Introduction to the Quantum defect theory QDT

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History and motivation

Non-relativistic energy of bound states in the poin-charge field

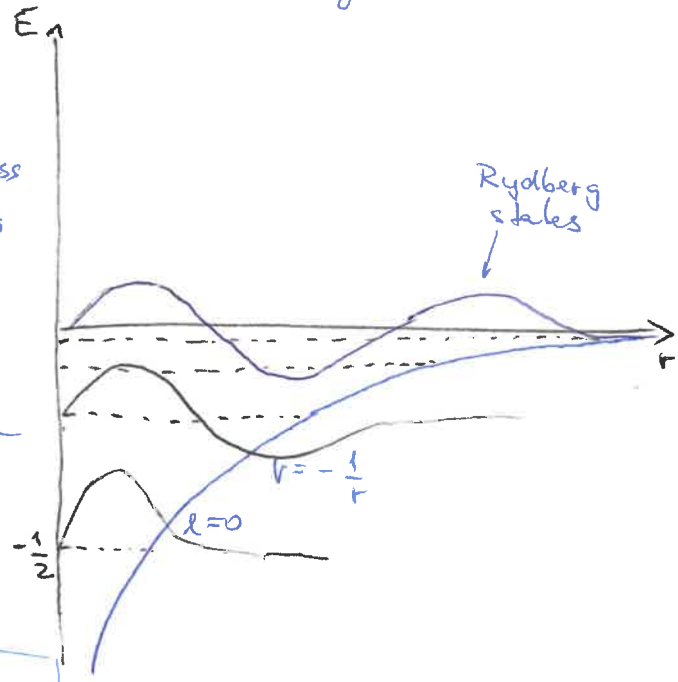
$$E_n = -\frac{Z^2}{2n^2} = -R\frac{Z^2}{n^2}$$

$$R = \frac{m e^4}{2\hbar^2} \; ; \quad m = \frac{m_e}{\left(1 + \frac{m_e}{M}\right)}$$

m_e ... electron mass

M ... nuclear mass

$$R = \frac{R(\infty)}{\left(1+\frac{m_e}{M}\right)} \; ; \; R(\infty) = \frac{m_e e^4}{2\hbar^2}$$ ... Rydberg constant



Transitions $n_0 \to n$ form séries in spectra

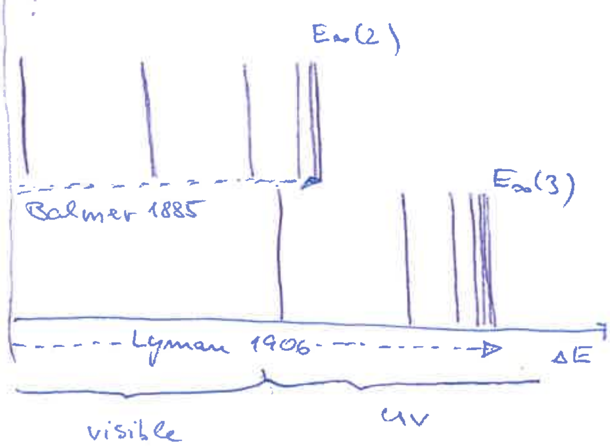
$$\Delta E = (E_n - E_0) = \frac{RZ^2}{n_0^2} - \frac{RZ^2}{n^2} = E_\infty - R\frac{Z^2}{n^2} = \Delta E$$

edge

Empiric formula before the quantum mechanics

Hydrogen atom series

Lyman, Balmer, Paschen, Brackett



Energy levels of alkali atoms: Li, Na, K, ...

