Lecture S 6 Nov 123 At the end of last class, we were discussing now these derivations will show how spectroscopy are We will see often how scattering physics, intinated such as phase shifts, connect to bound state physics, such as their energy levels. Learning has to extract these links will be key! In the present case, we will observe that poles of the scattering amplitude for S-matrix) determine the bound state energies! To see why, let's onelytically continue to ELO by setting k-s:K (K20) $\rightarrow E = -K^{2}/2.$ Doing this in our scattering solution gives $\Psi \rightarrow N(e^{-\kappa_{z}} + f(\kappa, \theta)e^{-\kappa_{x}})$ this diverges when 2 -> - >>, which is simply not acceptable! To fix this, we need f(ik,) to diverge even better! -> T(1+iQ) -> 80.

lest time: $f(b) = \frac{1}{(k(1-cos\theta))} \left(k^{2}\right)^{-iQ/k} e^{-\frac{2iQ}{k}g_{n}(1-cos\theta)} e^{-\frac{2iQ}{k}g_{n}(1-cos\theta)}$ This implies that 1+ R/K is a negative int. or zero $\rightarrow l + \frac{2}{k} = -(n-1), n = 1, 7, ...$ $\rightarrow k_n = \frac{z_1 z_2}{n}$ $-3 E_n = -\frac{Z^2}{2n}$, where $-Z = Z_1 Z_2$ What a coincidence! It's the Rydberg formula yet again! Loulomb Scottering in spherical coords Motivation: parabolic coords were very convenient to describe scattering, but atoms one still apherically symmetric! So when we really want to solve more complicated problems, especially for non-hydrogenic atoms, we will need to do this in 4ph. coords.

We already derived: $f_{coul(D)} = \frac{Z}{2Z} \frac{1}{1-cos\Theta} \frac{27T_0 + 25Z_0 n(1-cos\Theta)}{4}$ where $T_e = arg \Gamma(l+1-5Z/k)$ is the Coulomb phase shift. Note that this is a nice closed-form expression, nosms, no nothing!

If we had tried to do this in spherical coordinates, like in the typical way via a partial wave expansion, we would have gotten $M = \frac{2i\sigma_e}{f_{coul}(6) = \frac{2}{e=0}} (2li() \frac{e}{2ih} - \frac{1}{2ih} f_e(cos6)$

You can try to get this from our result above by Legendre P expansion in your vast spore sine!

But let is get it directly by working in sph. coords

The radial solves obey $-\frac{1}{2}u_{k}^{(1)}(r) + (\frac{l(l+l)}{2r^{2}} - \frac{k^{2}}{2})u_{k}(r) = 0$ 1

Agood way to solve equations such as this one is to factor out the long and short vange behavior we expect the solin to have: $U_{\ell}(r) \sim r^{\ell+1}, r = 20$ $U_{\ell}(r) \sim e^{ikr}, r = 30$ ~ ue(r) = rd+leikn Felr)

Patting this into O gives, after some algebra, $X F_{\ell}''(x) + (2l+2-X) F_{\ell}(x) - (l+1-i^{2}/k) F_{\ell}(x) = 0$ where x = - 2ikr. ASTOUNDINGLY, this is just the equation for our old friend, the Cont-Hypo-Geo-Func again! So we already know the radral solution:

 $u_{\ell}(r) = r^{\ell+1} e^{ikr} F(\ell+1-\frac{i2}{k}; 2\ell+2; -2ikr).$

Recall the asymptotic form we derived: $e^{-\chi/2}F(a,b,x) \longrightarrow \frac{\Gamma(b)}{\Gamma(b-a)} (-\chi) e^{-\chi/2} + \frac{T(b)}{\Gamma(b)} \frac{a-b}{\chi} \frac{\chi/2}{\Gamma(a)}$ $= \mathcal{U}_{e}(f) = \mathcal{U}_{e}(f)$ ter reasons, Martin 52(4) we call this the evergeg-analytic solution f. o (r). -> fe(r) -> (r(2/f2)) / r-> (r) her $(2k)^{l+1} [\Gamma(l+1-52/k)\Gamma(l+1+52/k)]^{1/2}$ $\circ \left(\underbrace{e^{\underline{k}\cdot \mathbf{r}} + \underbrace{i^{2}}_{k} \ln 2kr}_{\ell} - \frac{1}{\ell} - \frac{1}{\ell} \underbrace{e^{-\frac{1}{2}/2k}}_{\ell} \right)$ $\frac{1}{12} + e^{-ikr - i\frac{2}{2}kln2kr} + e^{-i\frac{2}{2}ln2kr} + e^{-i\frac{2}{$ $(2k)^{2+(17)(l+(1+2k))}$ · Sin / kr + Z lu 2kr - lit + Oz

