



Nederlandse Organisatie voor Wetenschappelijk Onderzoek

vrije Universiteit amsterdam



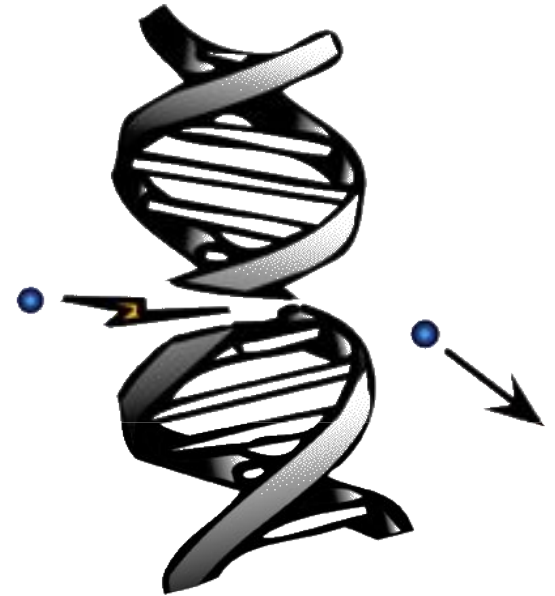
Electron scattering from simple potentials, atoms, and **molecules**

Meta van Faassen

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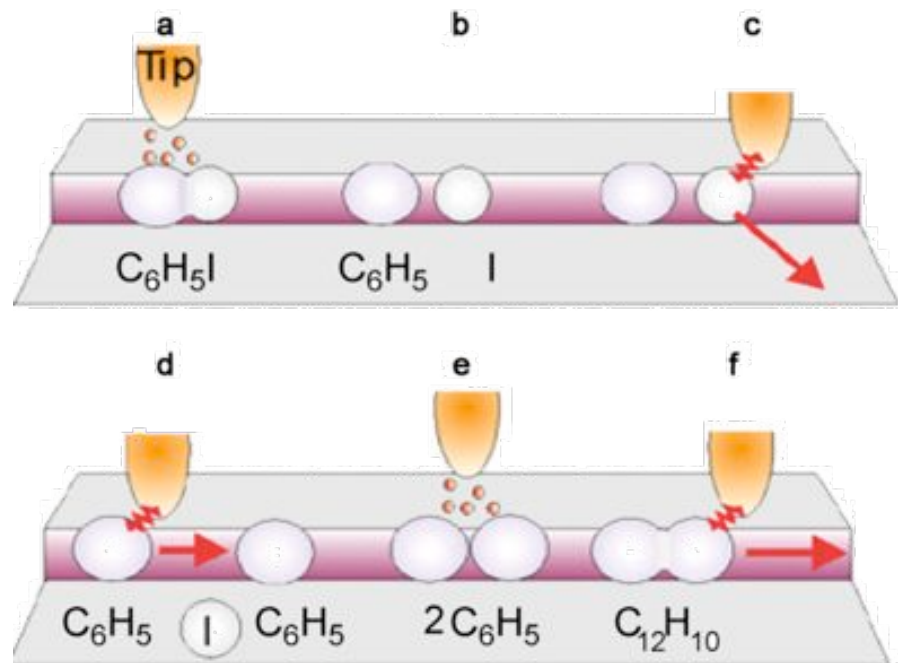
Why (low-energy) electron scattering is important

- DNA strand breaks
 - Leon Sanche and co-workers discovered in the year 2000 that when DNA strands (dried, on a surface) are bombarded with low-energy electrons (0-20 eV) single and double strand breaks can occur
 - The full mechanism of this process is still unknown
 - Calculations on a 10 base pair helix have been performed using very approximate methods
 - Present idea: electron attaches to base, travels to backbone, and breaks bond(s)



Why (low-energy) electron scattering is important

- Electron induced chemistry
 - Low-energy electrons can break bonds with 100% selectivity
 - This paves the way for an electron induced chemistry using for example STM tips as electron source



Electron scattering theory

- We assume elastic scattering during most of these lectures, that is, the energy of the scattering particle (electron) is the same before and after the collision
- Unless stated otherwise we assume potentials go faster to zero than $-1/r$, i.e. they are short-ranged and are effectively zero beyond some radius R
- First look at simple 1D systems that we can understand completely
- 3D spherical systems (effectively 1D)
- Atoms: application of density functional theory to scattering
- Molecules

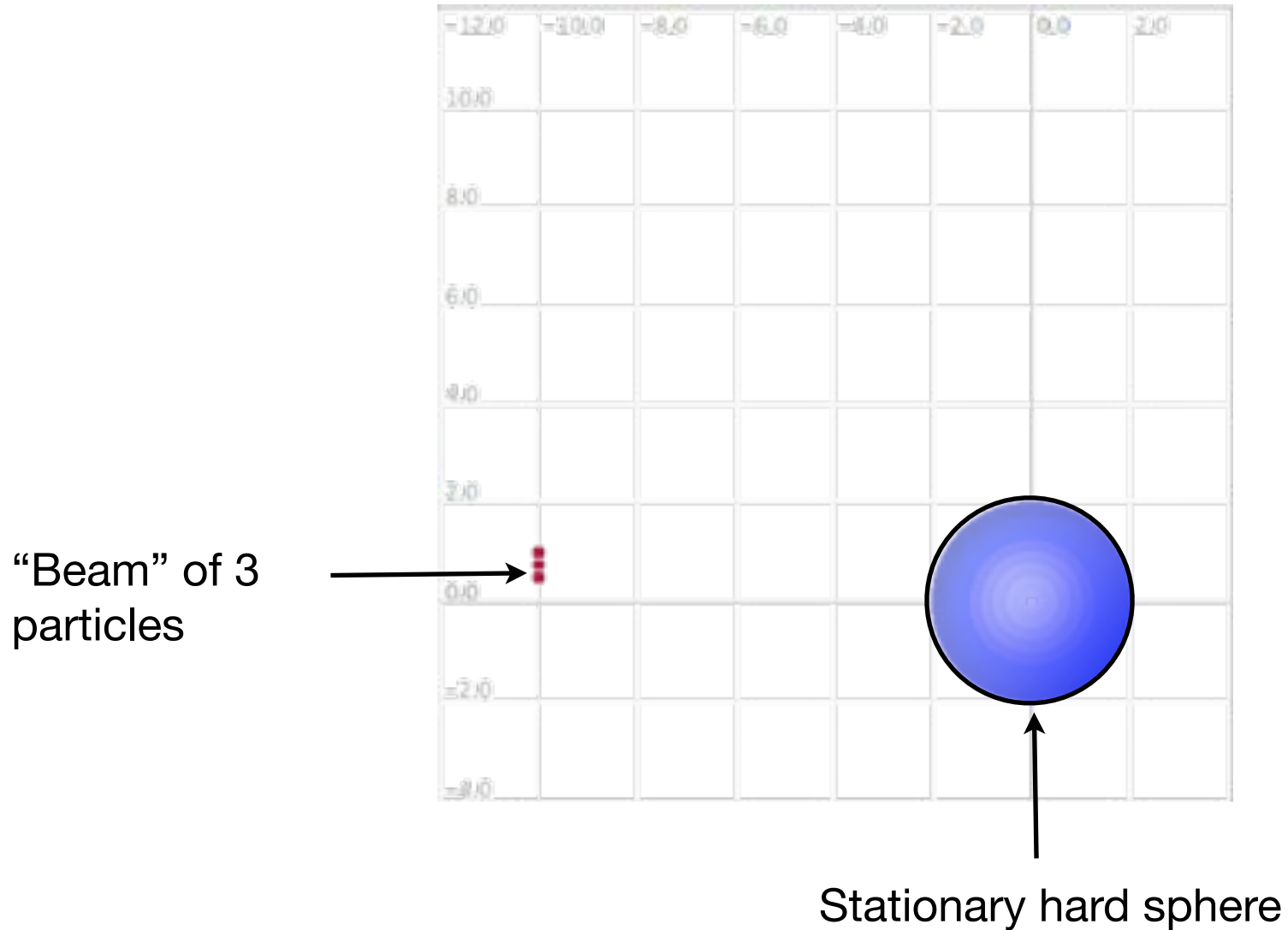
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MAJORITY OF
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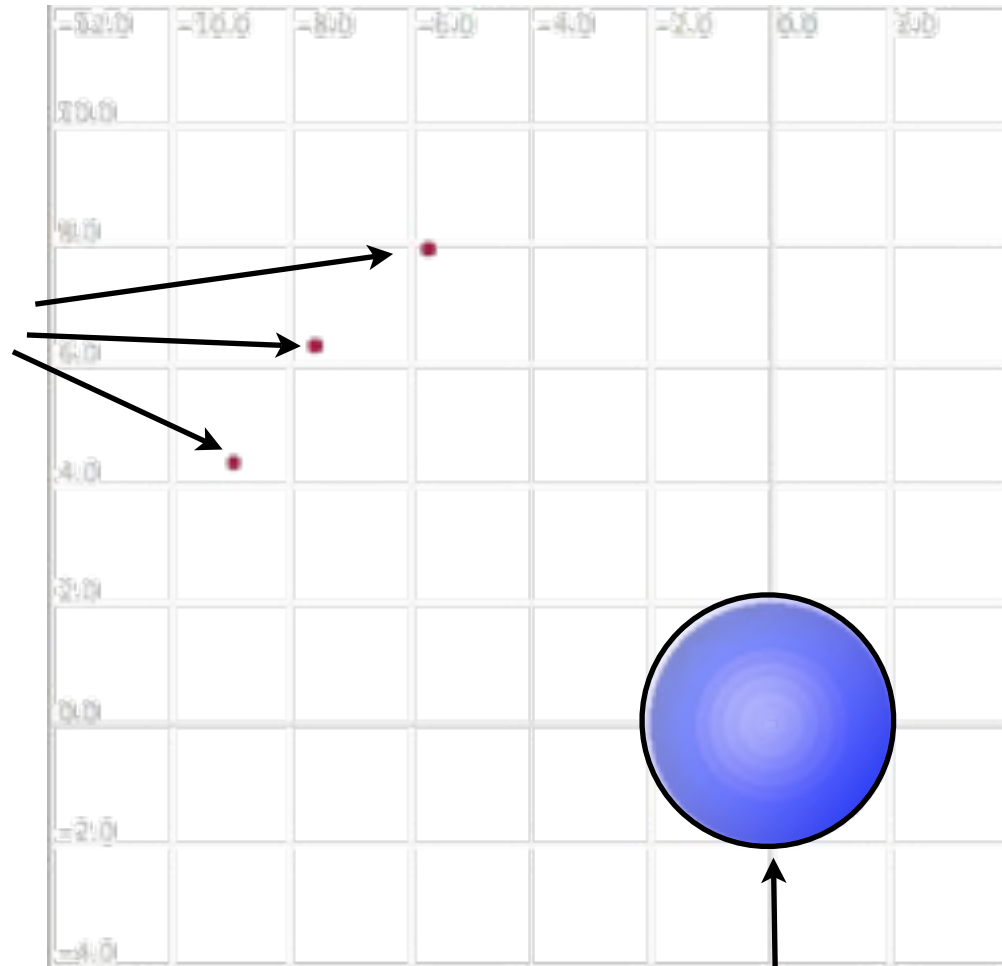
Classical scattering

Before



After

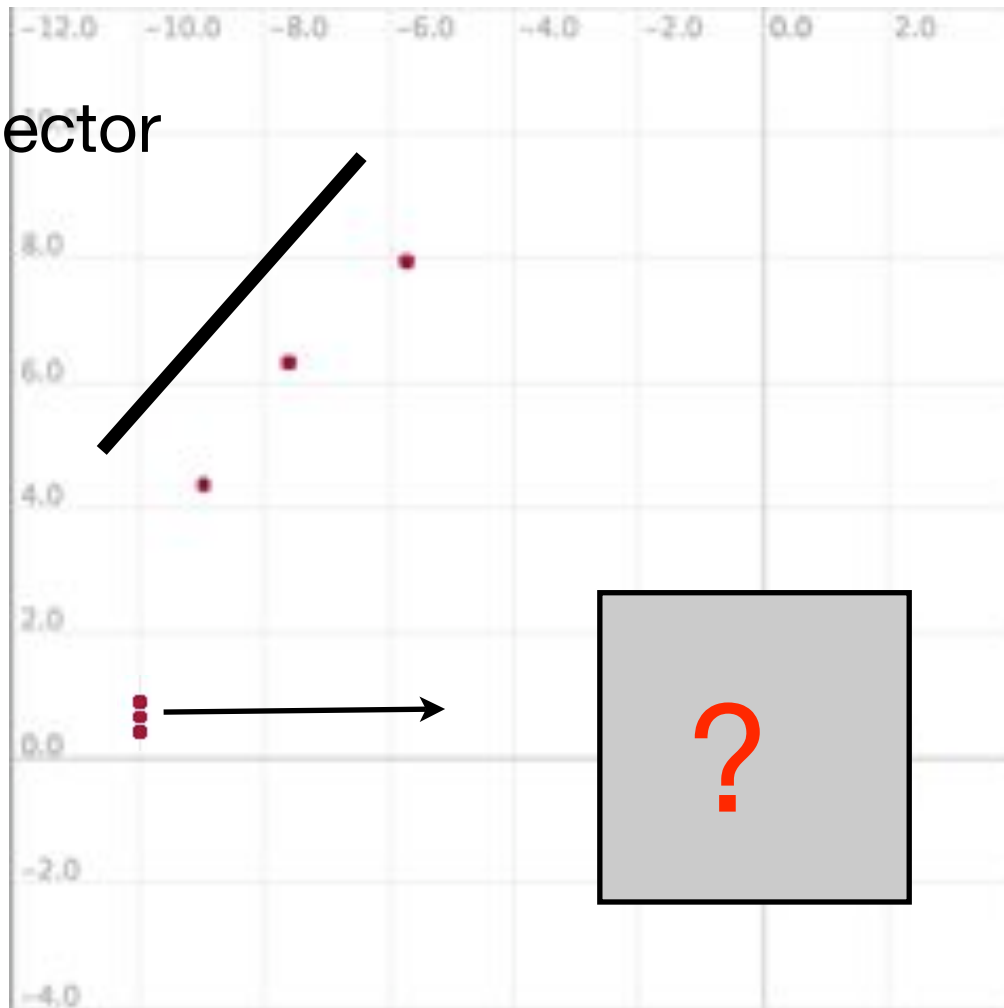
Scattered particles



Stationary hard sphere

Scattering experiment

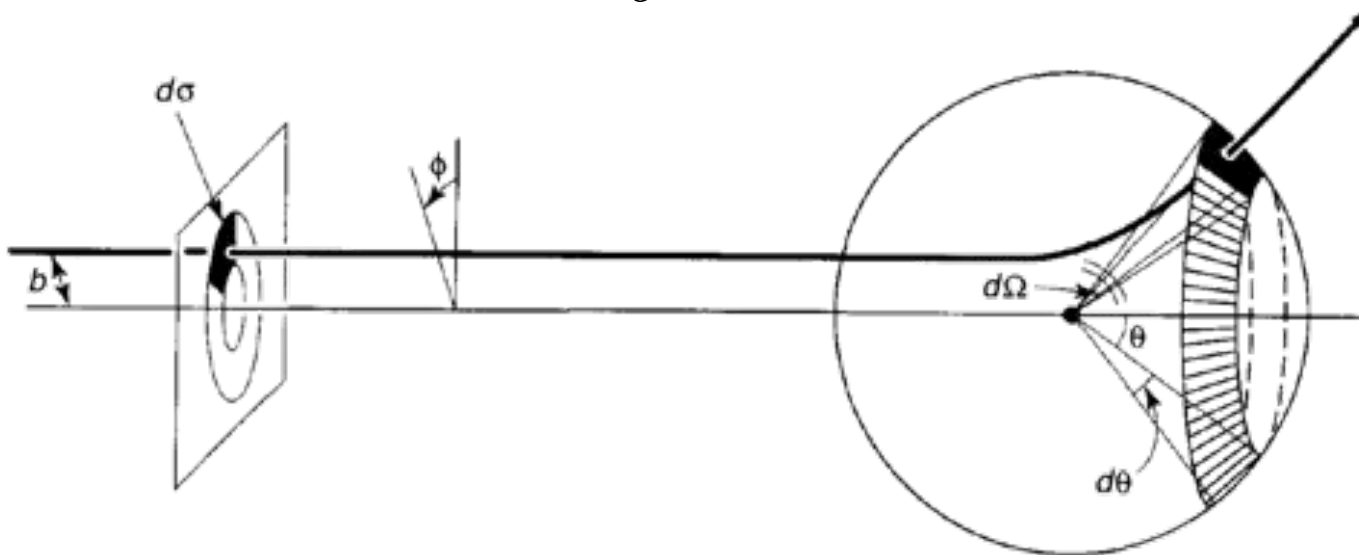
Detector



- The relation between the incoming beam and the detected particles tells us something about the properties (shape) of the target

The cross-section

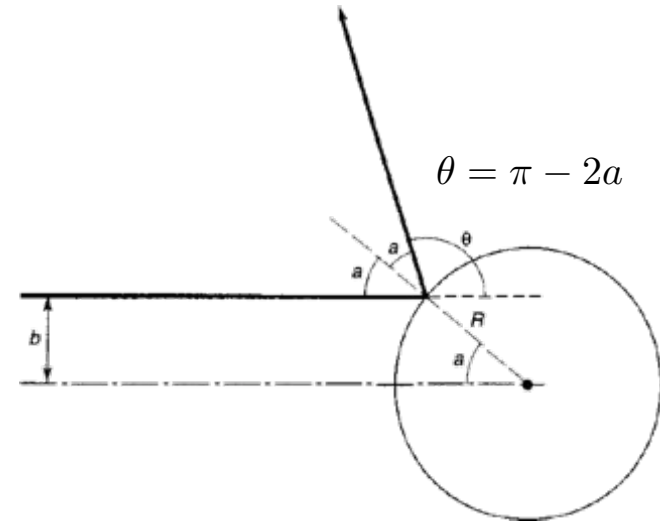
- Particles are incident within an patch of area $d\sigma$ with impact parameter b
- The particles scattering into a solid angle $d\Omega$
- The differential cross-section is defined as $d\sigma/d\Omega$
- From which the total cross-section σ can be obtained



The cross-section: hard-sphere

- Lets calculate the cross-section for the hard sphere

$$\begin{aligned} b &= R \sin a \\ &= R \sin \left(\frac{\pi}{2} - \frac{\theta}{2} \right) = R \cos \left(\frac{\theta}{2} \right) \end{aligned}$$



