi} + \frac{2m}{\hbar^2}(E-U)\overline{\Psi} - \frac{2m}{\hbar^2}\sum_i \overline{U_i \Psi}$$

where $\overline{\Psi} = \int d\vec{x}\,\Psi$

$\overline{U_i\Psi} = \int d\vec{x}_i\, U_i\Psi$

eval �
this
first!

To calculate ✳, recall the form of Ψ near a
perturber: it is <u>S-wave</u> locally and nearly
at Zero energy:

$$\Psi = \frac{u(r)}{r} Y_{00}(\theta,\phi)$$

$$u''(r) = \frac{2m}{\hbar^2}\left(V(r)u(r) - E\cancel{u(r)}\right)$$

$E=0...$

From a few pages ago: outside the range
r_0 of $V(r)$, we KNOW $u(r)$!!

$$u(r) = \underbrace{c(r-a)}_{\text{we don't yet know this.}}, \quad r \geq r_0.$$

Idea: outside $U(r)$, the avg of ψ is the same as ψ. Let's use this to find c.

Start w/ the E=0 SE:
$$\frac{\hbar^2}{2m} \nabla^2 \psi = V\psi, \quad \psi = \frac{u(r)}{r} Y_{00}(\hat{r}).$$

Integrate it over our averaging volume:
$$\rightarrow \int \nabla^2 \psi \, d^3r = \frac{2m}{\hbar^2} \int V\psi \, d^3r$$

$$= 4\pi Y_{00} \int_0^{r_0} u''(r) r \, dr \qquad \underset{\text{useful:}}{\overbrace{\qquad}}$$

$$\frac{d}{dr}\left(u' \cdot r\right) = u'' r + u'$$
$$\rightarrow u'' r = (u'r)' - u'$$

$$= 4\pi Y_{00} \left[u'(r) r \Big|_0^{r_0} - \int_0^{r_0} u'(r) \, dr \right]$$

$$= 4\pi Y_{00} \left[\underset{c}{\underbrace{r_0 u'(r_0)}} - 0 - \underset{c(r-a)}{\underbrace{u(r_0)}} - (-0) \right]$$

$$= 4\pi Y_{00} \left(c r_0 - c r_0 + c a \right)$$

$$\underline{= 4\pi Y_{00} \, c a} = \underline{\frac{2m}{\hbar^2} \int V\psi \, d^3r}$$

So: we have $\overline{\nabla \Psi}$. Now we need $\overline{\Psi}$:

$$\overline{\Psi} = \frac{\int d^3 r \, Y_{00} \, u(r)/r}{\int d^3 r} = \frac{4\pi Y_{00} \int_0^{r_0} \frac{c(r-a)}{r} r^2 \, dr}{\frac{4\pi}{3} r_0^3}$$

$$= \frac{3 Y_{00}}{r_0^3} \cdot \int_0^{r_0} c r^2 - c a r \, dr$$

here we use the
fact that the averaging
volume is <u>large</u> compared
to $a^3 \to \rho a^3 \ll 1$!

$$= \frac{3 Y_{00}}{r_0^3} \left(\frac{c r_0^3}{3} - \frac{c a r_0^2}{2} \right)$$

$$\approx c Y_{00}.$$

(strongly interacting
particles w/ $a \to \infty$ are
dubious!)

note: this gives us
c!

So: $0 = \nabla^2 \overline{\Psi} + \frac{2m}{\hbar^2} (\varepsilon - U) \overline{\Psi} - \frac{2m}{\hbar^2} \overline{\nabla \Psi}$

$c = \overline{\Psi}/Y_{00}$

$$= \nabla^2 \overline{\Psi} + \frac{2m}{\hbar^2} (E - U) \overline{\Psi} - 4\pi Y_{00} c a$$

ρ too!

And finally: $\Rightarrow -\frac{\hbar^2}{2m} \nabla^2 \overline{\Psi} + U \overline{\Psi} + \frac{4\pi a \hbar^2}{2m} \overline{\Psi} = E \overline{\Psi}$

This is just the SE for $\overline{\Psi}$ w/ an additional energy
term!