later on we will want the so-called "energy - normalized" form of this solution, which has to look like Un sin (state) as roo. Clearly, this is satisfied by $f_{22}(r) = \beta_{22} f_{22} r(r)$ where $\beta_{22} = \frac{1}{(12)} \frac{1}{(2)} \frac{2}{(12)} \frac{1}{(2)} \frac{2}{(12)} \frac{1}{(2)} \frac{1$ Billrart! While we are here, we will want to extend this solution to regative energies again using analytic continuation ... $f_{\ell}^{0}(r) = r^{\ell+1}e^{-Kr} F(\ell+1)^{-2/k}, 2\ell+2, 2Kr)$ $= \Gamma(2\ell+2)r^{\ell+1}\int (-2kr)^{2/k-\ell-1}e^{-Kr}$ Actel $f(2kr)^{-\frac{1}{2}/k-2-1} e^{\frac{1}{2}/k}$ This is again NOT OUL !!

So, let's kill :+ off! First, we define $\frac{Z}{K} = V$. V : S gonne be oar "effective quantum" number ". We proceed using yet another ["-func : dent ity, SINTZ This gives: $f_{i}(r) \rightarrow l(2l+2)r^{l+1} \left[\frac{2k}{2k} - \frac{l-1}{2k} - \frac{2k}{r} - \frac{2k}{r} - \frac{k}{r} + \frac{k}{r} \right]$ $= \frac{\Gamma(2\mu r_{0})}{\Gamma(2\mu r_{0})} + \frac{$ $-\frac{e^{\left[\left(\mathcal{V}-\ell\right)\right]}\left(2k\right)^{\nu}r^{\nu}e^{-k\nu}r^{\nu}2}{\left[\left(l+1+\nu\right)^{\prime\prime2}}\cdot\left(\left[\left(\mathcal{V}-l\right)\right]^{\prime\prime2}\right)^{\prime\prime2}\right)$ $= \frac{2(2k)}{\Gamma(1k+1+\nu)} \frac{-1/2}{(\pi k)^{-1/2}} \frac{\sqrt{2}}{\sin \pi(\nu-2)e^{k\nu} - \nu} \frac{\sqrt{2}k}{(12k)^{\nu}\pi^{1/2}} \frac{\sqrt{2}k}{\pi^{1/2}} \frac{1}{\Gamma(1k+\nu)} \frac{\sqrt{2}k}{\Gamma(1k+\nu)} \frac{\sqrt{2$ Dae

And so, finally: $f_{ze}(r) \longrightarrow A_{ze}^{-1/2} (tr K)^{1/2} \left[sin \pi (v - e) e^{kn - v - 1} \right]$ $= e^{2t\pi (v - e)} e^{-kn} v D_{ze} \left[e^{2t\pi (v - e)} e^{-kn} v D_{ze} \right]$ $A_{2e} = \frac{2\Gamma(l+(+\nu))}{\Gamma(2l+2)\Gamma(\nu-e)} (2K)^{2l+1}$ with $D_{2}e = (2k)^{\nu} \pi^{1/2} [\Gamma(l+(+\nu)\Gamma(\nu-e))^{1/2}]$ OK! Now we see how to remove these peaky divergences: $\sin \pi(v-1) = 0 \implies v-1 = \text{enteger}$ $\implies v = N_r + 1 + 1$ $\frac{1}{2} | k = \frac{2}{n} \rightarrow \frac{2}{2n^2}.$

VIL is important to remove the chance of [(V-l) blowing up, leaving us with no golucton. Going back to the definat K, V, etc, we see that we have once ogain obtained $E = -\frac{K^2}{E} = -\frac{2^2}{2} = -\frac{2^2}{2}$ 2 2n2 2(nn+l+1)2

Notice a weind feature of this asymptotic Corm: everything was real until the end, when suddenly we got an e^{itt(v-e)}!