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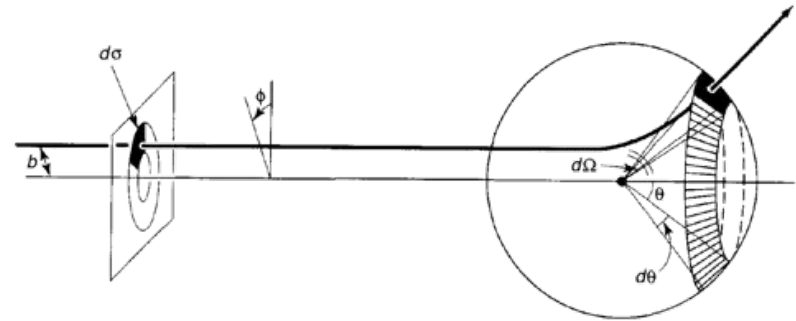
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$$\begin{aligned} b &= R \sin a \\ &= R \sin \left(\frac{\pi}{2} - \frac{\theta}{2} \right) = R \cos \left(\frac{\theta}{2} \right) \end{aligned}$$

$$d\sigma = b |db| d\phi$$

$$d\Omega = \sin \theta d\theta d\phi$$



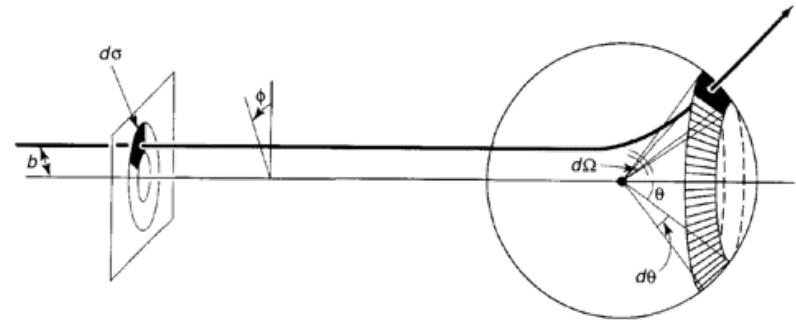
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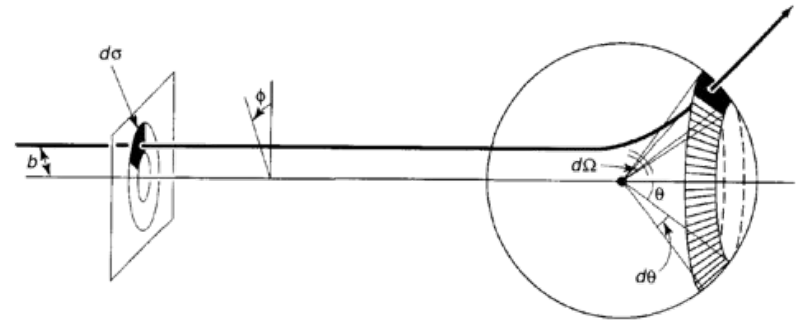
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$$\frac{d\sigma}{d\Omega} = \frac{R \cos(\theta/2)}{\sin \theta} \left| -\frac{1}{2} R \sin \left(\frac{\theta}{2} \right) \right| = \frac{R^2}{4}$$

$$\sin x \cos x = \frac{1}{2} \sin 2x$$



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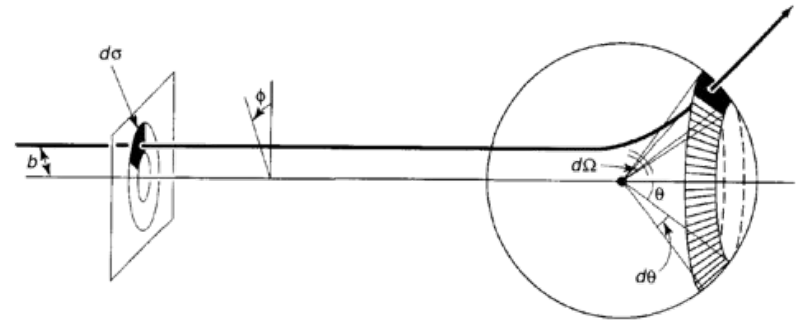
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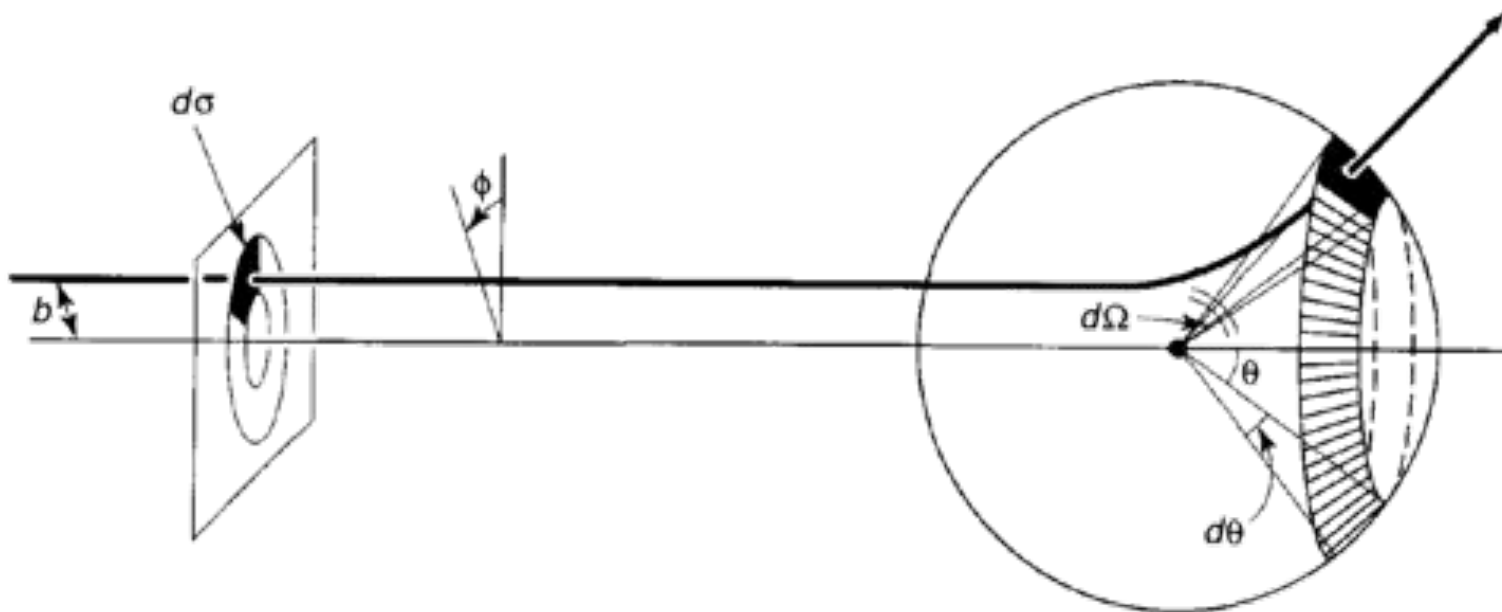
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$$\sigma = \int \frac{d\sigma}{d\Omega} d\Omega = \frac{R^2}{4} \int d\Omega = \pi R^2$$

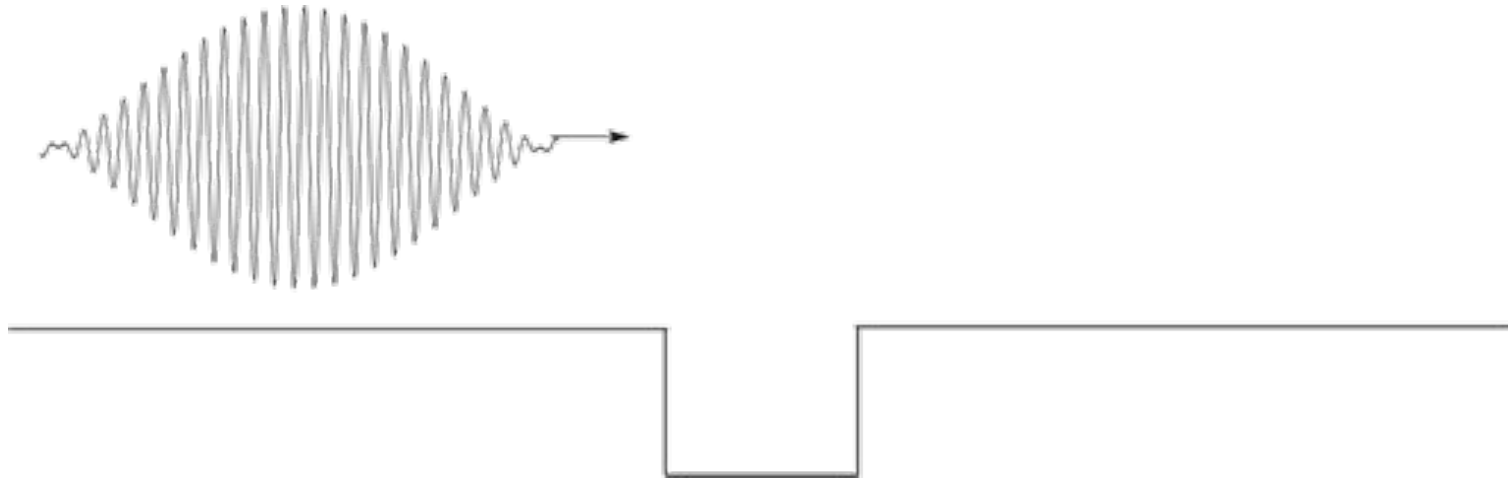
- The cross-sectional area of a sphere with radius R is:

$$\sigma = \int \frac{d\sigma}{d\Omega} d\Omega = \frac{R^2}{4} \int d\Omega = \pi R^2$$

- The meaning of the cross-section is that particles incident within this area hit the target, others miss it

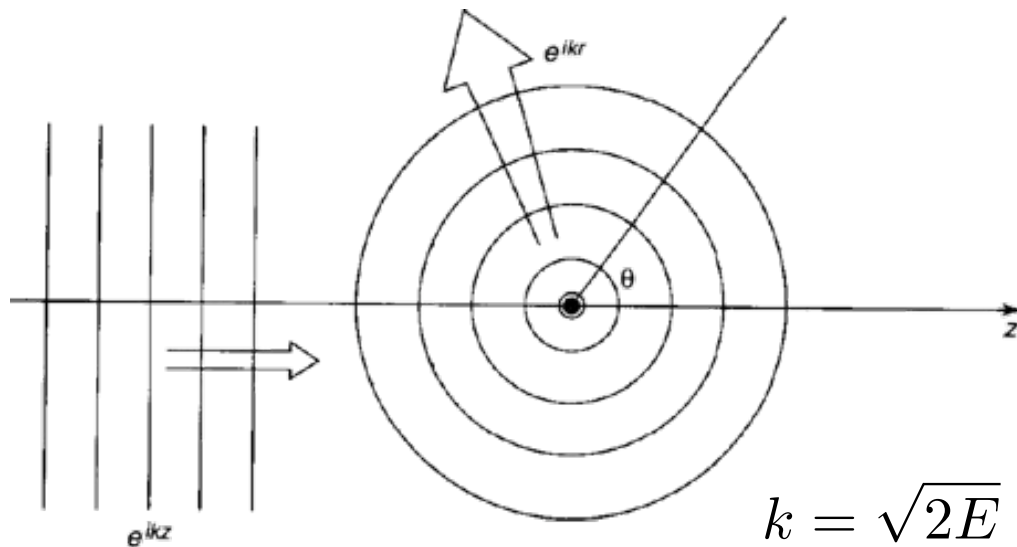


Quantum scattering theory



- Time dependent picture: wave packet comes in from the left, interacts with potential, and then moves away to the left (reflected) and to the right (transmitted)

- In the majority of experimentally realizable situations, the wave packets are so wide that treating them as infinitely wide, i.e., as plane waves, is an appropriate approximation.
- Our target is hit by an incoming plane wave (z-direction) and this produces an outgoing spherical wave after the scattering



Atomic units

We are looking for solutions of the SE of the following form:

$$\psi(r, \theta) \approx A \left[e^{ikz} + f(\theta) \frac{e^{ikr}}{r} \right]$$

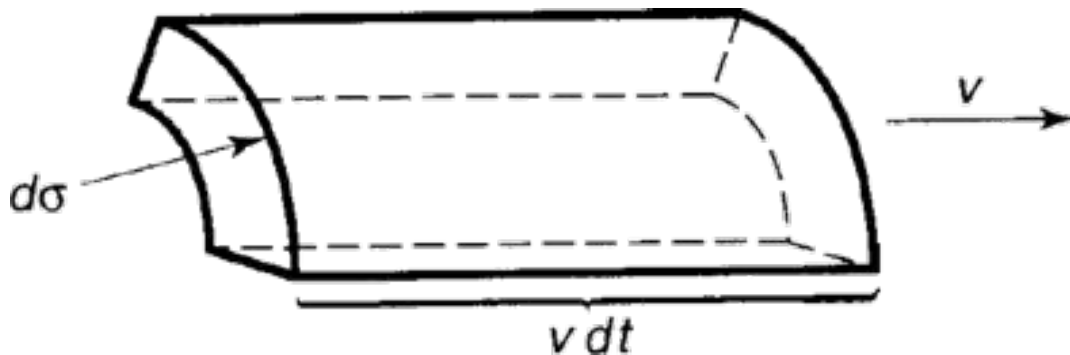
Quantum scattering cross-section

- The probability that the incident particle with speed v travels through the area $d\sigma$ in time dt is

$$dP = |\psi_{\text{inc}}|^2 dV = |A|^2 (v dt) d\sigma$$

- This must be equal to the probability that the particle emerges into the solid angle $d\Omega$

$$dP = |\psi_{\text{scatt}}|^2 dV = \frac{|A|^2 |f(\theta)|^2}{r^2} (v dt) r^2 d\Omega$$



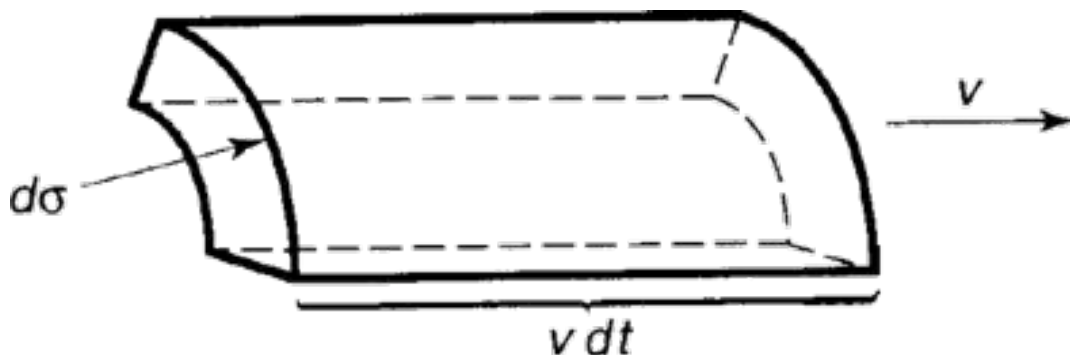
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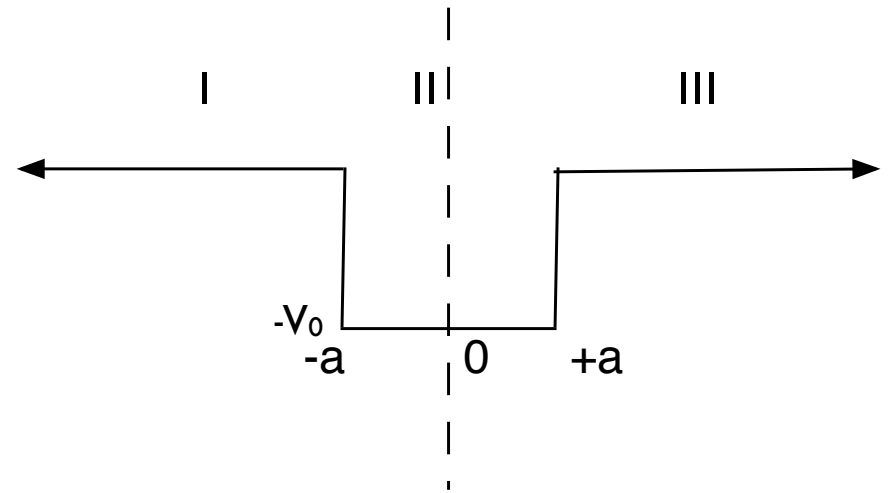
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$$dP = |\psi_{\text{scatt}}|^2 dV = \frac{|A|^2 |f(\theta)|^2}{r^2} (v dt) r^2 d\Omega \quad \Rightarrow \quad \frac{d\sigma}{d\Omega} = |f(\theta)|^2$$



Scattering from a potential in 1D: Reflection and transmission

- Particle coming in from the left, scattering from the potential, and leaving either to the right (transmission) or to the left (reflection)



$$\Psi_I = Ae^{ikx} + Be^{-ikx}$$

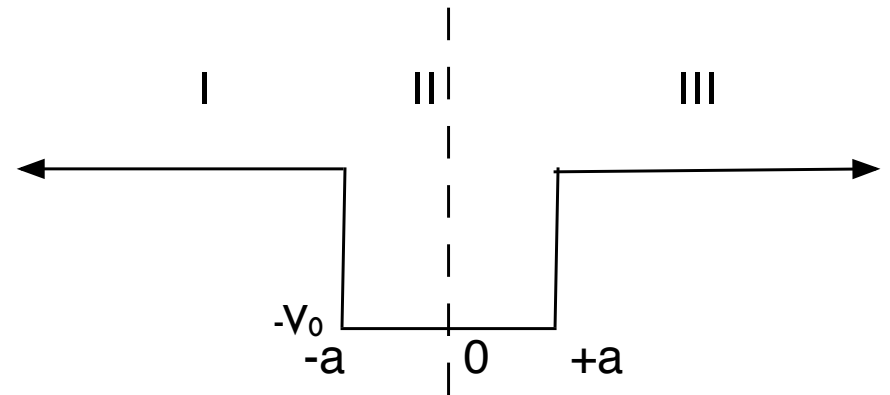
$$\Psi_{II} = C \sin(k'x) + D \cos(k'x)$$

$$\Psi_{III} = Fe^{ikx}$$

$$\begin{aligned} d\Psi^2/dx^2 &= -k^2\Psi & k &= \sqrt{2E} \\ d\Psi^2/dx^2 &= -k'^2\Psi & k' &= \sqrt{2(E + V_0)} \end{aligned}$$

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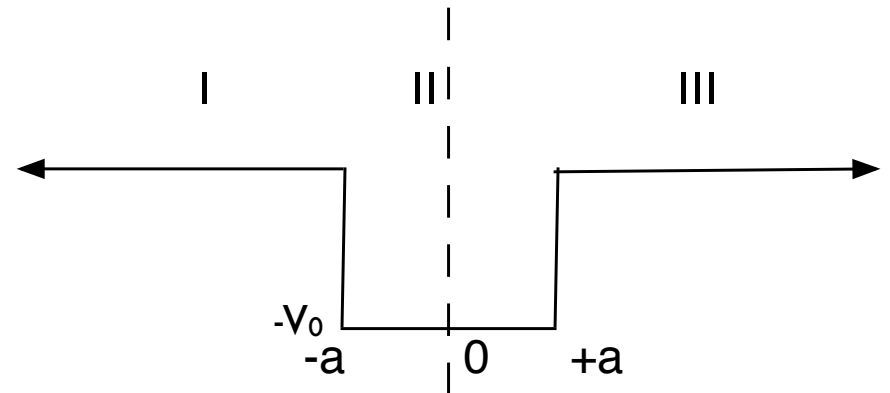
$$R = \frac{|\Psi_{\text{reflected}}|^2}{|\Psi_{\text{incident}}|^2} = \frac{B^* B}{A^* A}$$

$$T = \frac{|\Psi_{\text{transmitted}}|^2}{|\Psi_{\text{incident}}|^2} = \frac{F^* F}{A^* A}$$