Punchline: the effect of all these
perturbers is to shift the electrons energy
by $\boxed{\Delta E = \dfrac{2\pi \hbar^2}{m} a \rho}$

This term can be pos or neg, following
the sign of a, and typically dominates
the other due to the $\rho^{1/3}$ factor!

More globally useful punchline:

We showed that:

$$\frac{2m}{\hbar^2} \int v \Psi d^3 r = 4\pi a \overline{\Psi}$$

→ this equation would hold for any Ψ if
the real potential V was replaced by

$$V_{Fermi}(r, R) = \frac{2\pi \hbar^2}{m} a \, \delta^3(\vec{r} - \vec{R}).$$

This is the FAMOUS Contact (Fermi
potential!

Key physics insight from Fermi!

Squeeze everything you don't know
into an increasingly smaller volume
and characterize your lack of knowledge
by a single number a!

//   /   //

Some other checks / points:

1) The Fermi pseudopotential also guarantees
that we get the right scattering length
in the Born approx:

$$a = -\frac{\tan \delta_\ell}{k^{2\ell+1}} \underset{\text{Born}}{=} +\frac{\pi m}{\hbar^2 k^{2\ell+1}} \int \frac{f_{E\ell}(kr)^2}{r^2} |Y_{\ell m}(\theta, \varphi)|^2 V(\vec{r}) r^2 \sin\theta \, dr \, d\theta \, d\varphi$$

$$\underset{r \to 0}{=} +\frac{\pi m}{\hbar^2 k^{2\ell+1}} \int \frac{2 |Y_{\ell m}(\hat{r})|^2 (kr)^{2\ell+2}}{\pi \hbar r^2 [(2\ell+1)!!]^2} V(\vec{r}) r^2 \sin\theta \cdot dr \, d\theta \, d\varphi$$

$$V(\vec{r}) = \frac{\delta(r) \delta(\theta) \delta(\varphi)}{r^2 \sin\theta} \cdot \frac{2\pi a}{m}$$

$\rightarrow$ $l = 0$:

$$a = \frac{2\pi a}{m} \cdot \frac{\pi m}{k} \cdot \frac{2}{\pi k} \cdot k^2 \cdot \underbrace{|Y_{00}(0,0)|^2}_{= \frac{1}{4\pi}} \cdot \underbrace{\int_0^r \frac{r^2 \cdot r^2}{r^2} \cdot \frac{S(r)}{r^2} \, dr}_{= r}$$

$$= a \quad \checkmark$$

2) The pseudopotential is otherwise too singular to use in more exact calculations, for example when we try to use the actual wf (with phase shift) rather then $f_{el}(r)$.

That means we have (for $E \rightarrow 0$ and $l = 0$):

$$\Psi(r) \rightarrow C \frac{r-a}{r} \qquad \qquad ①$$

rather then

$$\Psi(r) = \frac{f_{el}(r)}{r} \rightarrow \frac{r'}{r} \rightarrow 1. \qquad ②$$

For ①, we might calculate matrix elements like: $\int V(r) \Psi(r) \, dr = \left. \frac{r-a}{r} \right|_{r=0} = \infty$!

This is cured by a more rigorous derivation which yields the regularization operator:

$$U_{Fermi} = \frac{2\pi a}{m} \delta^3(\vec{r}) \boxed{\frac{\partial}{\partial r} r}$$

Notice that this gives:

$$\int U(r) \psi \, dr = \int \delta(r) \frac{\partial}{\partial r} (r-a) \, dr$$

$$= \int \delta(r) [1] \, dr = 1.$$

This behaves as necessary. However, it's not necessary to include this reg. op. when we are doing mean-field or perturbative calcs, for example when the Fermi PP is used to derive:

1) The Gross-Pitaeuskii Eq. for BECs (see other course material)

2) Rydberg Moleccules