The reason for this is rather nessy... involving branch rats and other analying things. So we argue as plags: (? sts that our real solution to a real DE should inded be real, and take eITT (V-L) 3 COST (V-L).

To treat scattering from modified Coulomb potentials, we need the 2nd solution to this 2nd-order DE! - importantly this must be invertes independent to I to be any yenember: while $f \rightarrow r^{l+l} a_{3} r \rightarrow 0$, the other solin goes like $g \rightarrow r^{-l}$. good! One thing we could try, to define g, would be to define $l \rightarrow -l - l$. Note that this maps fing as rio and also leaves the SE unchanged, as $l(l+1) \rightarrow (-l-1)(-l-1+1) \rightarrow (l+1)(l).$ But, the power series solution that we used for Fla; b; x) was proportional to $\Gamma(b) = \overline{\Gamma}(2l+2) \xrightarrow{\rightarrow} \Gamma(-2l)$ This blows up for integer I, which is unfortunately the type of I we are interested in. Ack!

So that obviously a n't gonna work.

To derive the solin inregular at the origin exactly is rather (actually really) tedious.

> To check it out yourself, read: Seaton Rep. Pray. Phys. 46 167 '83 or Greene, Fanc, + Strinatt PRA 19 1485'79 on Greene, Rau, + Fano PRA 26 2441 '82

We'll do it approximately, following the WRB approach of GRF'82.

BRIEF DIVERSION: WRB?? The WEB (or JWEB or other permutations.)

approximation is a very metal tool to keep

in your "theorist's toolbox".

[here's not enough time to dive into this in detail, but høpefulle you alreade learned et in QM...

But Rydberg physics gives us a nice mot wation to study WRB malitle none detail.

Some useful formulas to remember: $\frac{U(x) = \frac{N}{p(x)}}{\frac{p(x)}{p(x)}} = \frac{(2m | E - U(x))}{(2m | E - U(x))} = \frac{V(x)}{x_1} = \frac{V(x)}{x_2}$ wave function everywhere, even in classically forbidden negions, we must satisfy the Bohr-Sommerfeld quantization viele: $\frac{1}{4} \int_{x_1}^{x_2} \rho(x) dx = (n + 1/2) T .$

The following sketch might help jog your WKB memory:

connection Dormale is derived so that Ciffer) dr t)(A this is a smooth match. E e f p(x)Lx exp. decreasing X

Now: WEB 15 a 10 approximation. And radeal SEs, although they look 1D, are not. At least, not purely: they have the additional BC that the radial sol'n Ual (r) = rd+(for small r, i.e. we have all problem w/ an infinite potential for all xco. for all XCO. This means we have to make some small adjustments, since the WKB connection formalog are all made to engine that u(x) -> 0 when x-s = 00 for bound states, whenever now we need ulx) > O when x >0. Fortunately, we can just be clever with a charge in variable to fix this: $\chi = ln r$ $\neg \cap = e^{k}$ (=) $k \rightarrow -\infty =$) $\gamma \rightarrow 0$ $\gamma \rightarrow \infty =$) $\gamma \rightarrow \infty$. Since $\frac{du}{dr} = \frac{du}{dx} \frac{dx}{dr} = \frac{1}{r} \frac{du}{dx} = \frac{e^{-x}}{dx} \frac{du}{dx}$ $\frac{\partial^2 \alpha}{\partial r^2} = \frac{1}{r^2} \frac{\partial^2 \alpha}{\partial x^2} - \frac{1}{r^2} \frac{\partial \mu}{\partial x} = e^{-2x} \left(\frac{\partial^2 \alpha}{\partial r^2} - \frac{1}{r^2} \frac{\partial^2 \alpha}{\partial x} - \frac{1}{r^2} \frac{\partial^2 \alpha}{\partial$