$\frac{d\Psi^2}{dx^2} = -k^2\Psi \quad k = \sqrt{2E}$
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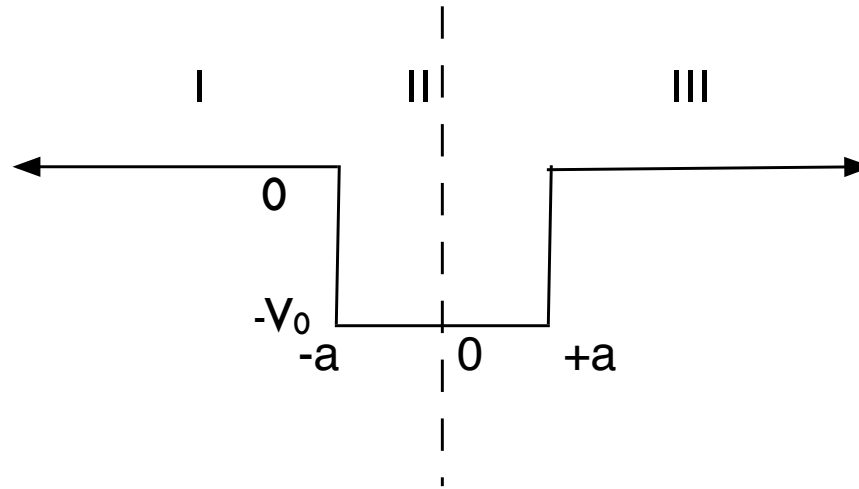
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Match functions
and derivatives at
 $x=a$ and $x=-a$



$$x = -a$$

$$\Psi(x) \rightarrow Ae^{-ika} + Be^{ika} = -C \sin(k'a) + D \cos(k'a)$$

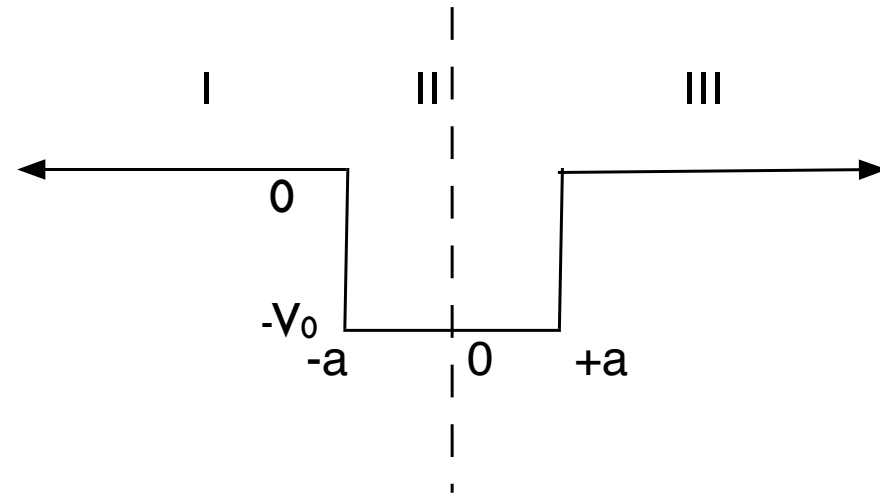
$$\frac{d\Psi}{dx} \rightarrow ik[Ae^{-ika} - Be^{ika}] = k'[C \cos(k'a) + D \sin(k'a)]$$

$$x = a$$

$$\Psi(x) \rightarrow C \sin(k'a) + D \cos(k'a) = Fe^{ika}$$

$$\frac{d\Psi}{dx} \rightarrow k'[C \cos(k'a) - D \sin(k'a)] = ikFe^{ika}$$

Use 2 equations to eliminate C and D and use the remaining 2 to solve for B and F



$$B = i \frac{\sin(2k'a)}{2kk'} (k'^2 - k^2) F$$

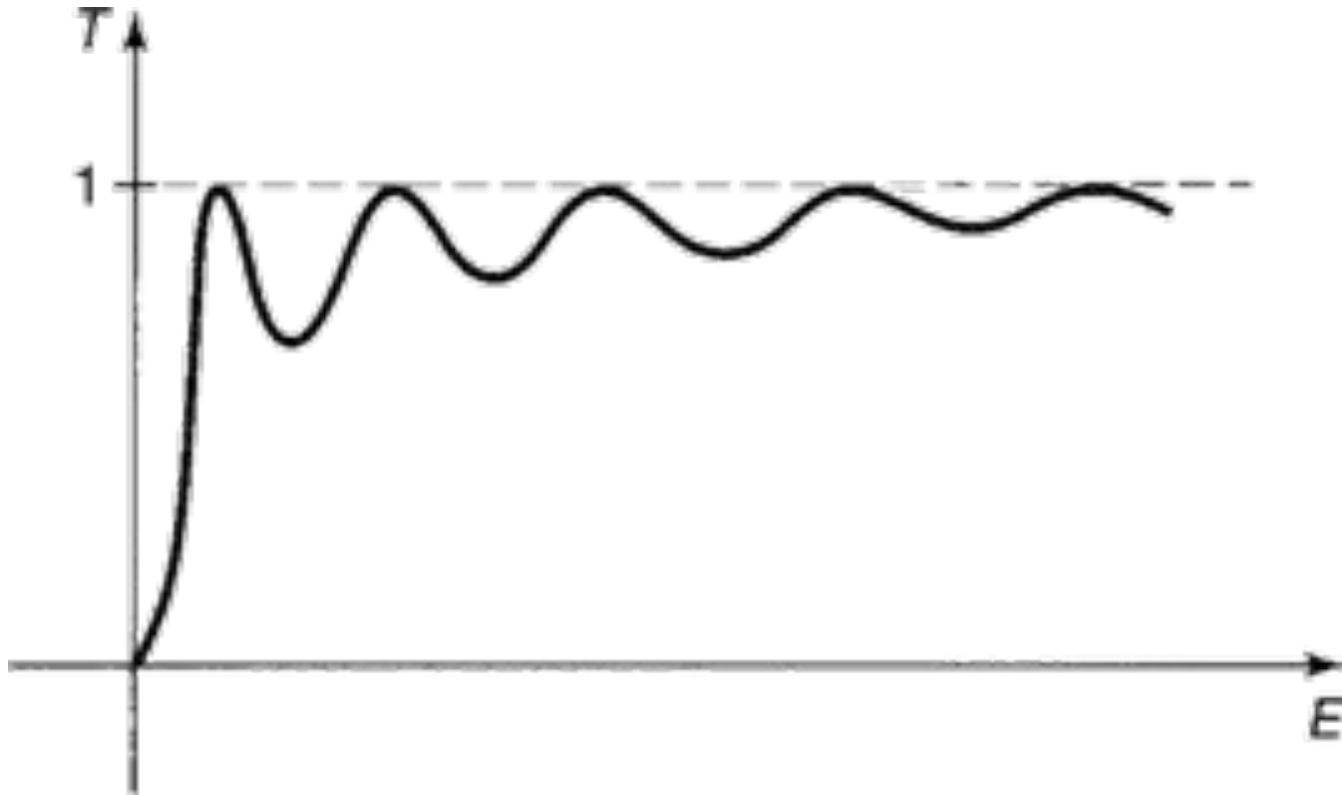
$$F = \frac{e^{-2ika} A}{\cos(2k'a) - i \frac{\sin(2k'a)}{2kk'} (k^2 + k'^2)}$$

$$T = \frac{F^* F}{A^* A} = \left[1 + \frac{V_0^2}{4E(E + V_0)} \sin^2 \left(2a \sqrt{2(E + V_0)} \right) \right]^{-1}$$

The sum of reflection and transmission is 1

$$R = 1 - T$$

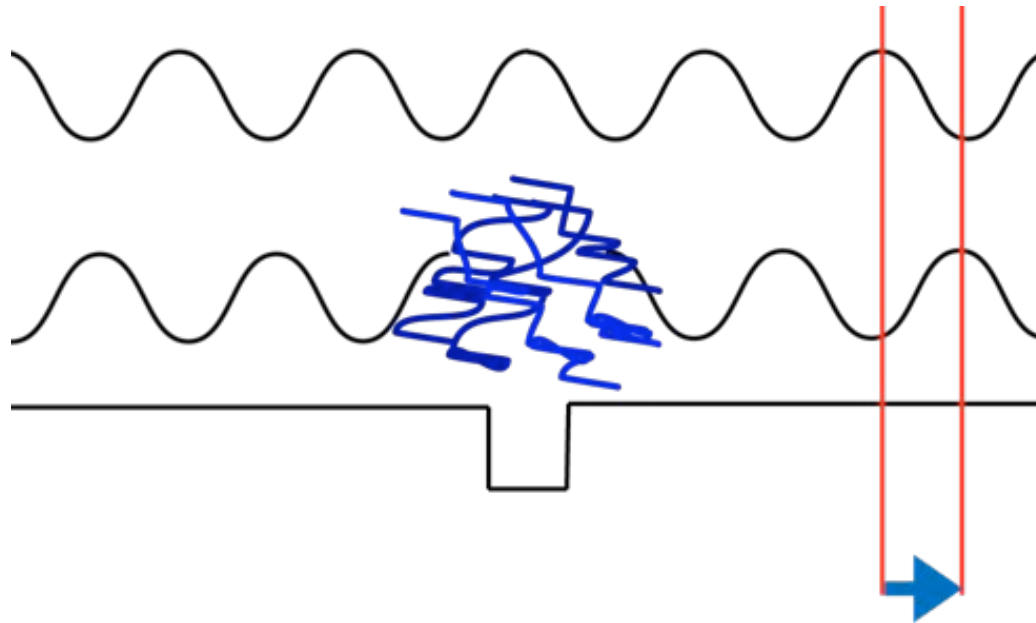
Transmission



$$T = \frac{F^* F}{A^* A} = \left[1 + \frac{V_0^2}{4E(E + V_0)} \sin^2 \left(2a\sqrt{2(E + V_0)} \right) \right]^{-1}$$

$$\left(2a\sqrt{2(E + V_0)} \right) = n\pi$$

Scattering from a potential in 1D: Phase shift analysis



- The phase shift is determined by the shape and strength of the potential
- The phase shift is obtained by studying the asymptotic region
- We need to know the form of the wave function in the asymptotic region

- Any analytic function in 1D can be written as the sum of even and odd functions

$$g(x) = g_e(x) + g_o(x)$$

$$r = |x| \quad g_o(-x) = -g_o(x) \quad \epsilon = \frac{x}{|x|}$$

- Any analytic function in 1D can be written as the sum of even and odd functions

$$g(x) = g_e(x) + g_o(x) = g_e(r) + \epsilon g_o(r)$$

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We can also write the function as the sum of two “partial waves”

$$g(x) = \sum_{l=0,1} \epsilon^l g_l(r)$$

The scattering wave function can also be written in terms of partial waves

$$\Psi_{\text{scatt}} = e^{ikx} + f e^{ik|x|}$$



$$f(\epsilon) = \sum_{l=0,1} \epsilon^l f_l$$

$$r = |x|$$

The scattering wave function can also be written in terms of partial waves

$$\begin{aligned}\Psi_{\text{scatt}} &= e^{ikx} + f e^{ik|x|} \\ &= \cos(kx) + i \sin(kx) + f_0 e^{ik|x|} + \epsilon f_1 e^{ik|x|}\end{aligned}$$



$$f(\epsilon) = \sum_{l=0,1} \epsilon^l f_l$$

$$r = |x|$$

The scattering wave function can also be written in terms of partial waves

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$$f(\epsilon) = \sum_{l=0,1} \epsilon^l f_l$$

$$r = |x|$$

- We can write the generalized wave function in the asymptotic region as a linear combination of odd and even functions, i.e. sine and cosine functions

$$\Psi_{\text{gen}} = \sum_{l=0,1} \epsilon^l A_l \cos(kr + \frac{1}{2}l\pi + \delta_l)$$

$$\cos(kr + \frac{\pi}{2}) = -\sin(kr)$$

- The δ_l are the odd and even phase shifts
- We can obtain f and A by matching the scattering and generalized wave functions

$$\Psi_{\text{scatt}} = \cos(kr) + f_0 e^{ikr} + \epsilon(i \sin(kr) + f_1 e^{ikr})$$

$$\Psi_{\text{gen}} = \sum_{l=0,1} \epsilon^l A_l \cos(kr + \frac{1}{2}l\pi + \delta_l)$$

Wave 0:

$$A_0 \cos(kr + \delta_0) = \cos(kr) + f_0 e^{ikr}$$

$$\frac{1}{2} A_0 e^{ikr} e^{i\delta_0} + \frac{1}{2} A_0 e^{-ikr} e^{-i\delta_0} = \frac{1}{2} e^{ikr} + \frac{1}{2} e^{-ikr} + f_0 e^{ikr}$$

Matching incoming (exp(-ikr)) and outgoing (exp(+ikr)) waves:

$$\frac{1}{2} A_0 e^{-ikr} e^{-i\delta_0} = \frac{1}{2} e^{-ikr} \longrightarrow A_0 = e^{i\delta_0}$$

$$\frac{1}{2} A_0 e^{ikr} e^{i\delta_0} = \left(\frac{1}{2} + f_0\right) e^{ikr} \longrightarrow f_0 = \frac{1}{2} (e^{2i\delta_0} - 1)$$

$$\Psi_{\text{scatt}} = \cos(kr) + f_0 e^{ikr} + \epsilon(i \sin(kr) + f_1 e^{ikr})$$

$$\Psi_{\text{gen}} = \sum_{l=0,1} \epsilon^l A_l \cos(kr + \frac{1}{2}l\pi + \delta_l)$$

- Wave 0: $f_0 = \frac{1}{2}(e^{2i\delta_0} - 1)$

- Wave 1: $-\epsilon A_1 \sin(kr + \delta_1) = \epsilon i \sin(kr) + \epsilon f_1 e^{ikr}$

- Same analysis as for wave 0 gives:

$$A_1 = -i e^{i\delta_1} \quad f_1 = \frac{1}{2}(e^{2i\delta_1} - 1)$$

$$A_l = (-i)^l e^{i\delta_l} \quad f_l = \frac{1}{2}(e^{2i\delta_l} - 1) \\ = i e^{i\delta_l} \sin(\delta_l)$$

$$f(\epsilon) = \sum_{l=0,1} i \epsilon^l e^{i\delta_l} \sin(\delta_l)$$

Cross section from phase shifts

$$\sigma = \sum_{\epsilon=\pm 1} |f(\epsilon)|^2$$

$$f(\epsilon) = \sum_{l=0,1} i\epsilon^l e^{i\delta_l} \sin(\delta_l)$$

$$\begin{aligned} |f(-1)|^2 &= |ie^{i\delta_0} \sin \delta_0 - ie^{i\delta_1} \sin \delta_1|^2 \\ &= \sin^2 \delta_0 + \sin^2 \delta_1 + 2e^{i(\delta_0 - \delta_1)} \sin \delta_0 \sin \delta_1 \end{aligned}$$

$$\begin{aligned} |f(+1)|^2 &= |ie^{i\delta_0} \sin \delta_0 + ie^{i\delta_1} \sin \delta_1|^2 \\ &= \sin^2 \delta_0 + \sin^2 \delta_1 - 2e^{i(\delta_0 - \delta_1)} \sin \delta_0 \sin \delta_1 \end{aligned}$$

$$\sigma = 2 \sum_{l=0,1} \sin^2 \delta_l$$

Phase shifts?

$$\Psi_{\text{gen}} = \sum_{l=0,1} \epsilon^l A_l \cos(kr + \frac{1}{2}l\pi + \delta_l)$$

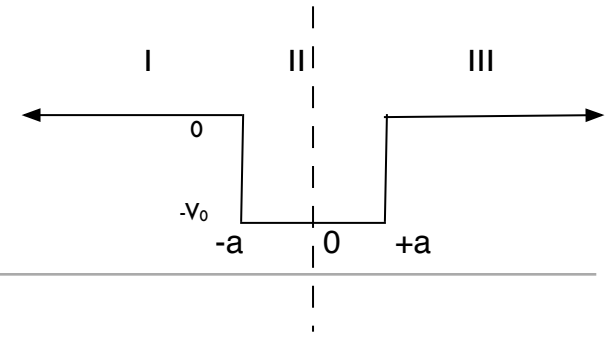
$$A_l = (-i)^l e^{i\delta_l}$$

$$\Psi_{\text{gen}} = \sum_{l=0,1} \epsilon^l (-i)^l e^{i\delta_l} \frac{1}{2} \left[e^{i(kr+l\pi/2+\delta_l)} + e^{-i(kr+l\pi/2+\delta_l)} \right]$$

$$= \sum_{l=0,1} \epsilon^l (-i)^l \frac{1}{2} \left[e^{i(kr+l\pi/2+2\delta_l)} + e^{-i(kr+l\pi/2)} \right]$$

- There is a relative phase difference of $2\delta_l$ of the outgoing wave compared to the incoming wave

Phase shifts for the square well



- Regions 1 and 3:

$$\Psi_{\text{gen}} = \sum_{l=0,1} \epsilon^l A_l \cos(kr + \frac{1}{2}l\pi + \delta_l)$$

- Region 2:

$$\Psi_{\text{int}} = \sum_{l=0,1} \epsilon^l B_l \cos(k'r + \frac{1}{2}l\pi)$$

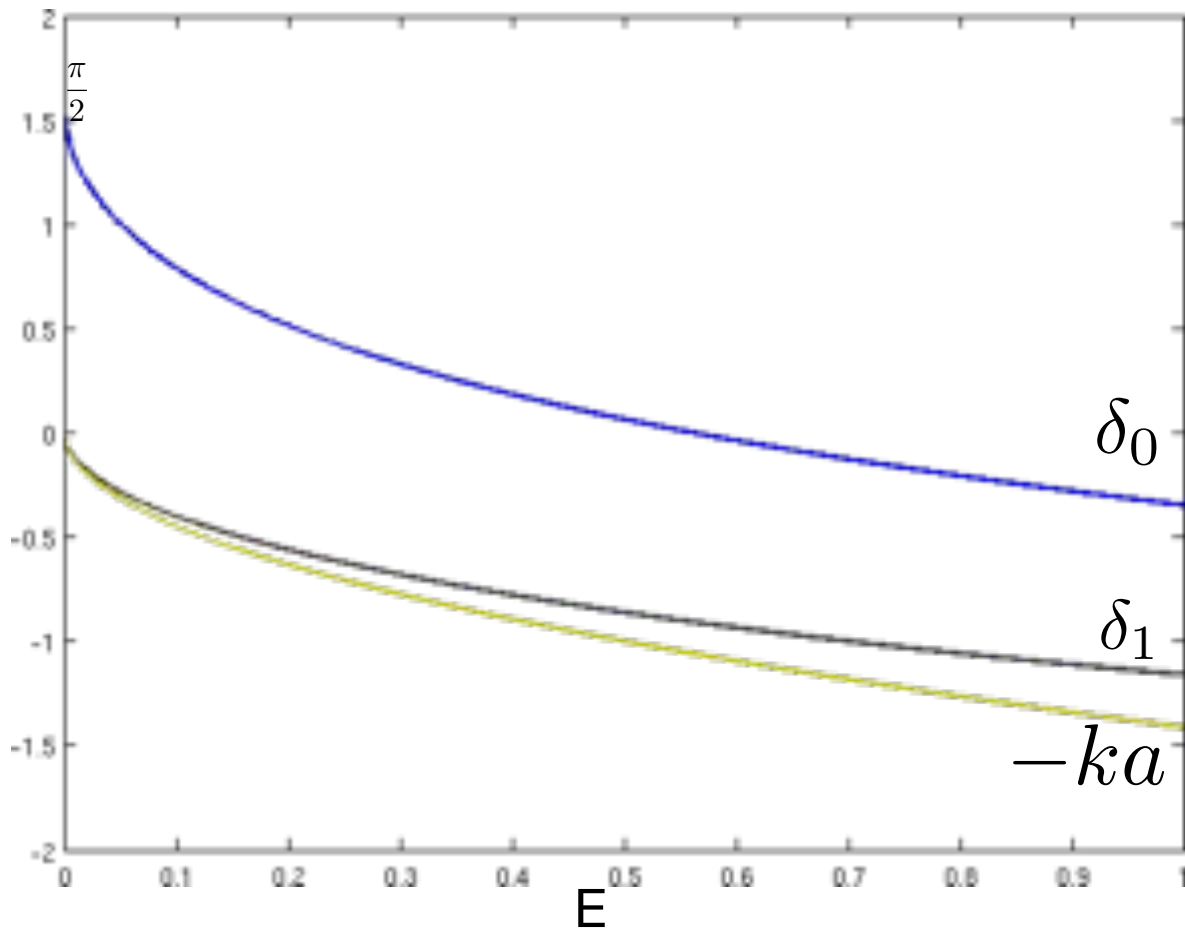
- We again match the odd and even wave function and its derivative at the boundaries between I, II and II, III

- Matching odd functions ($l=0$):

$$\begin{aligned}A_0 \cos(ka + \delta_0) &= B_0 \cos k'a \\ -kA_0 \sin(ka + \delta_0) &= -k'B_0 \sin k'a \\ k \tan(ka + \delta_0) &= k' \tan(k'a)\end{aligned}$$

- Matching even functions ($l=1$):

$$\begin{aligned}A_1 \sin(ka + \delta_1) &= B_1 \sin k'a \\ kA_1 \cos(ka + \delta_1) &= k'B_1 \cos k'a \\ k' \tan(ka + \delta_1) &= k \tan(k'a)\end{aligned}$$



- At low energies δ_0 dominates

$$\delta_0 = \tan^{-1} \left(\frac{k'}{k} \tan k'a \right) - ka$$

$$\delta_1 = \tan^{-1} \left(\frac{k}{k'} \tan k'a \right) - ka$$

Comparing with our previous results

- We found maximum transmission at: $\left(2a\sqrt{2(E + V_0)}\right) = n\pi$
- The cross section for back-scattering (to the left) is:

$$d\sigma = |f(-1)|^2 = \sin^2(\delta_0 - \delta_1)$$

- Maximum transmission when: $\delta_0 - \delta_1 = n\pi$
- This condition also applies to $\tan(\delta_0 - \delta_1)$:

$$\tan(\delta_0 - \delta_1) = \frac{\tan(ka + \delta_0) - \tan(ka + \delta_1)}{1 + \tan(ka + \delta_0)\tan(ka + \delta_1)} = \frac{1}{2} \left(\frac{k'}{k} - \frac{k}{k'} \right) \sin 2k'a$$

$$k' = \sqrt{2(E + V_0)} = \frac{n\pi}{2a}$$

Comparing with our previous results

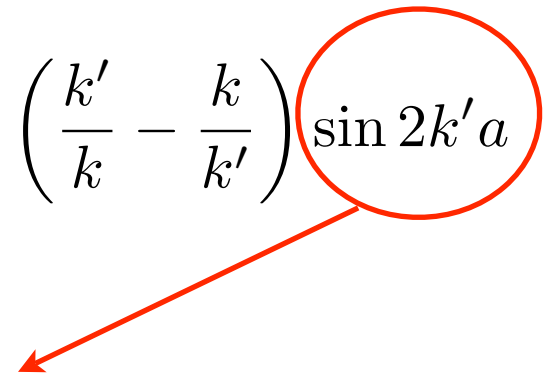
- We found maximum transmission at: $\left(2a\sqrt{2(E + V_0)}\right) = n\pi$
- The cross section for back-scattering (to the left) is:

$$d\sigma = |f(-1)|^2 = \sin^2(\delta_0 - \delta_1)$$

- Maximum transmission when: $\delta_0 - \delta_1 = n\pi$
- This condition also applies to $\tan(\delta_0 - \delta_1)$:

$$\tan(\delta_0 - \delta_1) = \frac{\tan(ka + \delta_0) - \tan(ka + \delta_1)}{1 + \tan(ka + \delta_0) \tan(ka + \delta_1)} = \frac{1}{2} \left(\frac{k'}{k} - \frac{k}{k'} \right) \sin 2k'a$$