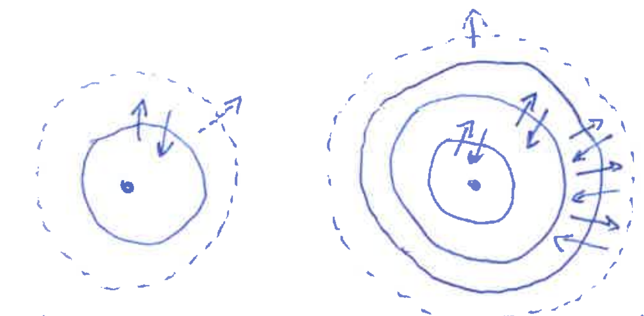
Empirical formula

$$\Delta E = E_\infty - R\frac{Z^2}{(n-\mu)^2}$$

(Mulliken formula)

1889 Rydberg

μ ... quantum defect



$Li^+ = 1s^2$ $\quad$ $Na^+ = 1s^2 2s^2 2p^6$

The single electron in the upper open shell "feels" the asymptotic Coulomb interaction with the remaining cation

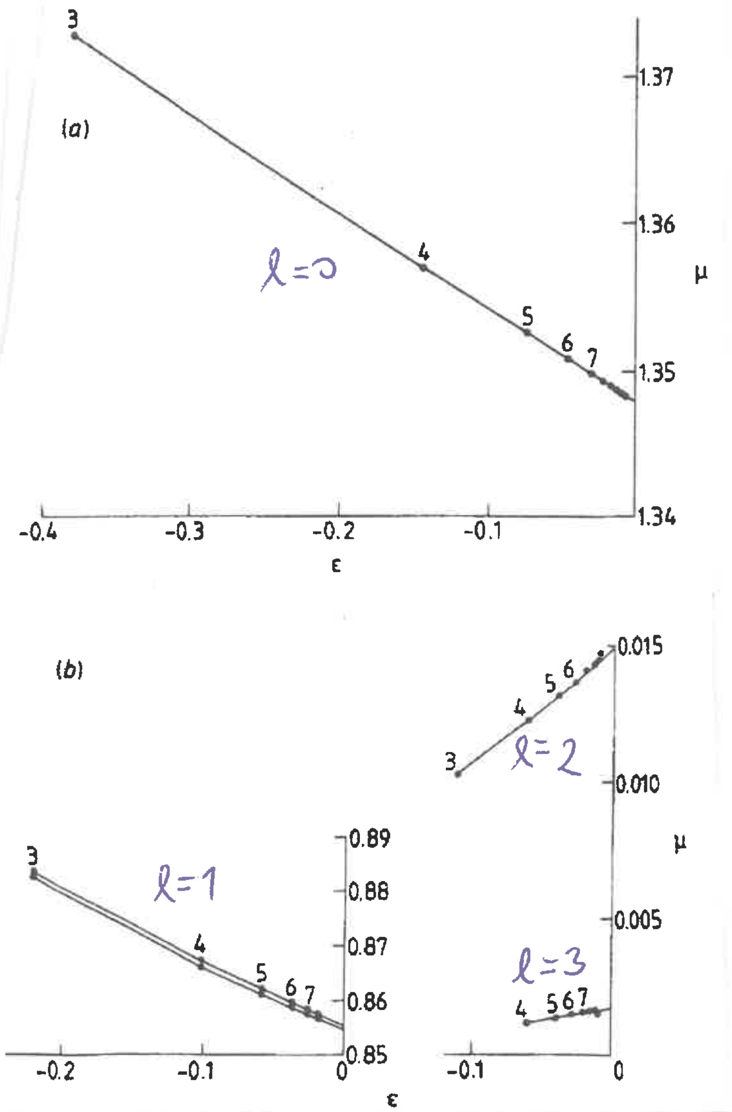
Later and more accurate measurements have shown that the quantum defect μ is not an exact constant. It exhibits a weak energy dependence $\mu(E_n)$ (for simplicity let's assume a.u. and $R = \frac{1}{2}$)

$$E_n = -\frac{Z^2}{2}\frac{1}{(n-\mu_n)^2} = -\frac{Z^2}{2}\frac{1}{(n-\mu(E_n))^2} = -\frac{1}{2\nu^2}$$

ν .... an effective (non-integer) quantum number $\nu = n - \mu$. $\mathcal{E}_n \equiv 2E_n = -\frac{1}{\nu^2}$

Importance of quantum defects

Na atom. Dependence of QD on the energy for $\ell = 0, 1, 2$



- fitting of the experimental transitions on

$$\mathcal{E}_n = -\frac{Z^2}{2\left[n - \mu(\mathcal{E}_n)\right]^2}$$

gives $\mathcal{E}_\infty$ .... ionization potential

- identification of atoms
- series of simple (linear) curves can describe infinite of Rydberg states
- prediction of transitions the have not been observed yet
- transition to continuum, prediction of the phase shift (later)