The radial SE becomes: $O = u^{(1)}(x) - u^{(1)}(x) + e^{2x} \left[\frac{1}{2} - 2 \frac{1}{2} \frac{1}{2} - \frac{1}{2} \frac{1}{2$ Mannoying: Set u(x)=e^{x/2}X(x) $\rightarrow u'' - u' = e^{X/2} \left(\chi'' - \frac{1}{4} \chi \right)$

 $\rightarrow 0 = \chi''(x) + e^{2\kappa} \left[k^2 - 2 \sqrt{e^{\kappa}} - \left(l \left(l + l \right) + \frac{1}{4} \right) e^{-2\pi} \right] \chi(x)$ $= l^{2} + l + l/\psi$ = $(l + l/z)^{2}$ $\equiv k^2(x)$

 $=> O = \mathcal{V}'(x) + \mathcal{K}^{2}(x)\mathcal{U}(x),$ which has the form of a truly ID SE suitable for WKB treatment, i.e. $\chi(x) = \frac{1}{e} e^{-\int_{x}^{e_{n}} \kappa(x) dx'}$ VKCX and quantization condition Jene K(x)dx = (u + 1/2)T.

It we take this equation and go back tor, we have $\int_{a}^{b} \int_{2E-2V(r)} - \frac{(l+1/2)^2}{r^2} dr = (n_r+1/2)\pi$ which is exactly what we would have raively used except that $l(l+1) \rightarrow ll+1/2)^2$. This is the Langer Correction, and we have to do it every time we want to get accurate WKB regults for a radial equation. Note that: $\frac{1}{2} \int_{a}^{b} \frac{1}{r} \left[-\frac{r^{2}}{v^{2}} + 2r - \left[1 + \frac{1}{2} \right]^{2} dr \frac{\text{lesing}}{\text{E} = -\frac{1}{2v^{2}}} \right]$ a, b are the turning pts, where V = 0. We would find sham by solving this quadratic eph, or simply by Ladoring _ = (r-a)(b-r). $= \int_{a}^{b} \frac{1}{r} \left[(r-a)(b-r) \right]^{1/2} dr = \frac{1}{2} \left(a+b-2\sqrt{ab} \right).$

a= v2 v Vv2 - (l+12)2 $b = v^2 + v \sqrt{v^2 - (u + i'z)^2}$ $\rightarrow \left(n_{r} + \frac{1}{2} \right) \pi = \frac{\pi}{2} \left[2 v^2 - 2 \sqrt{v'' - v^2 (v^2 - (l + \frac{1}{2})^2)} \right]$ $-7 2n_{r+1} = 22^{2} - 2(l+1/2)$ $\frac{\mathcal{V} = n_r \cdot l + l}{\mathcal{V} = \frac{-1}{2(n_r + l + l)^2}}$ or, My goodness, it is the Rydberg formula again! Exactly! Diversion punchlive: WRB is exact for Loulomb problem (for everyies at least) and Langer Correction is important! Bonus: there is a Supersymmetric WKB and papers arguing various fine points of general Langer correction Ideas. See e.g. Gangopadhyaya et al PLA 476 128 878 (2023) Hruška et al PRA 55 3345 (1996) Adhikarietal PRA 38 1679 (1986)

But now we have to get back to the original topic: what is the 2nd solution to the Coulomb SE?

In the classically allowed region, ricrerz,

We have $\int \frac{w_{kB}}{f_{ae}(r)} = \left(\frac{2}{t\tau k(r)}\right)^{1/2} \sin\left(\int_{r_{1}}^{r} \frac{k(r') dr' + tT/4}{f_{ae}(r')}\right) \cdot \frac{f_{ae}(r')}{f_{ae}(r')} + \frac$

This solly is regular at r=0 and 25 a smooth function of E at small r.

A+ ELD this becomes (using more WBB formulus)

fie (r)= fin Berr-v - cospre V DWKB $P^{WKB} = \int_{V_{1}}^{V_{2}} h(v') dv' + \frac{\pi}{2} = \pi (v - 2).$

Hun. compare with the exact fee behavior we obtained carlier. this has the some structure!