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1D Scattering

- Scattering information can be obtained from:
 - Reflection and transmission coefficients R and T -> 1D only
 - Cross sections -> also 3D
 - Phase shifts -> also 3D

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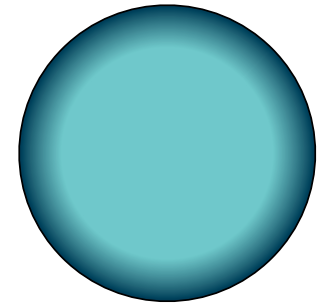
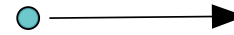
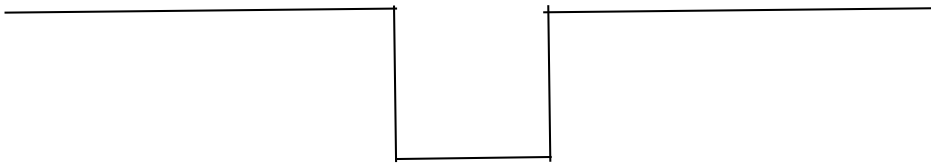
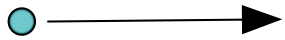
- Cross sections -> also 3D

- Phase shifts -> also 3D



From the phase shifts we can obtain the cross section

1D scattering -> 3D scattering



- In 1D scattering we expanded the wave functions in odd and even partial waves, which can be treated independently
- For a spherical potential we can also expand functions in partial waves, these partial waves will be based on the spherical harmonics

Scattering from a spherical potential

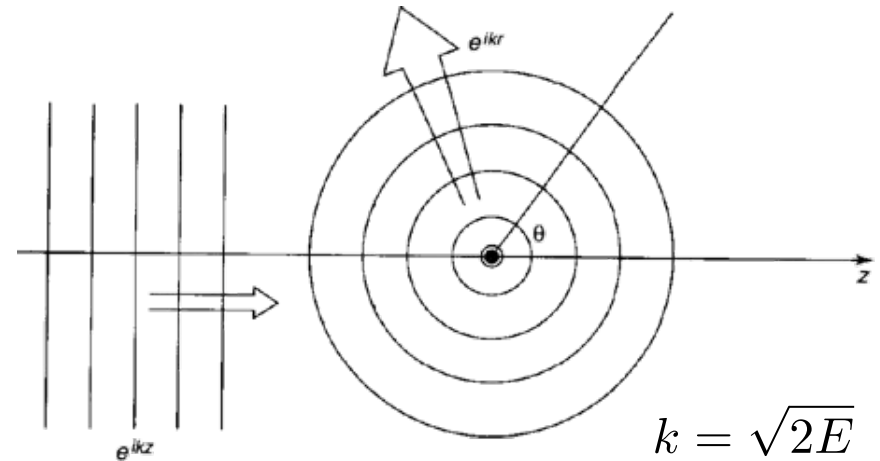
$$\psi(r) = e^{ikz} + f(\theta, \phi) \frac{e^{ikr}}{r} \quad r \rightarrow \infty$$

- Solutions of SE for a general spherical potential:

$$\psi(r, \theta, \phi) = R(r) Y_l^m(\theta, \phi)$$

$$\left[-\frac{1}{2} \frac{d^2}{dr^2} + V(r) + \frac{l(l+1)}{2r^2} \right] u(r) = E u(r) \quad u(r) = r R(r)$$

To describe scattering we need the continuum solutions to this equation



No centrifugal potential or $l=0$

- If we are very far away from the potential, the centrifugal potential has almost no influence and $V(r)=0$:

$$\frac{d^2 u(r)}{dr^2} + k^2 u(r) = 0$$

Also valid for a short-ranged potential with $l=0$ when $r > R$

- Two linear independent solutions: $u_s(r) = \sin kr$ $u_c(r) = \cos kr$
- In the asymptotic region we can write the general solution as

$$u(r) = Au_s(r) + Bu_c(r)$$

- A and B are obtained from matching inner and outer solutions for a specific potential $V(r)$

- We can rewrite this solution in the following way

$$\begin{aligned}u(r) &= Au_s(r) + Bu_c(r) \\&= \sqrt{A^2 + B^2} \left[\frac{A}{\sqrt{A^2 + B^2}} u_s(r) + \frac{B}{\sqrt{A^2 + B^2}} u_c(r) \right] \\&= \sqrt{A^2 + B^2} [\cos(\delta) u_s(r) + \sin(\delta) u_c(r)]\end{aligned}$$

- Plugging in u_s and u_c :

$$\begin{aligned}u(r) &= \sqrt{A^2 + B^2} [\cos(\delta) \sin(kr) + \sin(\delta) \cos(kr)] \\&= \sqrt{A^2 + B^2} \sin(kr + \delta)\end{aligned}$$

$$\tan \delta = \frac{\sin \delta}{\cos \delta} = \frac{B}{A}$$

- The asymptotic solution is again defined by a phase shift compared to the “free wave” solution u_s
- Note that we only looked at the stationary solution of the SE in the asymptotic region to obtain the phase shift!

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Spherical potential well: $l=0$

- In the inner region the wave function must vanish at $r=0$

$$\begin{aligned}u(r) &= \sin(k'r) & r \leq a \\ &= A \sin(kr + \delta) & r > a\end{aligned}$$

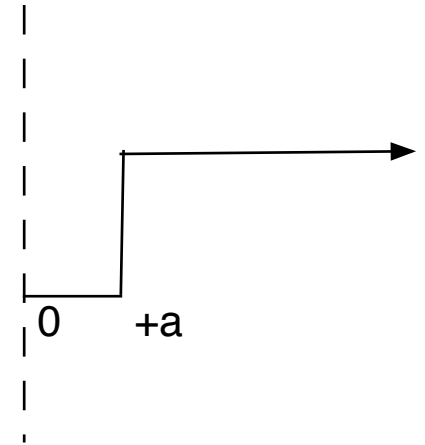
- Matching the functions and derivatives at $r=a$:

$$Ak \cos(ka + \delta) = k' \cos(k'a)$$

$$A \sin(ka + \delta) = \sin(k'a)$$

- Dividing the two expressions gives:

$$\tan(ka + \delta) = \frac{k}{k'} \tan(k'a)$$



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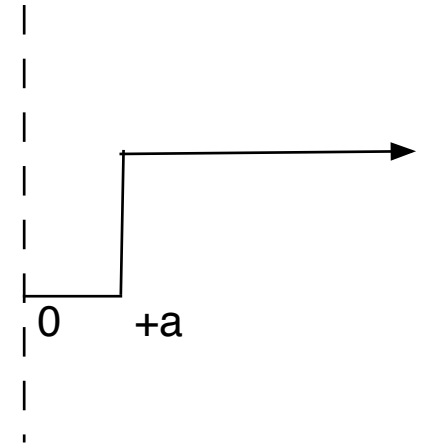
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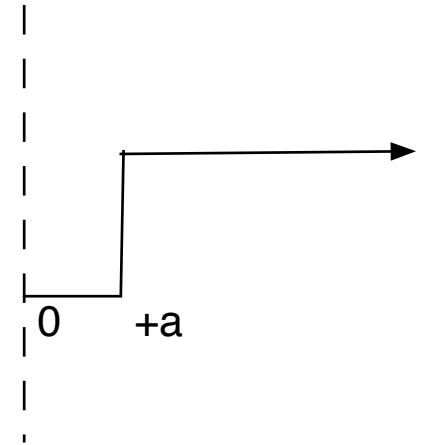
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$$\delta = \tan^{-1} \left[\frac{k}{k'} \tan(k'a) \right] - ka$$



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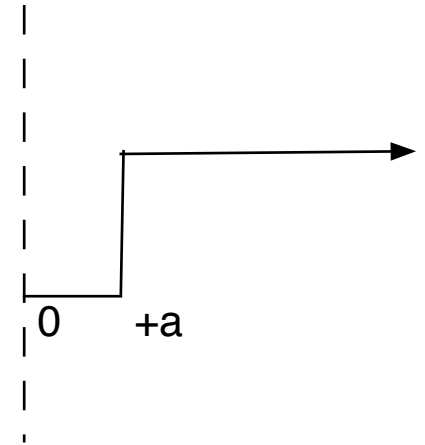
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$$\delta = \tan^{-1} \left[\frac{k}{k'} \tan(k'a) \right] - ka$$

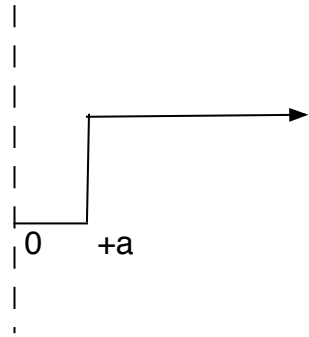
$$\delta_0 = \tan^{-1} \left(\frac{k'}{k} \tan k'a \right) - ka$$

$$\delta_1 = \tan^{-1} \left(\frac{k}{k'} \tan k'a \right) - ka$$

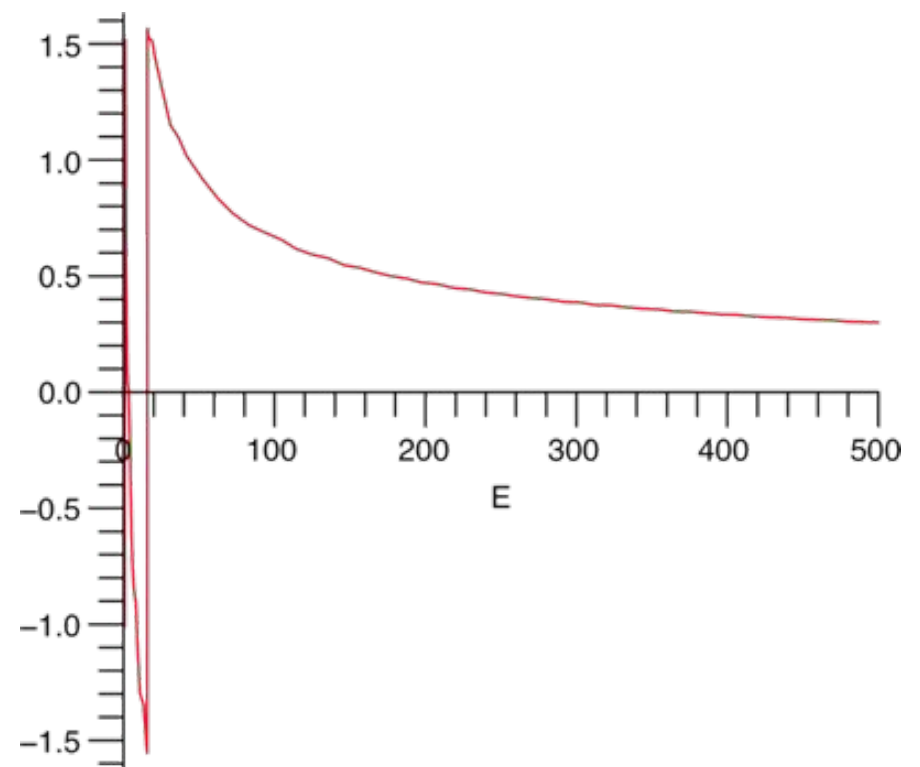
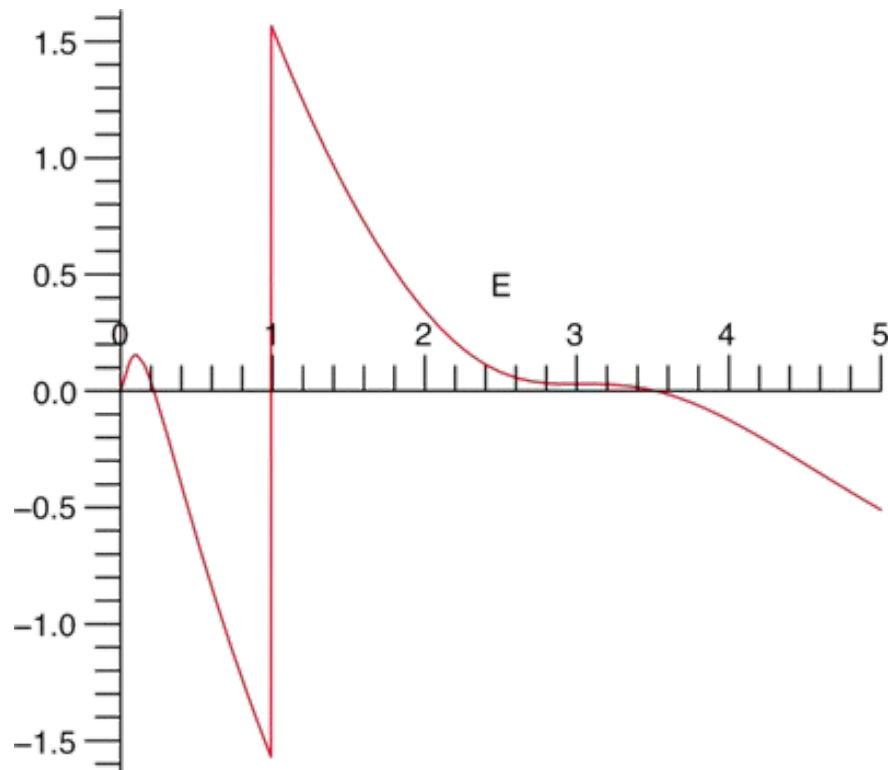
Odd solution is zero at $r=0$



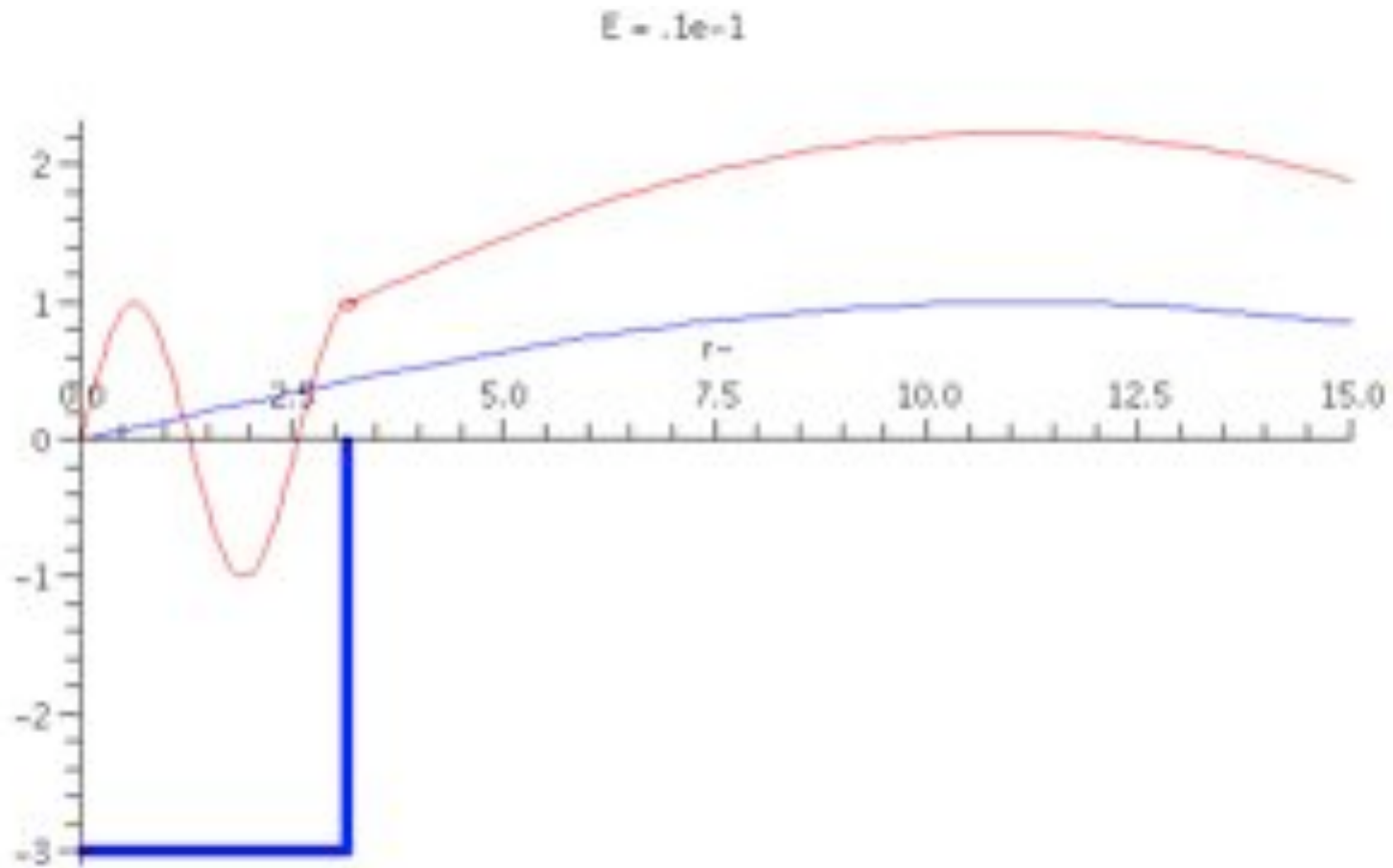
Phase shift: $a=3$ $V_0=3$



For very high energies we expect the potential to have less and less influence, the phase shift should go to zero



The wave function for energies between 0 and 5



Centrifugal potential

- We now generalize the results for the situation where the effective potential in the asymptotic region is the centrifugal potential
- We still assume $V(r)=0$ in the asymptotic region:

$$\frac{d^2 u(r)}{dr^2} + k^2 u(r) - \frac{l(l+1)}{r^2} u(r) = 0$$

- The linearly independent solutions of this equation are

$$u_s(r) = kr j_l(kr) \quad u_c(r) = kr n_l(kr)$$

- Spherical Bessel and Neumann functions

$$u_s(r) = kr j_l(kr) \quad u_c(r) = kr n_l(kr)$$

- $u_s(r)$ is the solution if we have only a centrifugal potential $V(r)=0$

- For $l=0$

$$j_l(kr) = \frac{\sin kr}{kr}$$

$$n_l(kr) = \frac{\cos kr}{kr}$$
 - This is exactly what we found before

- Asymptotic behavior are sines and cosines: we can do the same analysis as before

$$u_s(r) = \sin \left(kr - \frac{l\pi}{2} \right) \left[1 + O \left(\frac{1}{r} \right) \right]$$

$$u_c(r) = \cos \left(kr - \frac{l\pi}{2} \right) \left[1 + O \left(\frac{1}{r} \right) \right]$$

- And we again find the phase shift compared to the "free wave" $kr*j_l(kr)$

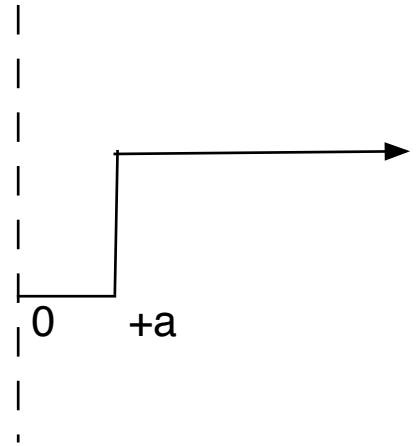
$$u(r) \propto \sin \left(kr - \frac{l\pi}{2} + \delta_l \right)$$

Spherical potential well: $l > 0$

- In the inner region the wave function must vanish at $r=0$

$$\psi(r) = A j_l(k' r)$$

$$\psi(r) = B j_l(kr) + C n_l(kr)$$



- Again replacing B and C with cosines and sines of the phase shift we get the matching conditions:

$$j_l(k' a) = \cos \delta_l j_l(ka) - \sin \delta_l n_l(ka)$$

$$k' j'_l(k' a) = k [\cos \delta_l j'_l(ka) - \sin \delta_l n'_l(ka)]$$

- Dividing the two expressions gives (omitting l):

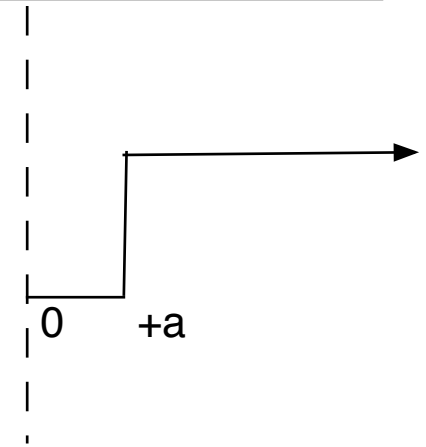
$$k' \frac{j'_l(k' a)}{j_l(ka)} = \frac{k j'_l(ka) - k \tan \delta_l n'_l(ka)}{j_l(ka) - \tan \delta_l n_l(ka)}$$