First attempts for theoretical understanding

a) H-atom Sommerfeld (1916, 1920) - eliptic trajectories, Bohr atomic model. Bohr quantum condition gives $\mathcal{E}_n = -1/n^2$

b) Alkali atoms 1 electron is excited on an eliptic trajectory and spends dominant time in the pure Coulomb field. Interaction is modified at the perihelium and hence precesion. Sommerfeld 1920 obtained $\mathcal{E}_n = -\frac{1}{(n-\mu)^2}$ but quantum defect μ depended on the frequency of the orbital precesion.

Correct explanation comes in the modern quantum mechanics by Hartree 1928

$$\left[-\frac{1}{2}\frac{d^2}{dr^2} + \frac{l(l+1)}{2r^2} + V(r) - E \right] F(E,r) = 0$$

$$V(r) \xrightarrow{r\to\infty} -\frac{z}{r}$$

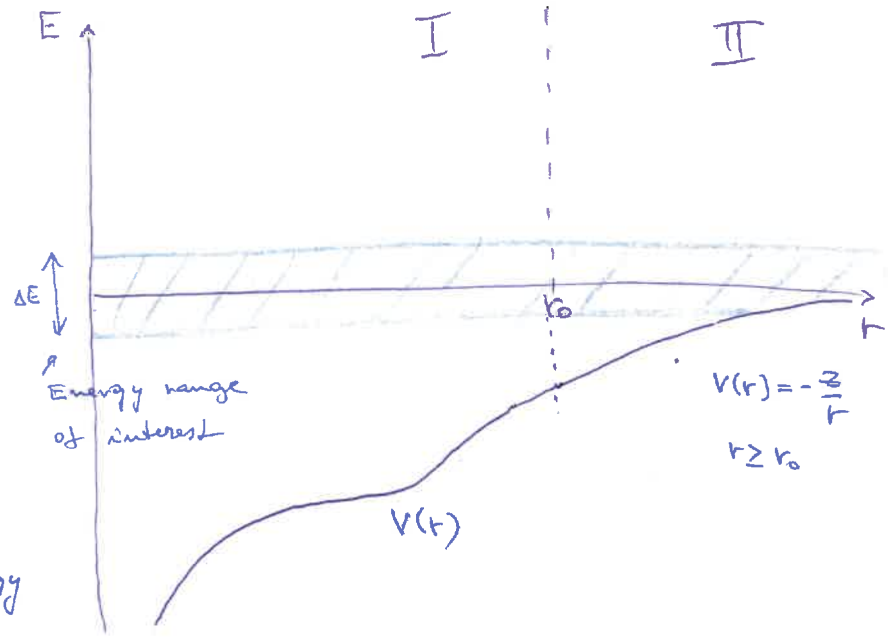
We have solutions in the region I and II

$F_I(E,r) = 0$ for $r \to 0$

$F_{II}(E,r) = 0$ for $r \to \infty$

At $E = E_n$ we have a smooth merge at r_0.

→ $F_I(E,r)$ can be normalized such that it does not depend on the energy much at ΔE



→ Generally $F_{II}(E,r)$ will depend on the energy E in the region ΔE for $r > r_0$. This is because nodal points are added for the higher bound states. But at the point r_0, if $|V(r_0)| \gg |E|$, then F_{II} can be normalized so, it does not depend on the energy at r_0 much.

→ General solution in the region II (not necessary bound) is written as a linear combination of 2 Coulomb functions $s(r)$ and $c(r)$. They are weakly dependent on the energy for $r \le r_0$ in the energy interval ΔE.