At large r, our 2nd linearly indep. gol'u should have the same amplitude as fee (s) but with a 90° phase laythink of an L=O zero potential case where the two solins one sin, -cos. Here, gee(r) - - - - Cosperr-2 + singer r Durke Durke And us it turns out, this matches the exact regult very well (in all the ways that matter, as we'll see.) For completeness: i' remember: remember: remember: remember: remember: remember: right (l+1-i/k) right (l+1+i/k) $g_{ke}(r) \longrightarrow \int \left(\frac{2}{\pi k}\right)^{1/2} \cos\left(hr + \frac{1}{\omega}\ln 2kr - \frac{2\pi}{2} + \sigma_{e}\right)$ $\int \frac{f_{0r} \epsilon_{>0}}{\left(r + k\right)^{1/2} \left[\cos \pi (v - e)e^{-v} D_{ee}^{-1} - \sin \pi (v - e)e^{-v} D_{ee}^{-1} - \sin \pi (v - e)e^{-v} D_{ee}^{-1}\right]}$ for 220.

We now have all the preliminarles out of the way. It's the to treat a non-hydrogen atom, s.e. solve the MODIFIED Loulomb potential to obtain energy levels of, say, Rb. The idea is: within the independent destron model, an electron in a multi-electron atom sees the potential: V(r) i r -1/rAt large , the other e's Screen the core and our electron sees a pure "Ir Coulomb potential. Inside all shells it sees the bull nucleus of 2 protons.

Vetween, the potential is Everywhere ch complaced!

Aside: one can fit model potentials very accurately to exp. energy levels in order to describe this complicated physic, see Marinescu, Sadeghpour, Dalgorno PRA 49 182 (1994)

They use ! $V(r) = -\frac{1}{r}$ (long - vange Coulomb) - (Z-1) c / (short-range coulomb) + (az + ayr) e (additional parameters) - de/2r4 (I-exp(-ring)) (polorization one polarizato; lity potential) and this works very well if I dependent as are used. But our potential can actually be the much more generic, yet conceptually simpler: $V(r) = \begin{cases} complicated, r < r_0 \\ - \frac{1}{r}, r \geq r_0. \end{cases}$

We have already solved the SE, at any energy but before applying any BCS, lor she pure Coulomb pert:

Mar (r)= Aze fiel(r) - Bze gre (r) $= \sqrt{A^{2} + B^{2}} \left[\frac{A}{\sqrt{A^{2} + B^{2}}} \int_{\mathbb{R}} \frac{A}{\sqrt{A^{2} + B^{2}}} \int_{\mathbb{R}} \frac{B}{\sqrt{A^{2} + B^{2}}} \int_{\mathbb{R}} \frac{B}{\sqrt$

Inside, the solution w/ U(r) = complicated is something complicated, but in principle Solvable: Uge(v) = Uge(v).

A continuous with exists when we match Cogarithme derivatives at ro: $\frac{1}{M} \left(\frac{u_{ne}(r)}{r_{er}} \right) = \frac{u_{ee}(r)}{r_{er}} = \frac{-f_{ee}(r)\cos\delta_{ee} - g_{ee}(r)\sin\delta_{ee}}{f_{ee}(r)} = \frac{-f_{ee}(r)\cos\delta_{ee} - g_{ee}(r)\sin\delta_{ee}}{f_{ee}(r)\sin\delta_{ee}},$ with at $r = r_{o}$

After some nearrangement, tansze = W(lze, uin) W(ger, uze), r=ro. We can rapidly finigh calculating f(0) now. Since $f \rightarrow sin()$ and $g \rightarrow cos()$, $bince f \rightarrow sin()$ and $g \rightarrow cos()$, base shift phase shift nodifiel $<math>base \rightarrow \int_{arc}^{2} \left[sin() cos \delta + cos() sin \delta \right]$, coulomb v trig identity f phase <math>coulomb v trig identity f phase <math>sift. $= \int_{arc}^{2} sin(kr + \frac{1}{h} ln 2kr - \frac{kr}{2} + be + See).$ -> We have a phase-shifted sive wave at large r, and they f(t) from the partial wave expansion derived in QM:s: $f(\theta) = \sum_{e=0}^{\infty} (2l+1) \frac{2i(l_e + \delta_{e,e})}{-l} - l P_e(\cos\theta).$ $\frac{\log_{e}}{\log_{e}} \frac{2ik}{factor}$

As stated last week, this does not converge well.