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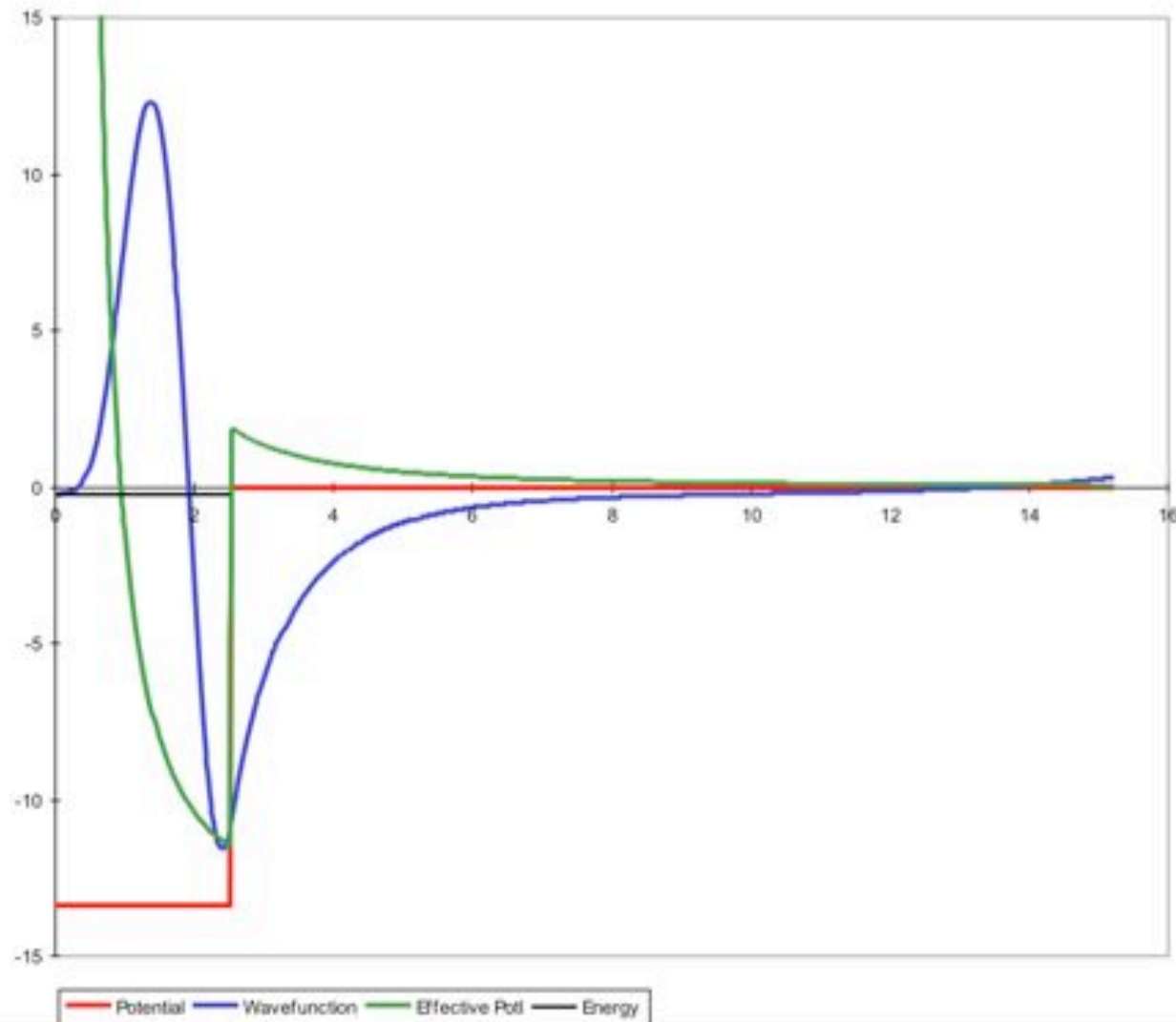
$$k' j'_l(k' a) = k [\cos \delta_l j'_l(k a) - \sin \delta_l n'_l(k a)]$$

- Dividing the two expressions gives (omitting l):

$$\delta = \tan^{-1} \left(\frac{k a j'_l(k a) - \gamma j_l(k a)}{k a n'_l(k a) - \gamma n_l(k a)} \right) \quad \gamma = k' a \frac{j'_l(k' a)}{j_l(k' a)}$$

Square well + centrifugal potential $l=3$

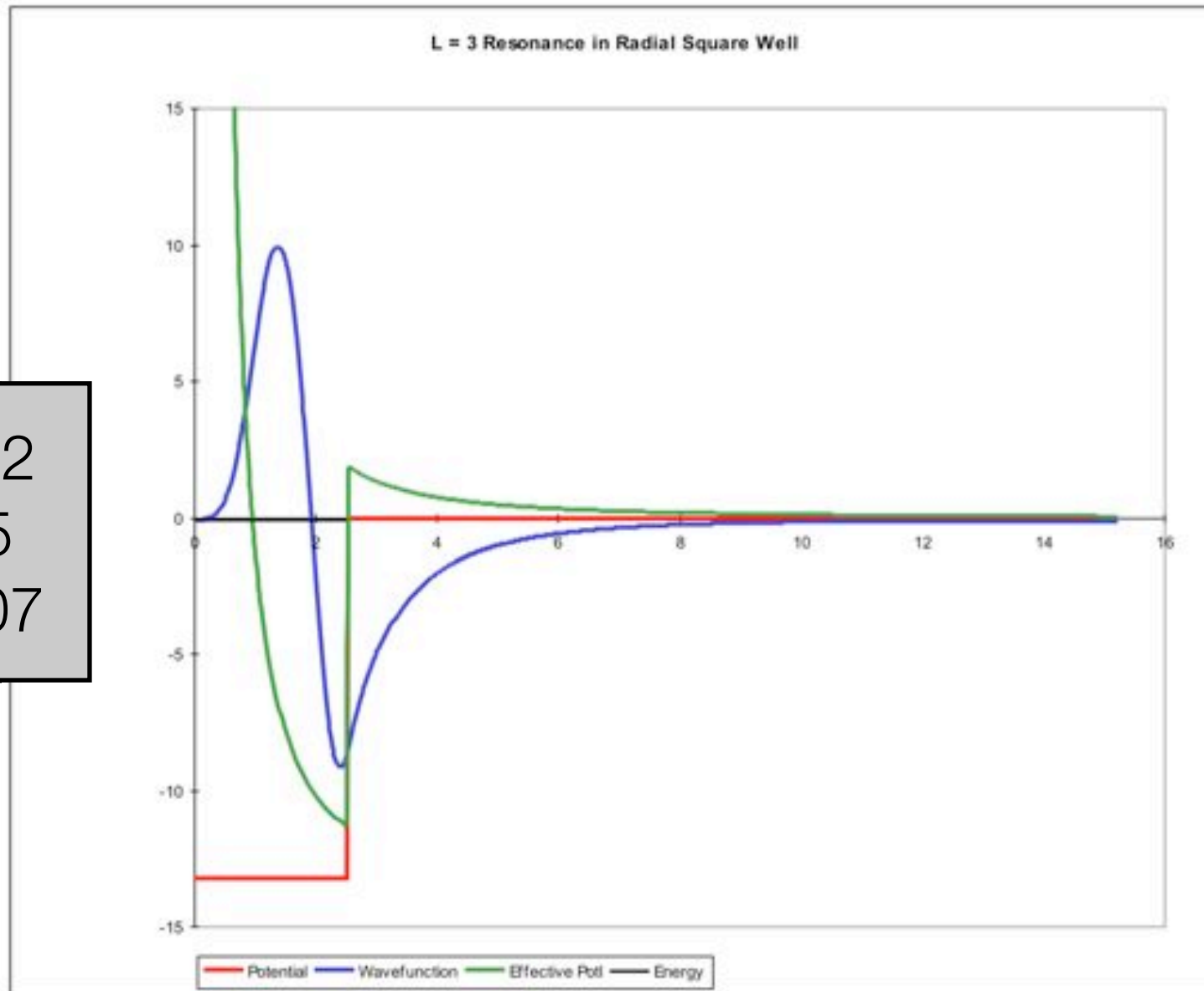
L = 3 Resonance in Radial Square Well



$D=13.4$
 $a=2.5$
 $E=-0.219$

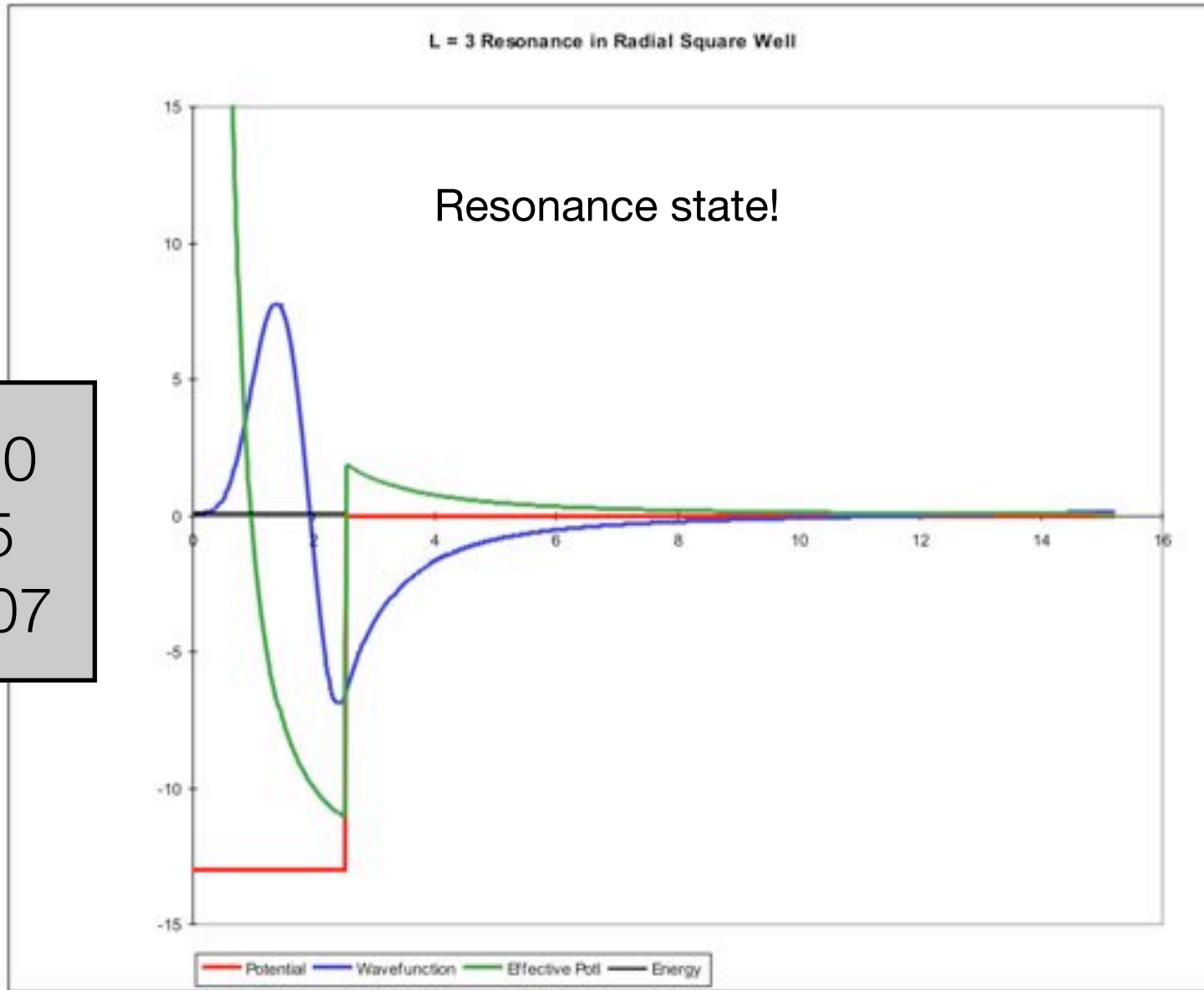
Square well + centrifugal potential $l=3$

$D=13.2$
 $a=2.5$
 $E=-0.07$



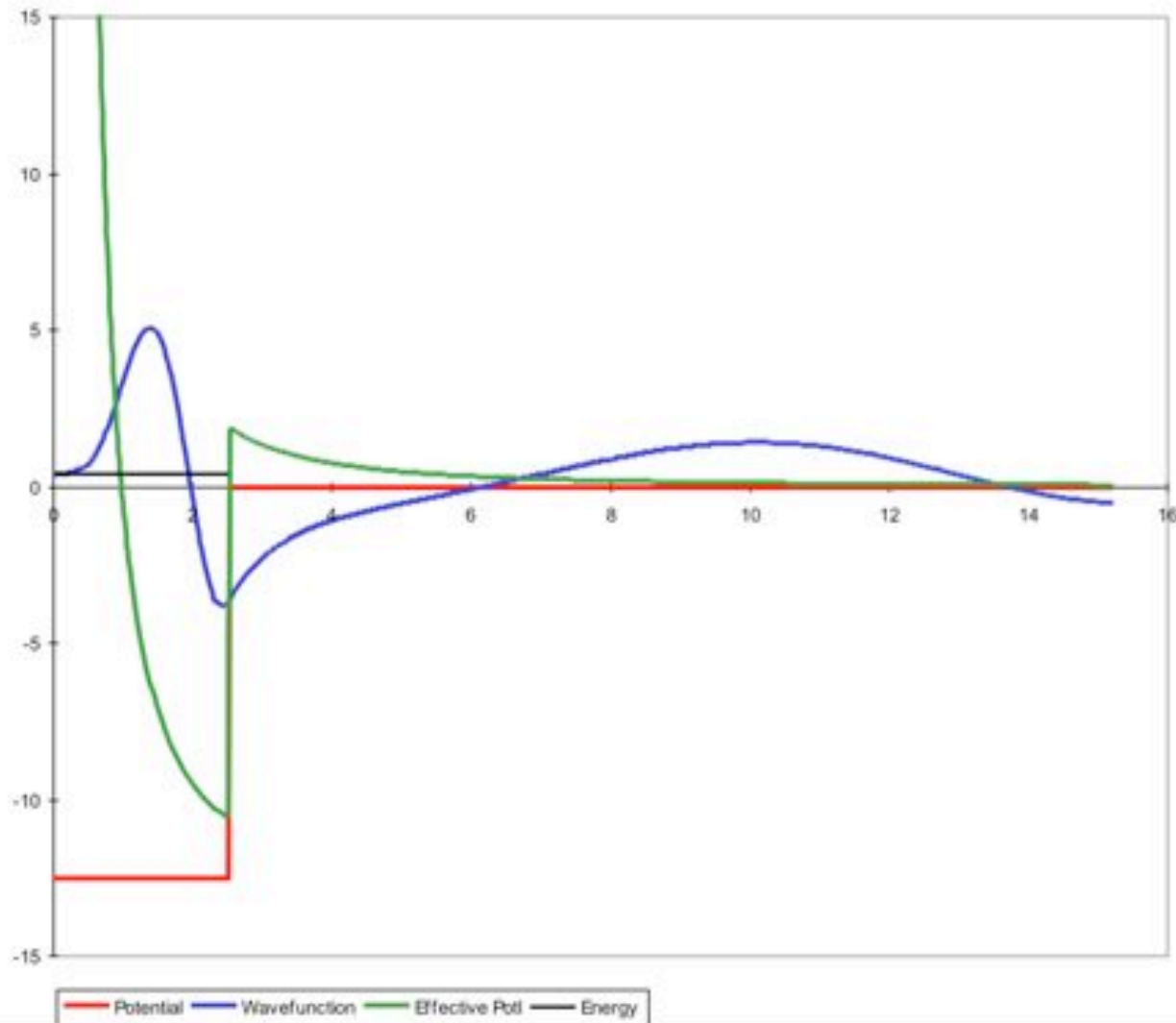
Square well + centrifugal potential $l=3$

$D=13.0$
 $a=2.5$
 $E=+0.07$

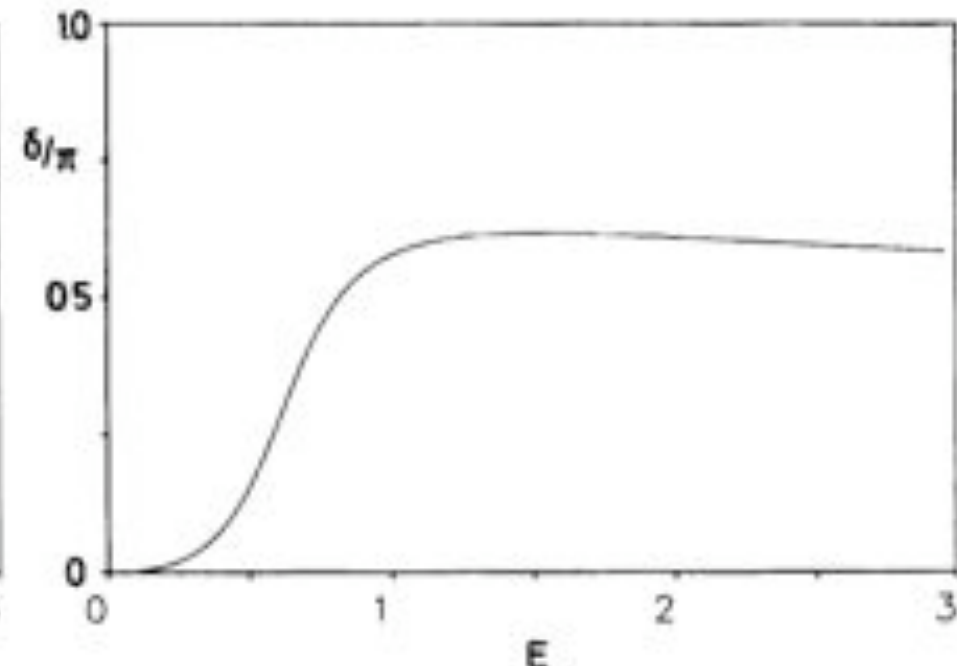
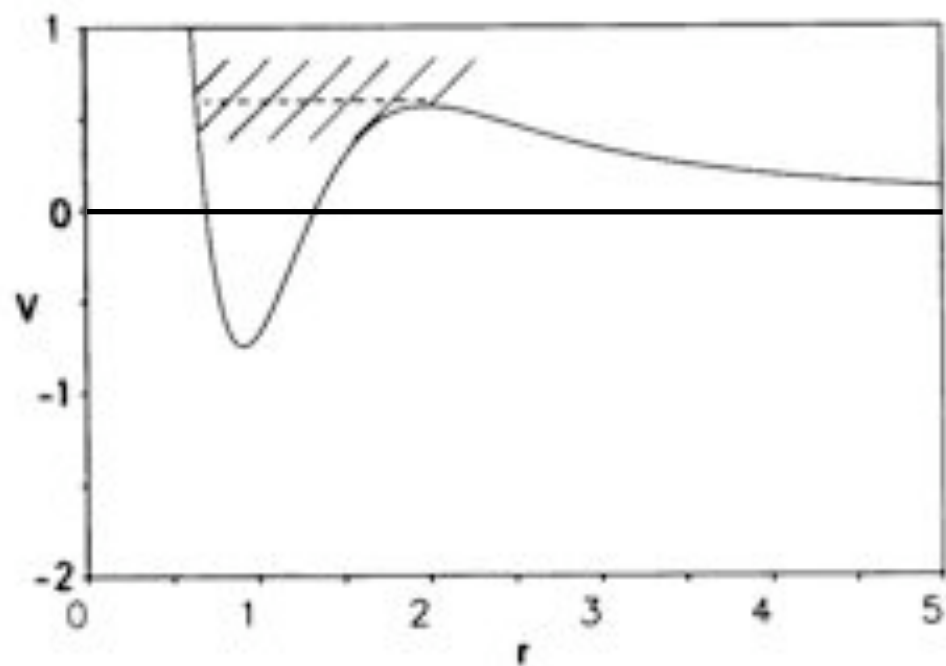
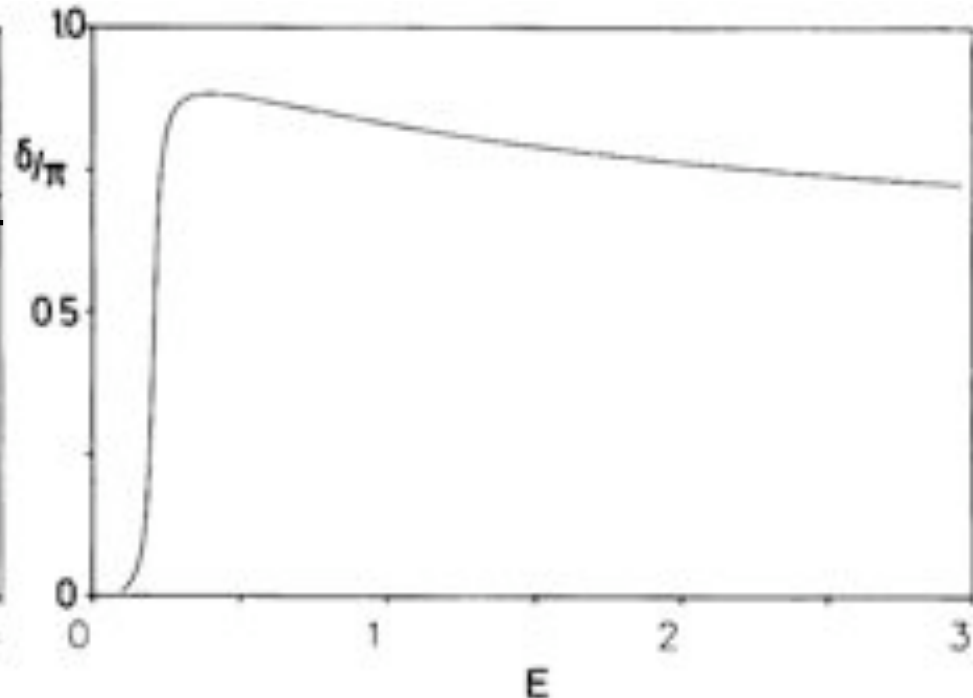
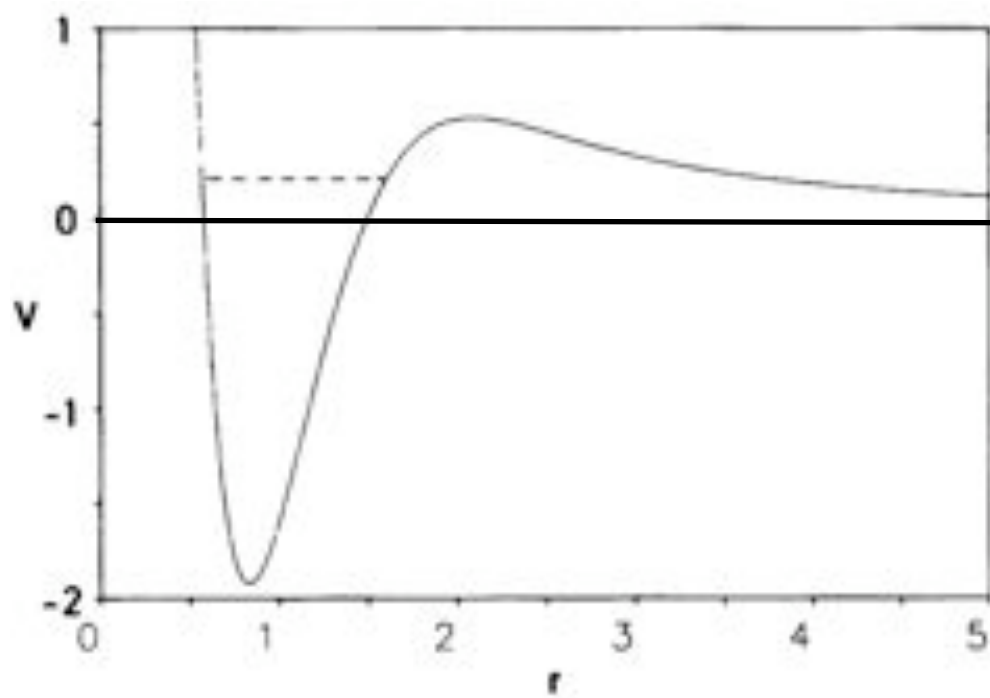