→ Hartree has shown

$$F_{II}(E,r) = -\cos(\pi\nu)\, s(r) + \sin(\pi\nu)\, c(r) \; ; \; E = -\frac{z^2}{2\nu^2}$$

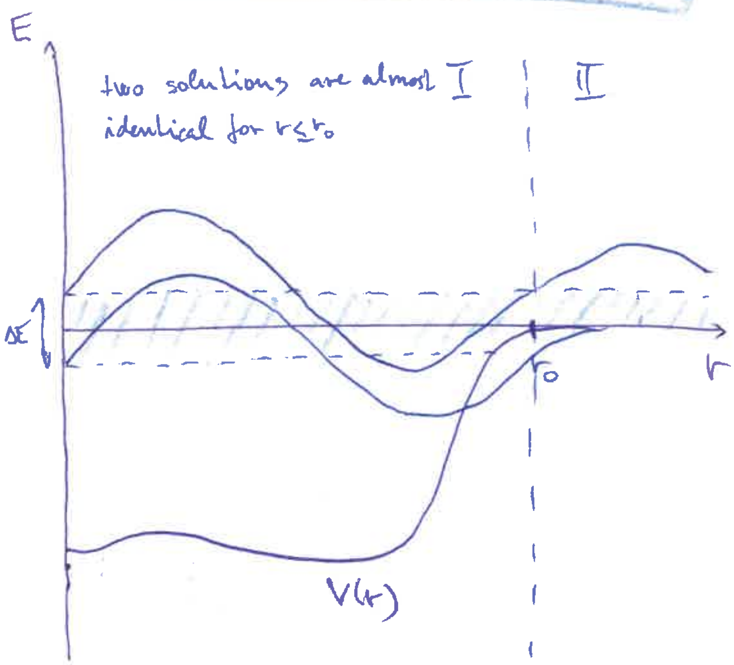
→ Seaton 1955 – 1960, extension of the QDT for $E > 0$, multichannel

Fano 1975, Greene 1979 – present – connection with the rovibrational frame transformation

For clarification an example is provided for a case without the Coulomb asymptotics

(what is meant by removal of the energy dependence by the normalization)

$$\left[-\frac{1}{2}\frac{d^2}{dr^2}+\frac{l(l+1)}{2r^2}+V(r)-E\right]u_l(r)$$, No Coulomb! $V(r)\xrightarrow{r\to\infty}0$



Solutions in II is a linear combination of the free solutions, i.e. Ricatti-Bessel functions $\hat{j}_l(kr)$ and $\hat{n}_l(kr)$ Neumann

Unfortunatelly: $\hat{j}_l(kr)\xrightarrow{k\to0}\frac{(kr)^{l+1}}{(2l+1)!!}$

$$\hat{n}_l(kr)\xrightarrow{k\to0}-\frac{(2l-1)!!}{(kr)^l}$$

This pair of independent solutions is UNSUITABLE for low energies as $s(r)$ and $c(r)$ because they exhibit this artificial energy dependece. They do not traverse E=0 smothly!

We can define: $f^0\equiv s(r)=\frac{1}{k^{l+1}}\hat{j}_l(kr)$ and $g^0\equiv c(r)=k^l\hat{n}_l(kr)$

Solution of the Coulomb problem for QDT

(a search for analytic, smooth functions $s(r)$ and $c(r)$)

Substitutions: $\rho=Zr$; $\varepsilon=\frac{2E}{Z^2}$ $\left[\frac{d^2}{d\rho^2}-\frac{l(l+1)}{\rho^2}+\frac{2}{\rho}+\varepsilon\right]F(\rho)=0$

solutions are found in 2 progression forms

A.) Series substitution $\lambda=\pm(l+1/2)$ => $\left[\frac{d^2}{d\rho^2}-\frac{\lambda^2-1/4}{\rho^2}+\frac{2}{\rho}+\varepsilon\right]F(\rho)=0$

$$F(\varepsilon,\lambda,\rho)=\sum_{n=0}^{\infty}a_n(\varepsilon,\lambda)\,\rho^{n+\lambda+1/2}$$ gives recurrence

$$a_n=-\frac{2a_{n-1}+\varepsilon a_{n-2}}{n(n+2\lambda)}\ ;\ a_1=-\frac{2a_0}{1+2\lambda}$$

a_0 = normalization, important in QDT!