But, we can choose to wr!te: $e^{2i\theta_{2} + \delta_{a,2}} = e^{2i\theta_{2}} e^{2i\theta_{2}} + e^{2i\theta_{2}} - e^{2i\theta_{2}}$ $= e^{2i\theta_{2}} (e^{2i\delta_{2}} - 1) + e^{2i\theta_{2}}$ $= e^{2i\theta_{2}} (e^{2i\delta_{2}} - 1) + e^{2i\theta_{2}}$ =0 for 124 pure Coulomb part

 $= f(\theta) = \left[\frac{\sum (2lH) e^{2i\theta}}{2ik} - l e^{i(\cos\theta)} \right] = f_c(\theta)$ + $\sum (21+i)e^{2i\theta i} \left[e^{2i\delta i e} -i \right] P_{e}(\cos \theta) ropidly$ $\sum i k conv!$

A comment: one thing that we have done under the rug in our devivation of f,q is to easine that they are smooth and almost-analytic finations whenever possible. The mathematical reasons for this can be a bit obscure (see the Scatcon paper refid previously for more details), but this is cruital for us as we can treat the phase Shift also as a vez smooth function of everyz. A picture helps ...

complicated for [Da.u. motching via See. E, JUN E=0.05 5-005 ~ V=3 USIN - 1/10. our outer solln is just a lever comb. of f +g and does not yet ober BCS at infinity. [V(r)]>>[E] at small r, so Use (r) is nearly everyz- in dependent (And thus: See must also be very a function of energy! smooth as

We can go ahead and analytically continue our whole scattering solution from EDO to ECO, Obtaining $\mathcal{U}_{ee}(r) \longrightarrow \frac{1}{\nabla \nabla r} \left[s \operatorname{En}(\nabla (\nu - e) + s_{ee}) r^{-\nu} e^{kr} \right]^{-1}$ -cos(tt(v-l)+See)rvero The full solution, at two arbitrary energies 200, the full solution, at two arbitrary energiesses, must look something (ike: exp diverge! 1 10 Bad! Uril) Uril) (wf's here are exp diverge! (wf's here are exp diverge! (wf's here are V. Bad! so rearly E-indep -that Sig hardly charges. Indue have no rapid Echarges. And we have no repid E. fluretuations because no BCS Dr-200

Looking at our long-range solly, we see that exp. growth is proportional to Sin[tt(v-l) + See]Now, we impose the BC and shut of this unphysical divergence. This will now lead to rapid energy-dependence in some parameters (think - V is correctly a continuous parameter and 1+1 the energy must become discrete!) but the key physics of the "complicated" port is contained in essentially a few numbers. STT (V-2) + SEE = NrT > n=l+np= V+ Sad/tt

or: $\mathcal{E}_{ne} = -\frac{1}{2(n - M_{ee})^2}$

By golly, we did it again! And better!

o Some notes: -> MER = SER/IT :5 the QUANTUM DEFECT! -) For alkali atoms: SER is constat (to~ 3 sig figs) already from n 50 or 50 ... - Infinite numbers of bound states are comparty described by one parameter, which is closely connected to the scattering phase shift!

> Core of QPT: we try our DARNDEST to put everything in terms of analytic (Smooth furctions of energy, and don't apply all BCs (which give rapid energy dependence) until the bitter end.

-> pac= 2 for safectathe high I (we cover polarization effects later) because l(lfi) ghields the e from the core.

Now to return to "Phenomenological evidence for SUS!". In his connent on thes PRL (PRL SG [1986]), Rau points out that comparisons of Rydberg series is kind of Gilly to do via energies; it should really be done using quantum defects.

And here, Mg = 0.4 for Li and Ms=O for H. These are not similar! Even though the transition evergles Rostelechy + Nieto mention seen to get closer, 0.4 never yets close to O.

Furthermore, the agreement blu & states is lettle more than an adenowledgement that Mesi~O.

The authors to reply in that save reference. See what you think!