Square well + centrifugal potential $l=3$

L = 3 Resonance in Radial Square Well



$D=12.5$
 $a=2.5$
 $E=+0.409$



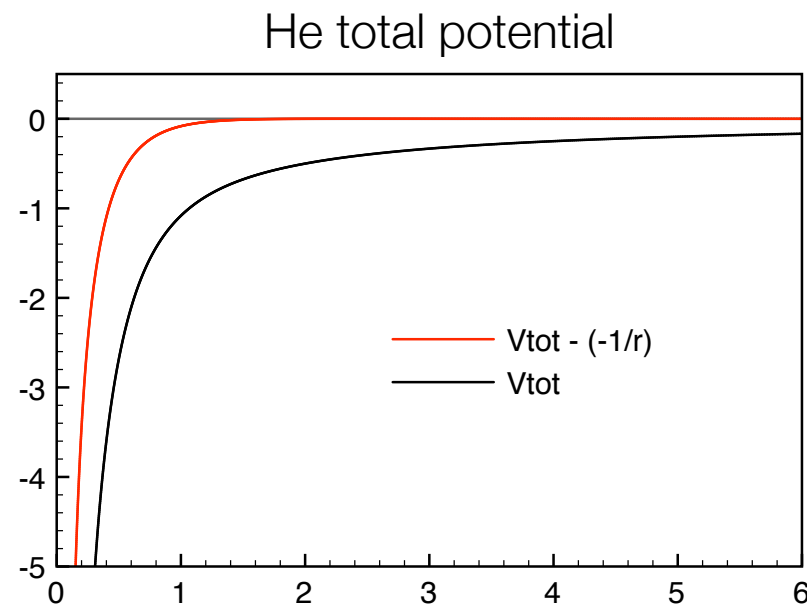
$$V = -V_0 e^{-r^2} + \frac{l(l+1)}{2r^2}$$

Coulomb potential

- A special case is when we include a Coulomb potential. The potential can never be considered zero also not at infinity

$$\frac{d^2 u(r)}{dr^2} + k^2 u(r) - \frac{l(l+1)}{r^2} u(r) + \frac{C}{r} u(r) = 0$$

- We can still do the previous analysis when we can write the total potential as a short range potential plus a pure Coulomb potential



$$\frac{d^2 u(r)}{dr^2} + k^2 u(r) - \frac{l(l+1)}{r^2} u(r) + \frac{C}{r} u(r) = 0$$

- In this case the linearly independent solutions are

$$u_s(r) = F_l(\eta, kr) \quad u_c(r) = G_l(\eta, kr)$$

- Regular and irregular Coulomb functions
- The Coulomb parameter eta determines the relative strength of the Coulomb term in the Hamiltonian

$$\eta = -\frac{1}{ka_0}$$

- Asymptotically

$$F_l(\eta, kr) \rightarrow \sin \left(kr - \eta \ln 2kr - \frac{l\pi}{2} + \sigma_l \right)$$

$$G_l(\eta, kr) \rightarrow \cos \left(kr - \eta \ln 2kr - \frac{l\pi}{2} + \sigma_l \right)$$

- The r-dependent term ensured that the Coulomb wave never acquires a constant wave length.

- The Coulomb phases are given by

$$\sigma_l = \arg[\Gamma(l + 1 + i\eta)]$$

$$u(r) \propto \sin \left(kr - \eta \ln 2kr - \frac{l\pi}{2} + \sigma_l + \delta_l \right)$$

Partial wave analysis

- We can obtain the phase shifts from just looking at the stationary states, but to find the relation with the cross section we do need to look explicitly at the scattering wave function
- Just like in the 1D case we can write any 3D function in terms of partial waves
- This time we do not have odd and even partial waves, but we have a partial wave for each angular momentum quantum number l :

$$\psi(\mathbf{r}) = \sum_{l=0}^{\infty} \frac{u_l(r)}{r} Y_{l,0}(\theta)$$



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$$\psi(\mathbf{r}) = \sum_{l=0}^{\infty} \frac{u_l(r)}{r} Y_{l,0}(\theta) = \sum_{l=0}^{\infty} \frac{u_l(r)}{r} \sqrt{\frac{2l+1}{4\pi}} P_l(\cos \theta)$$

- Remember that we are looking for a scattering function of the form:

$$\psi(r) = e^{ikz} + f(\theta) \frac{e^{ikr}}{r} \quad r \rightarrow \infty$$

- We can use the identity:

$$e^{ikz} = \sum_{l=0}^{\infty} (2l + 1) i^l j_l(kr) P_l(\cos \theta)$$

- We assume the scattering amplitude can be expanded as:

$$f(\theta) = \sum_{l=0}^{\infty} f_l P_l(\cos \theta)$$

- So we obtain the following expression:

$$\psi(\mathbf{r}) = \sum_{l=0}^{\infty} \left[(2l + 1) i^l j_l(kr) + f_l \frac{e^{ikr}}{r} \right] P_l(\cos \theta)$$

$$\psi(\mathbf{r}) = \sum_{l=0}^{\infty} \left[(2l+1)i^l j_l(kr) + f_l \frac{e^{ikr}}{r} \right] P_l(\cos \theta) = \sum_{l=0}^{\infty} \frac{u_l(r)}{r} \sqrt{\frac{2l+1}{4\pi}} P_l(\cos \theta)$$

- Asymptotically: $j_l(kr) = \frac{\sin(kr + l\pi/2)}{kr} + O\left(\frac{1}{r^2}\right)$

$$u_l(r) = i^l \sqrt{\frac{4\pi}{2l+1}} \left[\left(\frac{2l+1}{k} + if_l \right) \sin\left(kr - l\frac{\pi}{2}\right) + f_l \cos\left(kr - l\frac{\pi}{2}\right) \right]$$

- We have derived that in the asymptotic region

$$u_l(r) \propto \sin\left(kr - l\frac{\pi}{2} + \delta_l\right) = \sin\left(kr - l\frac{\pi}{2}\right) \cos \delta_l + \cos\left(kr - l\frac{\pi}{2}\right) \sin \delta_l$$

- Comparing the two equations we are able to extract the scattering amplitude (and hence, the cross section) in terms of the phase shifts

$$\cos \delta_l = c_l \left(\frac{2l+1}{k} + if_l \right) \quad \sin \delta_l = c_l f_l$$

$$\cos \delta_l = c_l \left(\frac{2l+1}{k} + i f_l \right) \quad \sin \delta_l = c_l f_l$$

- Converting the sine and cosine into their exponential forms, we can combine the two equations above and extract f_l and c_l and obtain:

$$f_l = \frac{2l+1}{k} e^{i\delta_l} \sin \delta_l \quad c_l = \frac{k}{2l+1} e^{-i\delta_l}$$

1D expression:

$$f_l = i e^{i\delta_l} \sin(\delta_l)$$

$$\frac{d\sigma}{d\Omega} = |f(\theta)|^2 = \frac{1}{k^2} \sum_{l,l'} e^{i(\delta_{l'} - \delta_l)} (2l+1) \sin \delta_l (2l'+1) \cos \delta_{l'} P_l(\cos \theta) P_{l'}(\cos \theta)$$

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$$\int_{-1}^{+1} P_i(\mu) P_j(\mu) d\mu = \frac{2}{2i+1} \delta_{ij}$$

$$\sigma = \int \frac{d\sigma}{d\Omega} d\Omega = \frac{4\pi}{k^2} \sum_{l=0}^{\infty} (2l+1) \sin^2 \delta_l$$

Low-energy quantum scattering from a hard sphere

$$V(r) = \begin{cases} \infty & r < a \\ 0 & r > a \end{cases}$$

- At low energies ($ka \ll 1$) we can safely assume that the $l=0$ solution dominates
- The wave function must be zero at a

$$u(a) = C_0 \sin(ka + \delta_0) = 0$$

$$\delta_0 = n\pi - ka$$

Taking $n=0$:

$$\sigma = \frac{4\pi}{k^2} \sin^2(ka) \approx 4\pi a^2$$

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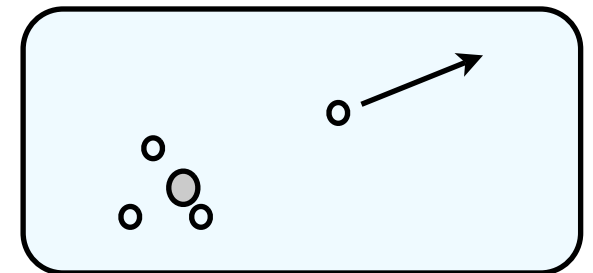
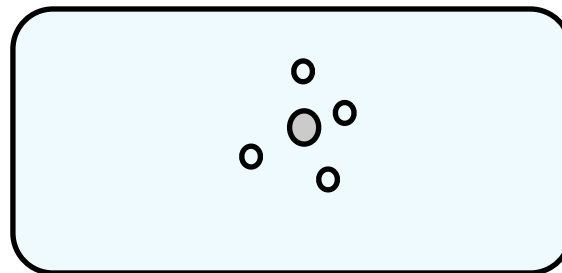
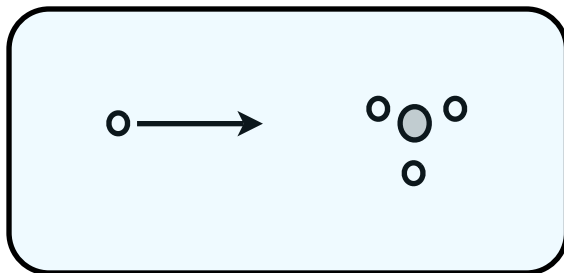
REMEMBER

Classical: $\sigma = \pi a^2$

The long-wavelength waves “feel” the whole surface of the sphere

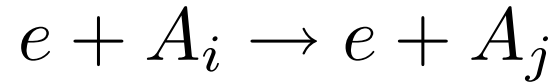
From potential scattering to many-electrons

- Until now we just looked at how to obtain the phase shifts and cross sections for scattering from empty 1D and spherical potentials
- Real systems like atoms and molecules in general contain many-electrons
- When we scatter a low-energy electron from a target with other electrons, the electrons become indistinguishable close to the target
- We need to include the interaction of the scattering electron with the other electrons



Electron-atom scattering

- We consider an electron scattering from an atom A:



- The Schrödinger equation describing this process is

$$H_{N+1} \Psi = E \Psi$$

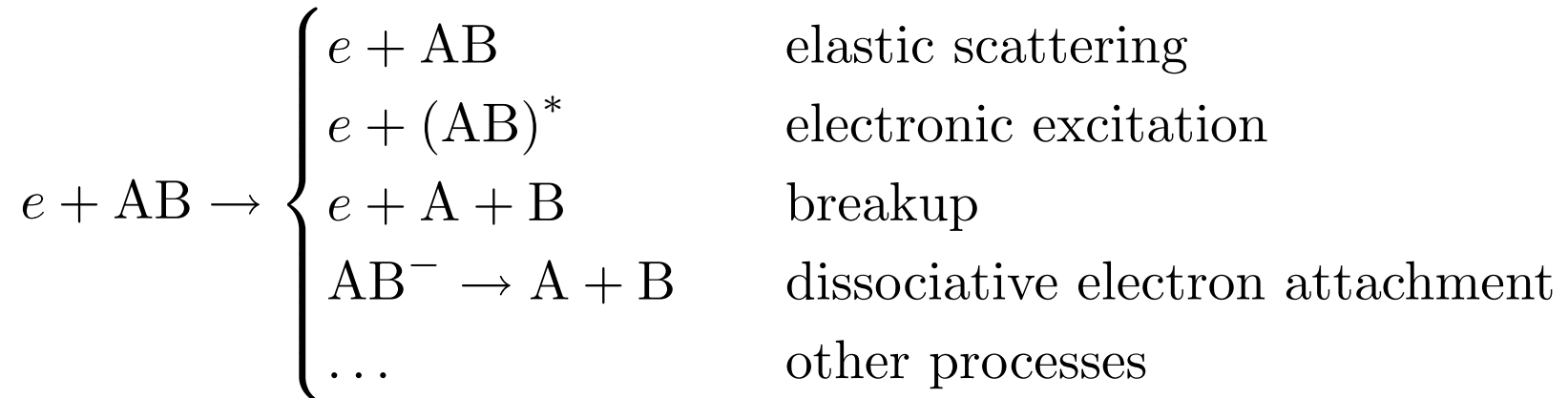
- With the N+1 electron Hamiltonian

$$H_{N+1} = \sum_{i=1}^{N+1} \left(-\frac{1}{2} \nabla_i^2 - \frac{Z}{r_i} \right) + \sum_{i>j=1}^{N+1} \frac{1}{r_{ij}}$$

$$r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$$

Intermezzo: Channels

- When an electron collides with a molecule, several processes can take place, these are called *Channels*:



- During electron-atom scattering, only elastic scattering and electronic excitations can take place
- Which channels can be accessed is dependent on the energy of the incoming electron. We say that accessible channels are *open* and the others are *closed*
- In low-energy electron scattering, elastic scattering is usually the dominant channel

- We introduce the target eigenfunctions that only describe the N-electron target by the equation

$$\langle \Phi_i | H_N | \Phi_j \rangle = \varepsilon_i \delta_{ij}$$

- We know that for a scattering process, the solution of the N+1 electron SE has the following asymptotic form

$$\Psi_i \rightarrow \Phi_i e^{ik_i z} + \sum_j \Phi_j f_{ji}(\theta, \phi) \frac{e^{ik_j r}}{r}$$

$$E = \varepsilon_i + \frac{1}{2}k_i^2 = \varepsilon_j + \frac{1}{2}k_j^2$$

$$\frac{d\sigma_{ji}}{d\Omega} = \frac{k_j}{k_i} |f_{ji}(\theta, \phi)|^2$$

elastic:

$$\Psi_i \rightarrow \Phi_i e^{ik_i z} + \Phi_i f_i(\theta, \phi) \frac{e^{ik_i r}}{r}$$

$$\frac{d\sigma_i}{d\Omega} = |f_i(\theta, \phi)|^2$$

Practical wave function calculations

- One often approximates the wave function by the following expansion

$$\Psi_k = \mathcal{A} \sum_{ij} a_{ijk} \Phi_i^N \eta_{ij} + \sum_m b_{mk} \Phi_m^{N+1}$$

Anti-symmetrizer

Target functions

1-electron continuum functions


(N+1) electron short-range functions (Gaussians)

- This expression can be used as a trial wave function in a variational calculation (like we do for bound-state calculations)
- The coefficients a and b are variationally determined

One-channel: static approximation

- The simplest approximation we can make is:
 - only consider one channel (elastic)
 - the projectile electron only sees the static field of the target (Coulomb)

$$\Psi_k = a_{jk} \Phi^N \eta_j + \sum_m b_{mk} \Phi_m^{N+1}$$


frozen

- The η_j must be orthogonal to the target states.
- The sum over $N+1$ electron functions allows for relaxation of orthogonality

One-channel: static-exchange approximation

- The static approximation is only reasonable for very high energies
- At low-energies the scattering electron and target electrons are *indistinguishable* we need to allow for exchange effects
- The wave function must be antisymmetric

$$\Psi_k = \mathcal{A} \sum_j a_{jk} \Phi^N \eta_j + \sum_m b_{mk} \Phi_m^{N+1}$$

- The sum over N+1 electron functions allows for relaxation of orthogonality

One-channel: static-exchange + polarization

- The incoming electron polarizes the target
- We can account for this by allowing the N+1 electron functions to include excited state configurations

$$\Psi_k = \mathcal{A} \sum_j a_{jk} \Phi^N \eta_j + \sum_m b_{mk} \Phi_m^{N+1}$$

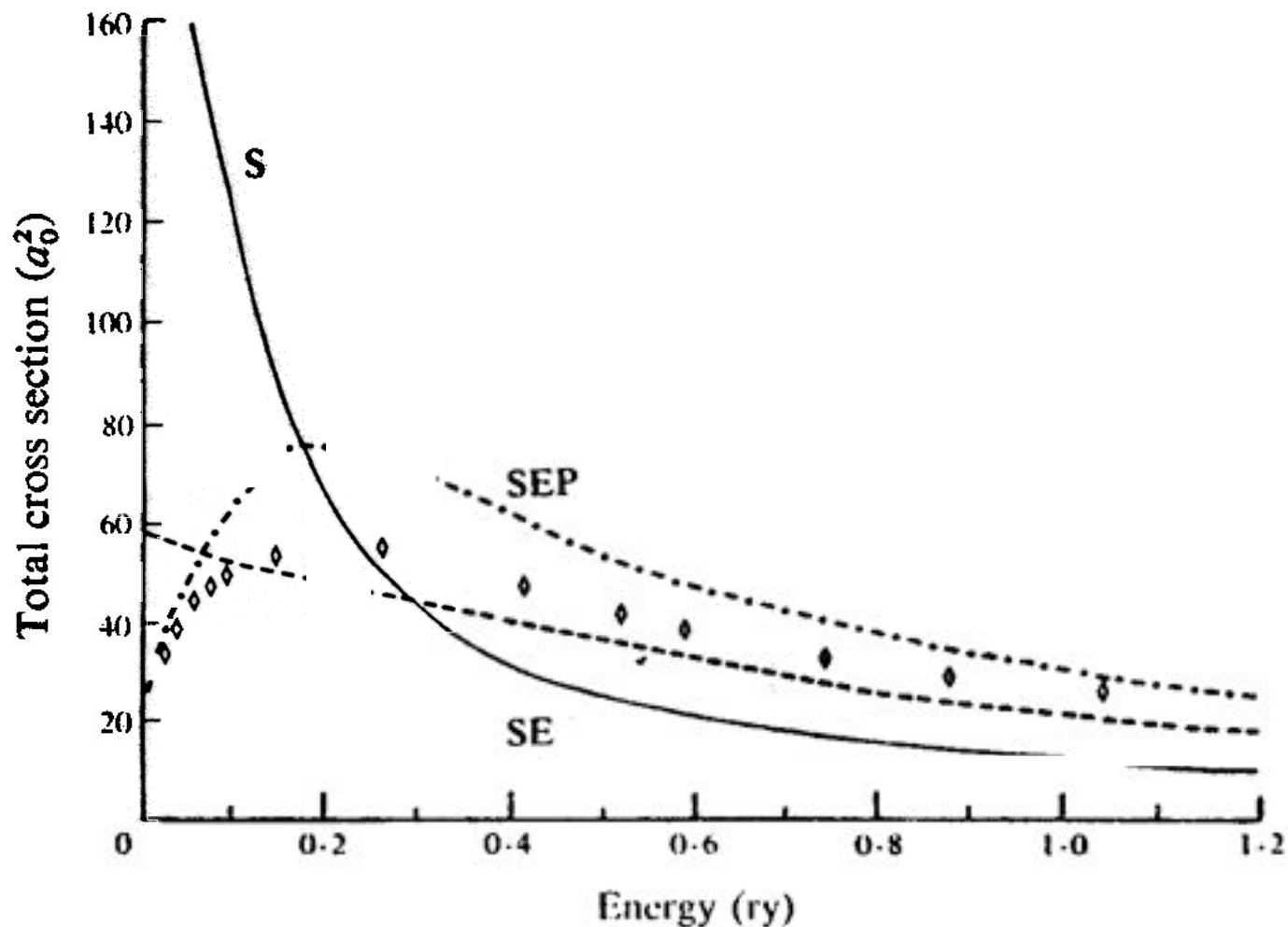


Fig. 14. Total cross sections for e-H₂ collisions calculated using the fixed-nuclei approximation employing three model interaction potentials: S, static only; SE, static and exchange; SEP, static, exchange and polarization. The diamonds are the experimental data of Golden *et al.* (1966). (The theoretical results shown here were calculated using rather crude model potentials. They are designed to show *qualitative* behaviour only. (Note: 1 ry = 27.212 eV.)