Clearly, $F(\varepsilon,-\lambda,\rho)$ is also a solution. Expect troubles for $\lambda\to-(l+1/2)$

B) Series

$\varepsilon = -\frac{1}{\varkappa^2}$; $z = \frac{2\rho}{\varkappa}$

$$y(\varkappa,\lambda,z) = \frac{(\varkappa z)^{\lambda+1/2}\, e^{-z/2}}{\Gamma(\lambda+1/2+\varkappa)} \sum_{n=0}^{\infty} \frac{\Gamma(\lambda+1/2+\varkappa+n)}{\Gamma(2\lambda+1+n)} \frac{z^n}{n!}$$

solution, proof by the direct insertion.

absolutely and uniformly converging series $\Leftrightarrow$ the product $e^{-z/2} \times \sum_{n=0}^{\infty}$ can be rearranged to the form A.). Then the first term:

$$\frac{(\overbrace{\varkappa z}^{2\rho})^{\lambda+1/2}}{\Gamma(\lambda+1/2+\varkappa)} \cdot \frac{\Gamma(\lambda+1/2+\varkappa)}{\Gamma(2\lambda+1)} = a_0 \rho^{\lambda+1/2} \Rightarrow a_0 = \frac{2^{\lambda+1/2}}{\Gamma(2\lambda+1)}$$

← Does not depend on energy.

⇒ Solution does not depend on the energy for $r \to 0$

We have found the regular QDT solution $s_\ell(r)$

From A.) Series it is clear the $a_n^{(\varepsilon)}$ is a polynomial of the order $n-1$ in the energy ε. That means, that series A.) can be rearranged to

$$F(\varepsilon,\lambda,\rho) = \sum_{n=0}^{\infty} b_n(\rho,\lambda)\,\varepsilon^n \quad \ldots \text{ analyticity in } \varepsilon$$

Search for the irregular solution $c_\ell(r)$ – very complicated

Why?

1.) $y(\varkappa,-\lambda,z)$ is a good candidate, because it is really independent from $y(\varkappa,\lambda,z)$ except for $\lambda = \pm(\ell+1/2)$

Using series B) it is easy to show that

$$y(\varkappa,-\ell-1/2,z) = A(\varkappa,\ell)\, y(\varkappa,\ell+1/2,z)$$, where $A(\varkappa,\ell) = \frac{\Gamma(\varkappa+\ell+1)}{\varkappa^{2\ell+1}\,\Gamma(\varkappa-\ell)} = \prod_{p=0}^{\ell}(1+p^2\varepsilon)$

⇒ $y(\varkappa,-\ell-1/2,z)$ and $y(\varkappa,\ell+1/2,z)$ are linearly dependent

2.) Special linear combination and limit

$$\eta(\varkappa,-\ell-1/2,z) = \lim_{\lambda\to-\ell-1/2} \eta(\varkappa,\lambda,z)$$

$$\eta(\varkappa,\lambda,z) = \frac{A(\varkappa,\lambda)\cos(2\pi\lambda)\, y(\varkappa,\lambda,z) - y(\varkappa,-\lambda,z)}{\sin(2\pi\lambda)}$$

Linear combination is still a solution. In the limit $\frac{0}{0}$, higher order remains as the solution

3.) η is non-analytic in ε → $g = \eta - G$, however G still contains part of $s(r)$

→ $h = -g + A\,s(r)$ and h is almost the sough $c(r)$

Asymptotic forms of $s_\ell(r)$ and $c_\ell(r)$

$\varepsilon > 0$ $\qquad \varepsilon = k^2$

$$s_\ell(r) \xrightarrow{r\to\infty} \left(\frac{1}{\pi k}\right)^{1/2} \sin\left(k\rho - \frac{\ell\pi}{2} + \sigma_\ell(k)\right)$$

$$c_\ell(r) \xrightarrow{r\to\infty} \left(\frac{1}{\pi k}\right)^{1/2} \cos\left(k\rho - \frac{\ell\pi}{2} + \sigma_\ell(k)\right)$$

$$\sigma_\ell(k) = \frac{1}{k}\ln(2k\rho) + \arg\Gamma(\ell+1-i/k)$$

$\varepsilon < 0$ $\qquad \varepsilon = -\frac{1}{\nu^2};\ \nu = \frac{i}{k}$

$$s_\ell(r) \xrightarrow{r\to\infty} (-1)^\ell\left[\frac{\sin\pi\nu}{(2\nu)^{1/2}\pi K}\,\xi_\nu(\rho) - \cos\pi\nu\left(\frac{\nu^3}{2}\right)^{1/2} K\,\theta_\nu(\rho)\right]$$