Multichannel: close coupling (coupled states)

- When we allow for more channels we obtain the close-coupling (coupled-states, N-state) expansion

$$\Psi_k = \mathcal{A} \sum_{ij} a_{ijk} \Phi_i^N \eta_{ij}$$

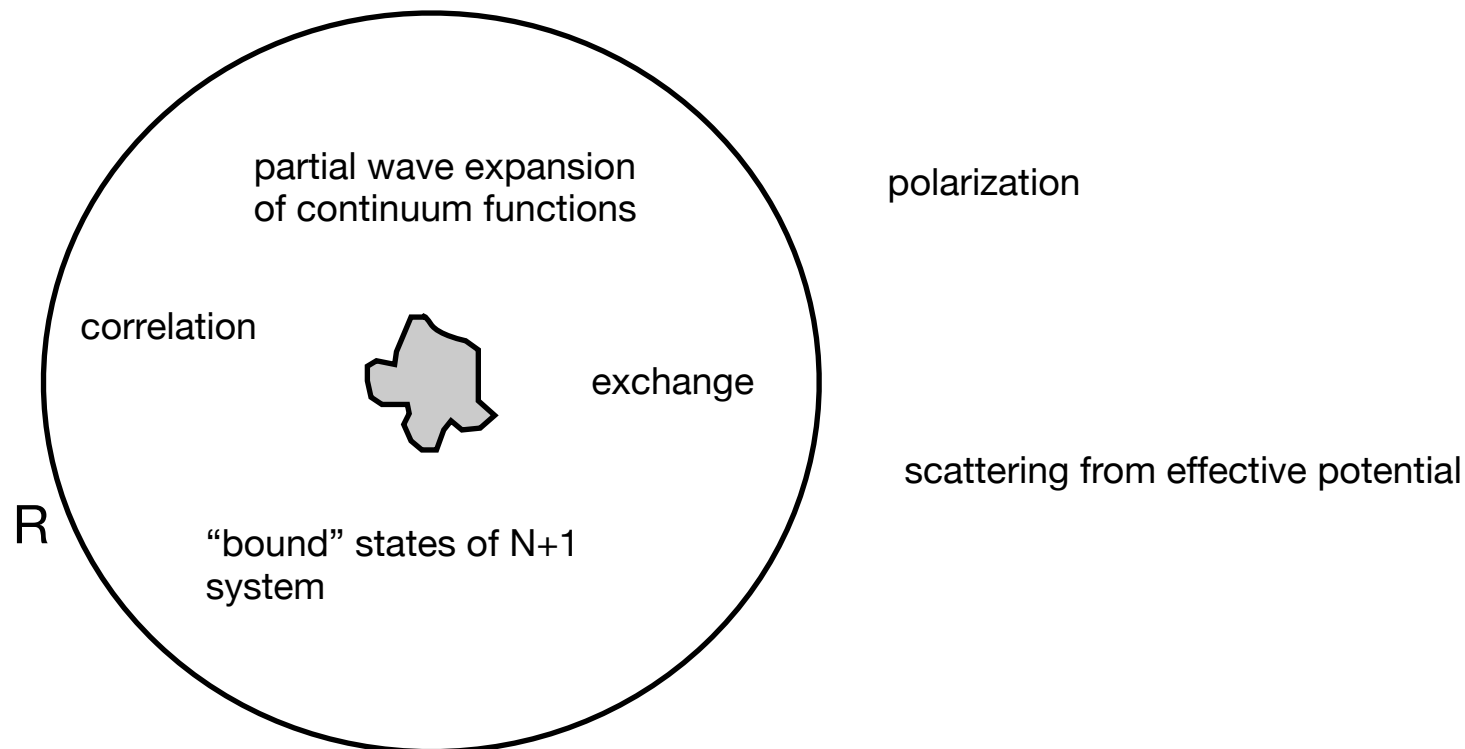
- For flexibility and polarization we again need to include N+1 electron functions

$$\Psi_k = \mathcal{A} \sum_{ij} a_{ijk} \Phi_i^N \eta_{ij} + \sum_m b_{mk} \Phi_m^{N+1}$$

- In practice it is not possible to include an infinite amount of channels, we need to choose which ones we think are important

Practical methods: R-matrix

- Over the past decades many methods have been developed for the practical solution of the close-coupling equations
- Currently the most popular (since it allows for the calculation of relatively large systems) is the R-matrix theory



Practical methods: local potential

- The non-local nature of exchange effects makes scattering methods very expensive
- Also, including correlation effects is non-trivial
- In practice one “borrows” an idea from DFT: construct an effective local potential that can also include polarization effects
- approximate the exchange effects by a local potential
- unlike in DFT, the use of such an effective potential for scattering is not justified, it is done only to make calculations on systems with many electrons at all possible

Optical potential

- Exchange: use free-electron gas orbitals (within the LDA) to obtain a local-exchange potential. A popular form of this potential is the *Hara exchange potential*

- Polarization (correlation):
$$V_{\text{pol}} = -\frac{\alpha}{2r^4} \left[1 - e^{(-r/r_p)^n} \right]$$

- Close to the target this potential is nonlocal, but in practice again approximated by a local potential based on DFT
- These are so-called correlation-polarization potentials that also approximate a part of correlation

DFT approach

- Since scattering calculations are expensive, and they already borrow stuff from DFT, why not do scattering with (TD)DFT itself?
- Kieron Burke (UCI CA), Neepa Maitra (Hunter College NY), Adam Wasserman (Perdue University IN), and Fan Zhang (now works in finance NY) started pioneering work (first paper 2005) on obtaining continuum states and low-energy electron scattering phase shifts from simple potentials and He^+
- As a postdoc with Kieron in 2005-2007 (at Rutgers University NJ) I continued this work and we developed a scattering method that avoids using continuum states: we can obtain phase-shifts for any atom easily
- VENI: 2007-now taking baby-steps to extend the method to molecules

Outline DFT part

- A few slides on DFT and TDDFT
- How to approach the scattering problem with TDDFT
- The world in a box: obtaining continuum information from bound states
 - ➔ The square well potential revisited
- Box calculations with (TD)DFT: another 1D example, the delta potential well
- Results for atoms

Ground state DFT

Hohenberg-Kohn:

Hohenberg-Kohn (1964) proved that the ground-state energy can be completely determined from the density; $E_0[r]$.

P. Hohenberg and W. Kohn, Phys. Rev. 136, B864 (1964)

Ground state DFT

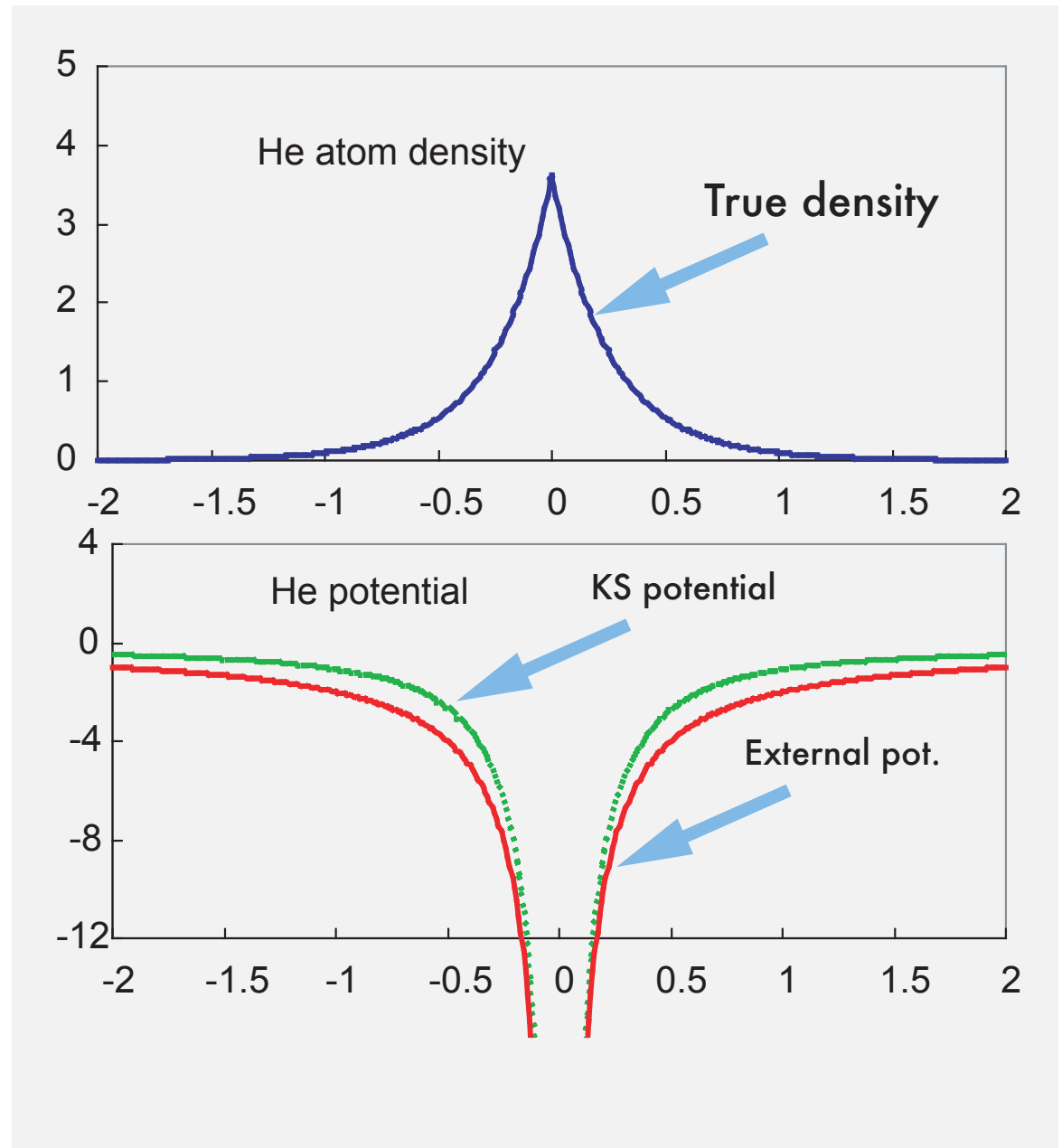
- Kohn-Sham (KS):
 - A non-interacting many-body system in an effective potential gives the true ground state density of the interacting system

$$\left(-\frac{1}{2} \nabla^2 + v_{\text{ext}}(\mathbf{r}) + \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + v_{\text{xc}}(\mathbf{r}) \right) \phi_i(\mathbf{r}) = \epsilon_i \phi_i(\mathbf{r})$$

$$\rho(\mathbf{r}) = \sum_{i=1}^N |\phi_i(\mathbf{r})|^2$$

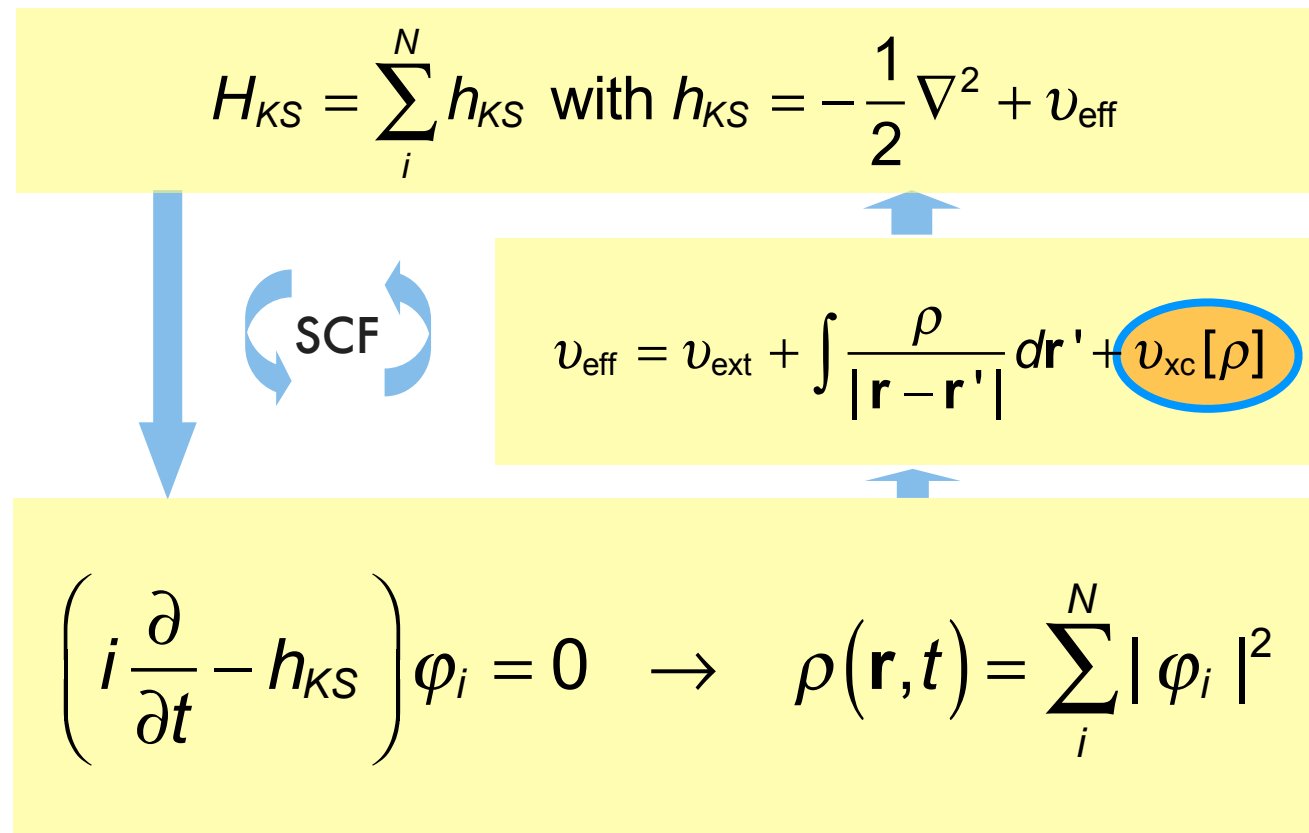
- The KS orbitals do not correspond to the true orbitals of the system

- 2 non-interacting electrons in the KS potential will have the same density as 2 interacting electrons in the true potential

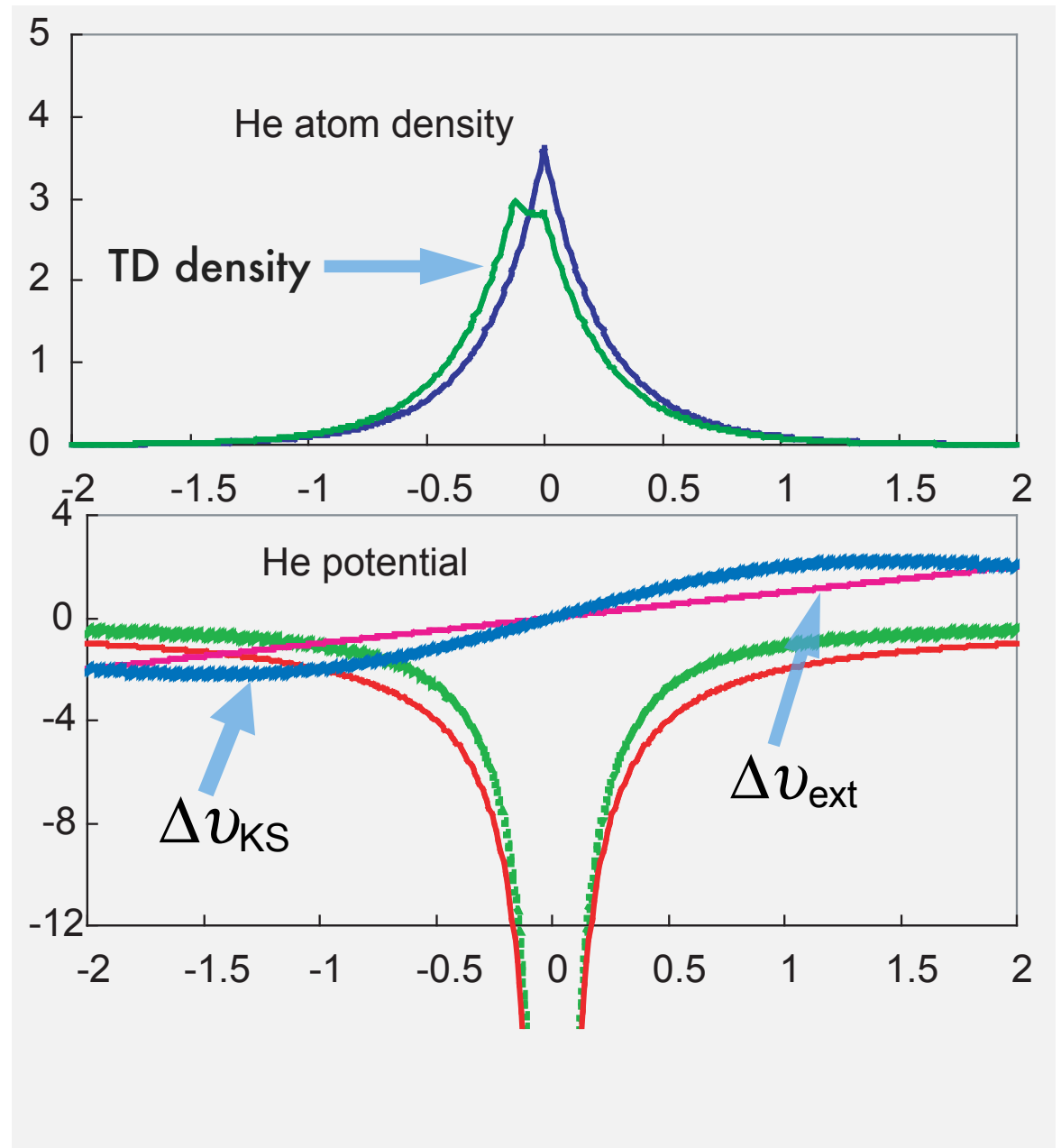


Time-dependent DFT

- Runge-Gross: A non-interacting many-body system in an effective potential gives the true time-dependent density of the interacting system