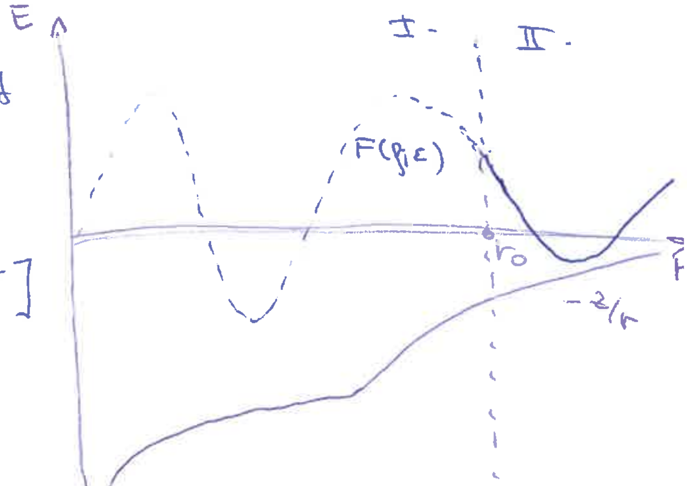
$$c_\ell(r) \xrightarrow{r\to\infty} (-1)^\ell\left[\frac{\cos\pi\nu}{(2\nu)^{1/2}\pi K}\,\xi_\nu(\rho) - \sin\pi\nu\left(\frac{\nu^3}{2}\right)^{1/2} K\,\theta_\nu(\rho)\right]$$

$$\theta_\nu(\rho) = \left(\frac{2\rho}{\nu}\right)^{\nu} e^{-\rho/\nu}$$

$$\xi_\nu(\rho) = \left(\frac{2\rho}{\nu}\right)^{-\nu} e^{\rho/\nu}$$

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

Once we have the pair $s_\ell(r)$ and $c_\ell(r)$ of the 2 independent solutions that are not energy-dependent in the limit $r\to 0$, we can expand the Hartree problem



parametrization of $K = \mathrm{tg}\,\sigma$

$\varepsilon \geq 0$

$$F_{II}(\rho,\varepsilon) \xrightarrow{r\geq r_0} s(r) + c(r)K$$

$$F_{II}(\rho,\varepsilon) \longrightarrow \frac{1}{(\pi k)^{1/2}}\left[\sin(k\rho - \ell\pi/2 + \sigma) + \cos(k\rho - \ell\pi/2 + \sigma)\,\mathrm{tg}\,\delta\right]$$

$$F_{II}(\rho,\varepsilon) \longrightarrow \left(\frac{1}{\pi k}\right)^{1/2}\frac{1}{\cos\delta}\left[\sin(k\rho - \ell\pi/2 + \sigma + \delta)\right]$$

δ ... short-range phase shift

$\varepsilon \leq 0$ $\quad$ Smooth transition through the zero energy gives the same linear combination

$$F_{II}(\rho,\varepsilon) \xrightarrow{r\geq r_0} s(r) + c(r)K$$

$F_{II}(\rho,\varepsilon)$ is a linear combination of $s(r)$ and $c(r)$, both exponentially growing (and decaying). The exponentially growing part: $\frac{(-1)^\ell}{(2\nu)^{1/2}\pi K}\,\xi_\ell(\rho)\left[\sin\pi\nu + \cos\pi\nu\, K\right]$

must disappear for the bound states, i.e. $\sin\pi\nu + \cos\pi\nu\,K = 0 \iff \mathrm{tg}\,\pi\nu = -\mathrm{tg}\,\delta$

If we write $\delta = \pi\mu$ then $\nu = n - \mu$; $\varepsilon = -1/\nu^2 = -\frac{1}{(n-\mu)^2}$

Phase shift δ for positive energies becomes quantum defect $\pi\mu$ for negative energies. Seaton's theorem

Difficulties of the Seaton's theorem lie in finding the irregular solution and deriving asymptotic behaviors of $s_e(r)$ and $c_e(r)$ for positive and negative energies. We can apply it for the non-Coulomb problem, where the functions are known.

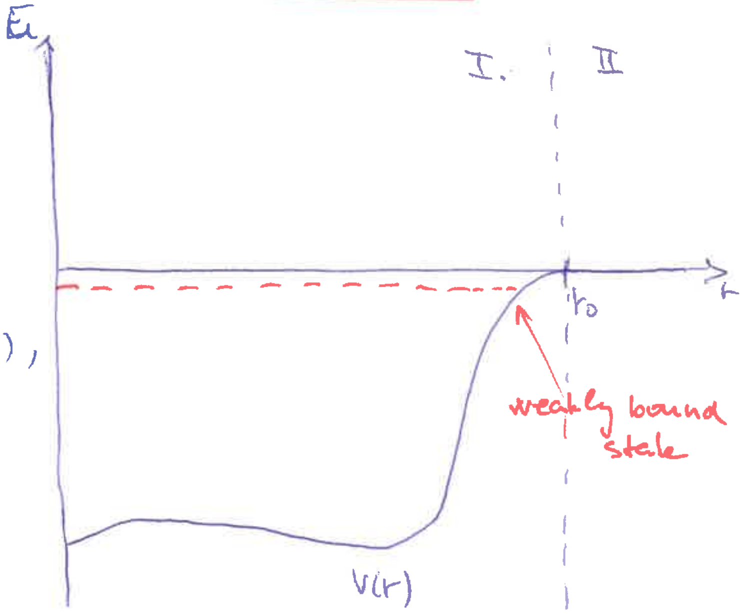
Non-Coulomb problem, Bessel asymptotics

Analytic pair of functions

$$f_e^0 \equiv s_e = \frac{1}{k^{l+1}} \hat{j}_l(kr)$$

$$g_e^0 \equiv c_e = k^l \hat{n}_l(kr)$$

We will use $f^0(r)$ and $g^0(r)$ instead of $s(r)$ and $c(r)$, because $s(r)$ and $c(r)$ are typically used for the Coulomb functions. For simplicity we also assume $l = 0$.



For $\varepsilon \geq 0$

$$f^0(r) = \frac{1}{k}\hat{j}_0(kr) = \frac{\sin kr}{k} = \frac{1}{2ik}\left[e^{ikr} - e^{-ikr}\right]$$

$$g^0(r) = \hat{n}_0(kr) = \cos kr = \frac{1}{2}\left[e^{ikr} + e^{-ikr}\right]$$

Solution in the sector II

$$F_{II}^{*}(k,r) = f^0 + g^0 K^0$$

$K^0 = \operatorname{tg} \pi\mu_0 = \operatorname{tg}\delta^0$ — analytic phase shift δ^0

For $\varepsilon \leq 0$

$\varepsilon = -\varkappa^2$; $k = i\varkappa$; $\varkappa \geq 0$

$$f^0(r) = -\frac{1}{2\varkappa}\left[e^{-\varkappa r} - e^{\varkappa r}\right]$$

$$g^0(r) = \frac{1}{2}\left[e^{-\varkappa r} + e^{\varkappa r}\right]$$

solution in sector II:

$$F_{II}^{\varkappa}(k,r) = f^0 + g^0 K$$

For a possible bound state, the exponential part of $F_{II}(\varkappa, r)$

$$\frac{e^{\varkappa r}}{2}\left[\frac{1}{\varkappa} + \operatorname{tg}\delta^0\right]$$

must disappear. Therefore, $\operatorname{tg}\delta^0 = -\frac{1}{\varkappa}$ for the bound state $\varepsilon = -\varkappa^2 = -\frac{1}{\operatorname{tg}^2\delta^0} = -\frac{1}{a_0^2}$

$\operatorname{tg}\delta^0$ = scattering length from the effective range theory

The ~~stor~~ analytic (short-range) phase shift is not the physical phase shift δ.

Physical δ is defined by asymptotics: $kF = \hat{j} + \hat{n}\frac{K^0 k}{\operatorname{tg}\delta}$ $\Rightarrow$ $\operatorname{tg}\delta = k \operatorname{tg}\delta^0$