- Runge-Gross theorem illustrated for the He atom



Linear response

- Excitation energies can be obtained from the following equation:

$$\Omega^{S/T} \mathbf{F}_i = \omega_i^2 \mathbf{F}_i$$

$$\Omega_{ia,jb}^S = \delta_{ab}\delta_{ij}(\varepsilon_a - \varepsilon_i)^2 + 2\sqrt{\varepsilon_a - \varepsilon_i} \left(K_{ia,jb}^{\uparrow\uparrow} + K_{ia,jb}^{\uparrow\downarrow} \right) \sqrt{\varepsilon_b - \varepsilon_j}$$

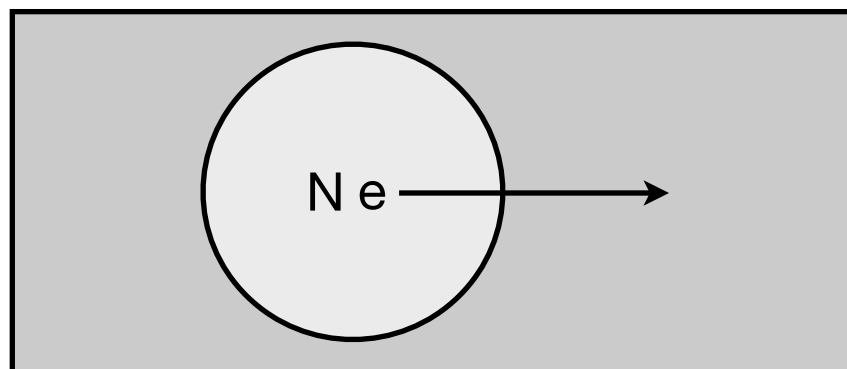
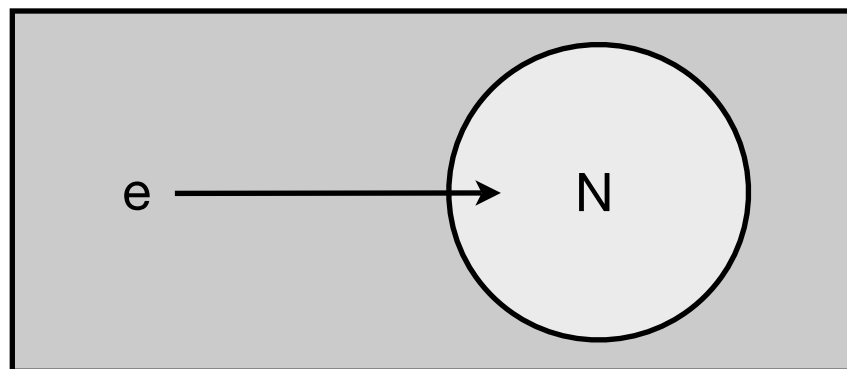
$$\Omega_{ia,jb}^T = \delta_{ab}\delta_{ij}(\varepsilon_a - \varepsilon_i)^2 + 2\sqrt{\varepsilon_a - \varepsilon_i} \left(K_{ia,jb}^{\uparrow\uparrow} - K_{ia,jb}^{\uparrow\downarrow} \right) \sqrt{\varepsilon_b - \varepsilon_j}$$

- The coupling matrix contains only ground state properties, apart from the xc-kernel f_{xc}

$$K_{ia,jb}^{\sigma\tau}(\omega) = \iint \phi_{i\sigma}(\mathbf{r})\phi_{a\sigma}(\mathbf{r}) \left[\frac{1}{|\mathbf{r} - \mathbf{r}'|} + f_{xc}^{\sigma\tau}(\mathbf{r}, \mathbf{r}', \omega) \right] \phi_{b\tau}(\mathbf{r}')\phi_{j\tau}(\mathbf{r}') d\mathbf{r}d\mathbf{r}'$$

Scattering properties from TDDFT

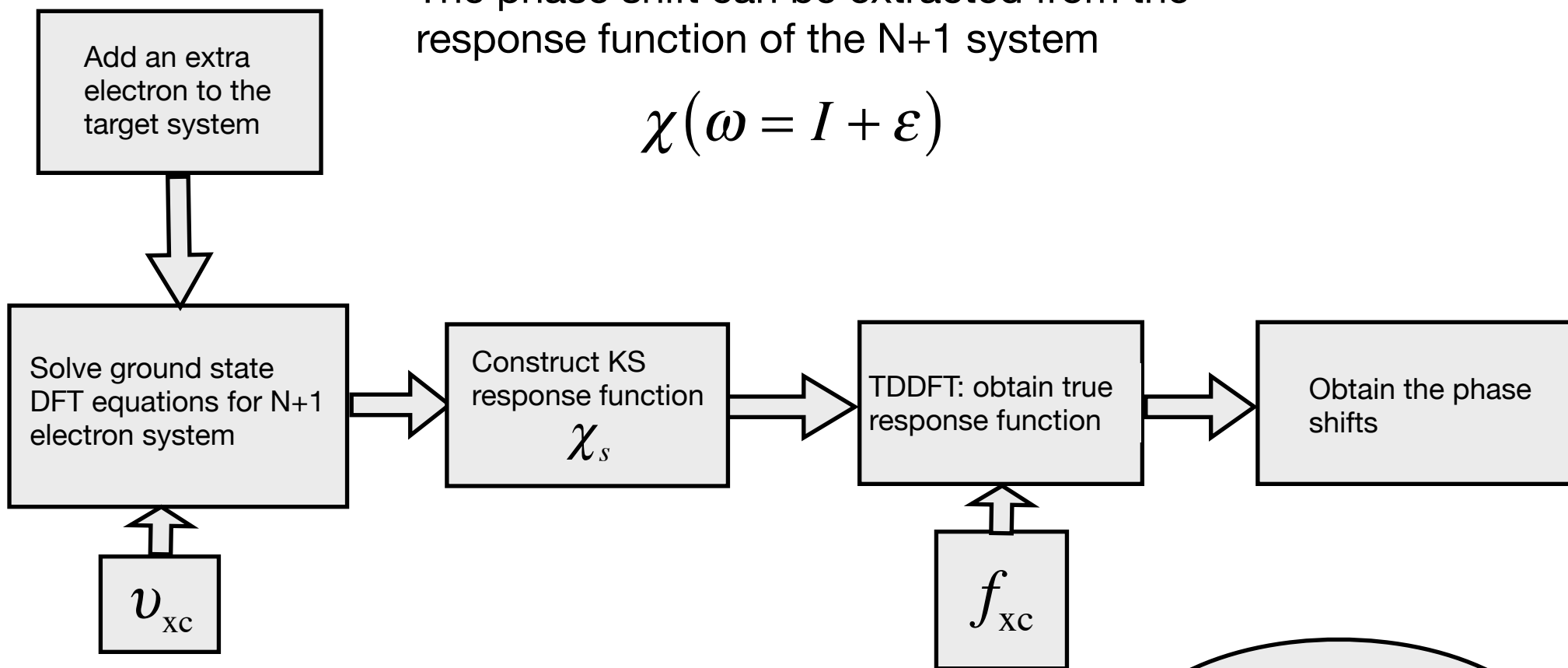
- Basic Idea: The incoming electron and the N -electron target combined are an excited state of the $(N+1)$ -electron system
- We start from the ground state of the $(N+1)$ -electron system and excite one electron into the continuum (TDDFT)



Scattering with TDDFT

The phase shift can be extracted from the response function of the N+1 system

$$\chi(\omega = I + \varepsilon)$$

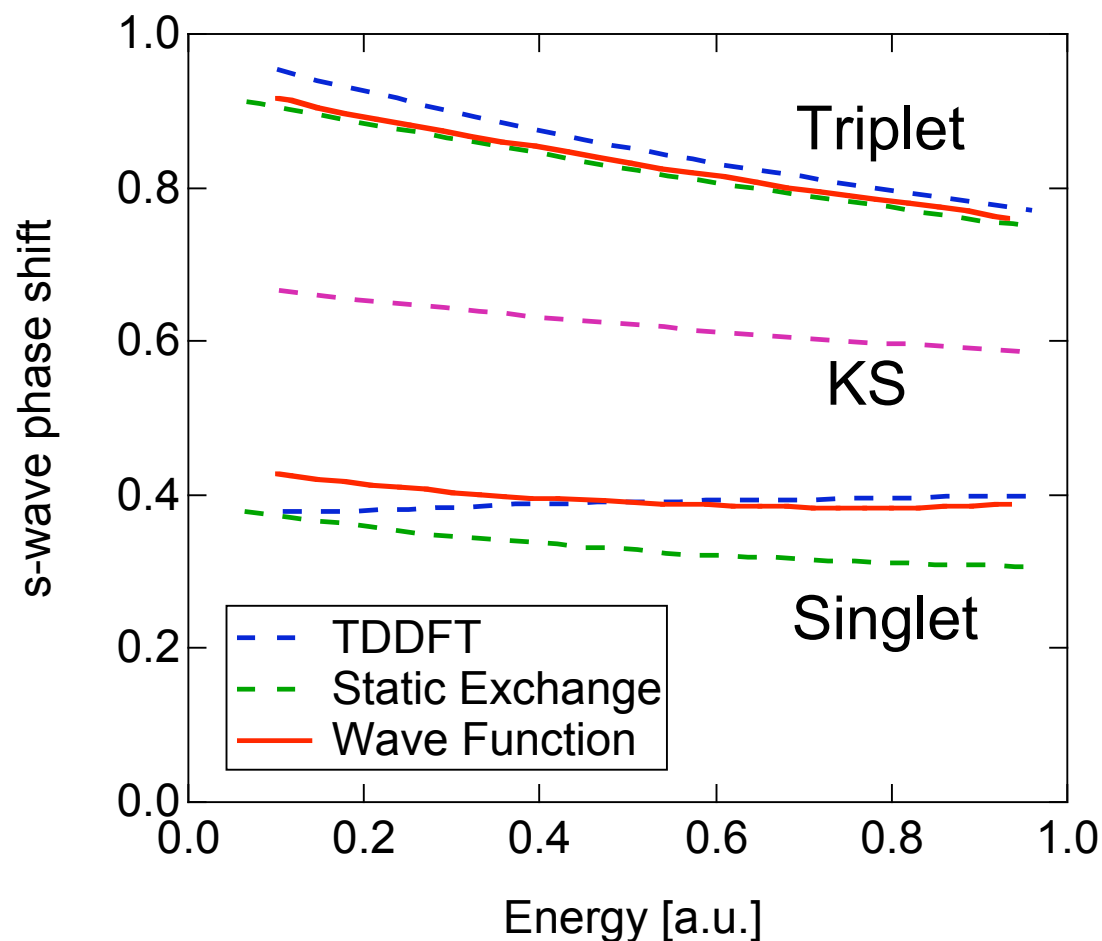


$$\chi = \chi_s + \iint \chi_s(\mathbf{r}_1) \left[\frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} + f_{xc} \right] \chi(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2$$
$$\delta = \delta_s + \text{correction}$$

Works for both short and long range potentials

e-He⁺ scattering

- TDDFT results of same (or better) quality as static exchange calculations, computational costs are equal or less
- KS result is good starting point for TDDFT calculation
- Results obtained by Adam Wasserman



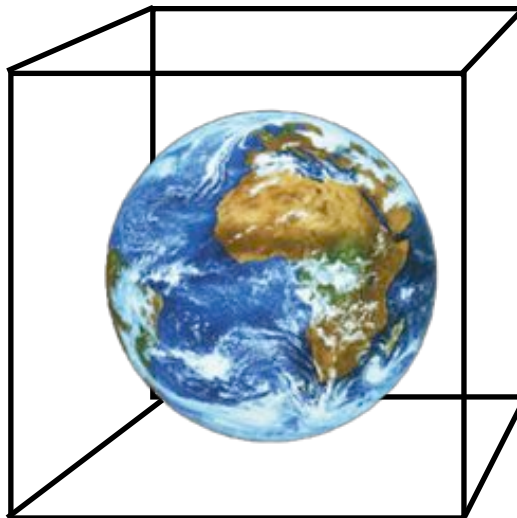
DFT method was still cumbersome...

- The TDDFT method developed by Burke and Wasserman is still cumbersome
- Reason is that continuum states are involved that don't occur naturally in DFT
- Also, not all DFT xc-potentials and TDDFT xc-kernels can be used

- Can we get away with just considering bound states somehow?

Continuum states from a box

- The idea of enclosing a system in a box to discretize the continuum keeps popping up in the literature
- We enclose our potential (atom, molecule) in a hard walled box. In this way we discretize the continuum and obtain a finite set of what are called “pseudo-states”



The spherical potential well: $l=0 \rightarrow$ revisited

- In the inner region the wave function must vanish at $r=0$

$$\begin{aligned}u(r) &= \sin(k'r) & r \leq a \\ &= A \sin(kr + \delta) & r > a\end{aligned}$$

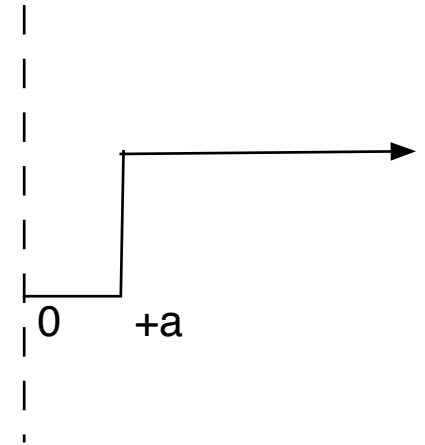
- Matching the functions and derivatives at $r=a$:

$$Ak \cos(ka + \delta) = k' \cos(k'a)$$

$$A \sin(ka + \delta) = \sin(k'a)$$

- Dividing the two expressions gives:

$$\tan(ka + \delta) = \frac{k}{k'} \tan(k'a)$$



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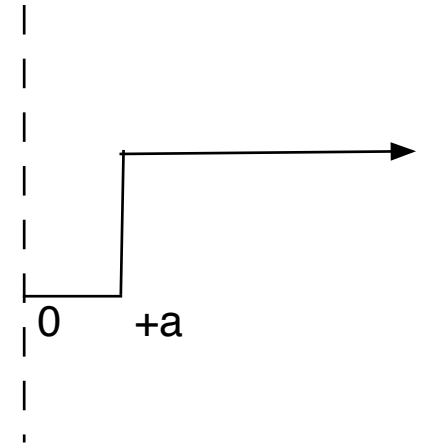
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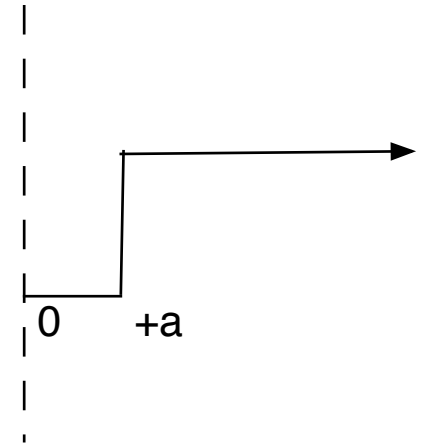
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$$\delta = \tan^{-1} \left[\frac{k}{k'} \tan(k'a) \right] - ka$$



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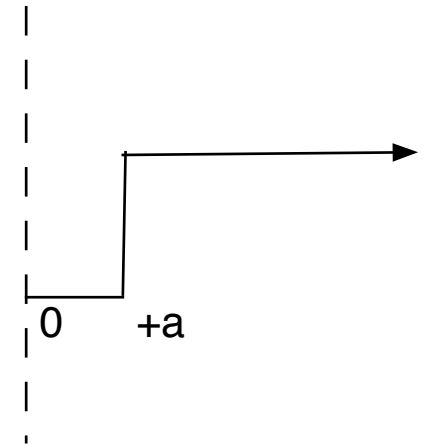
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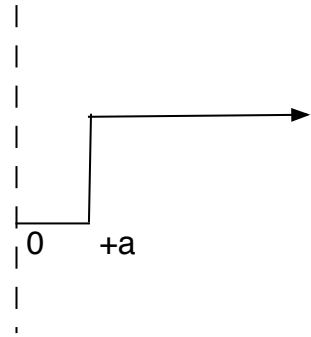
$$\delta_0 = \tan^{-1} \left(\frac{k'}{k} \tan k'a \right) - ka$$

$$\delta_1 = \tan^{-1} \left(\frac{k}{k'} \tan k'a \right) - ka$$

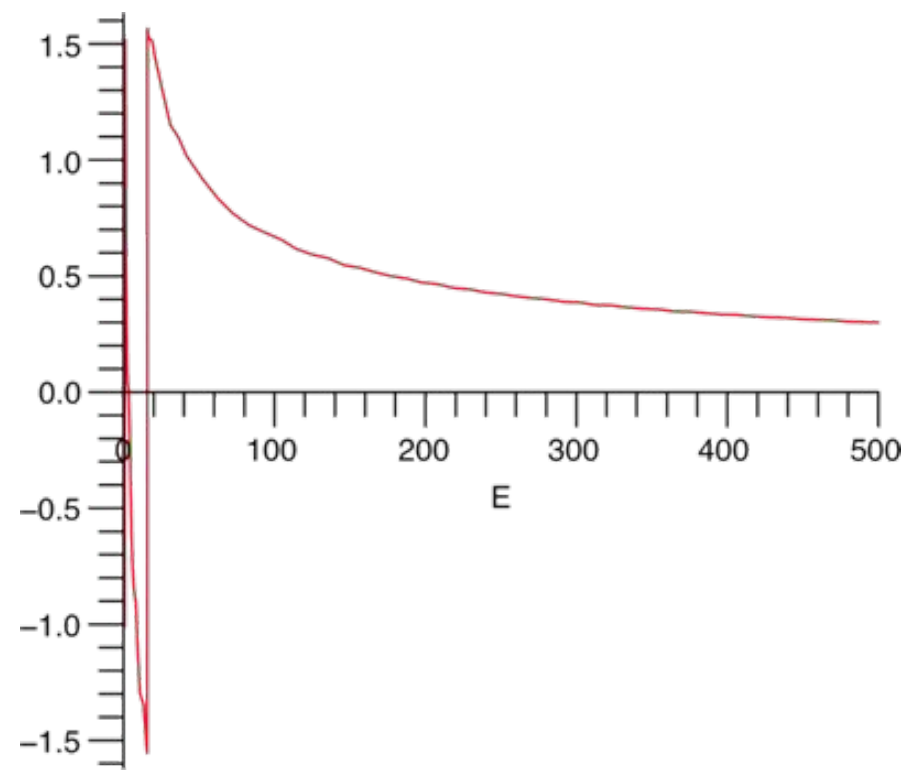
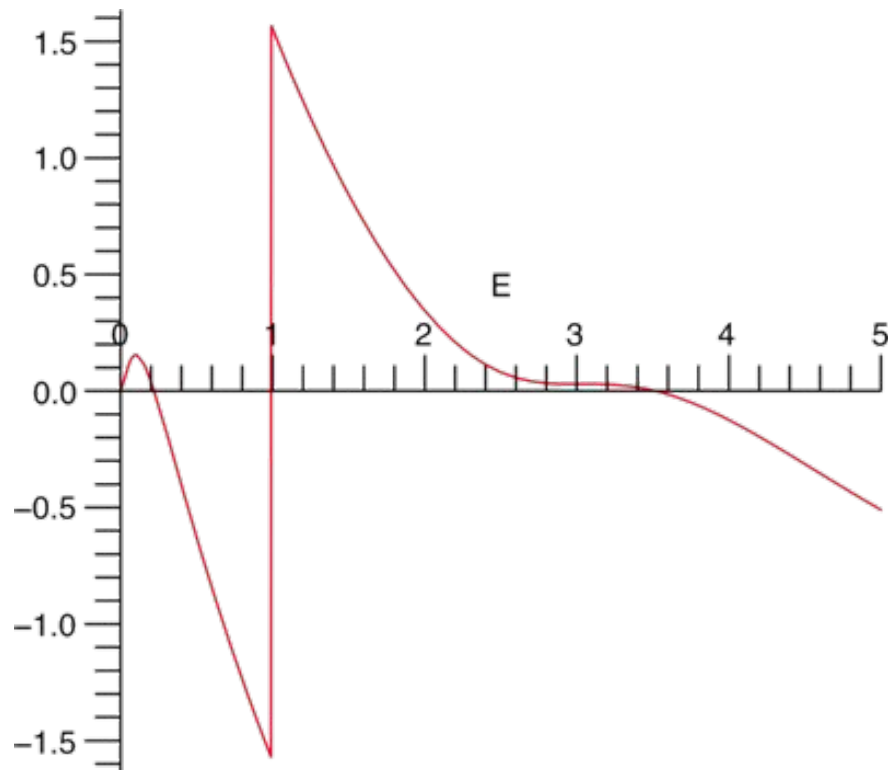
Odd solution is zero at $r=0$



Phase shift: $a=3$ $V_0=3$

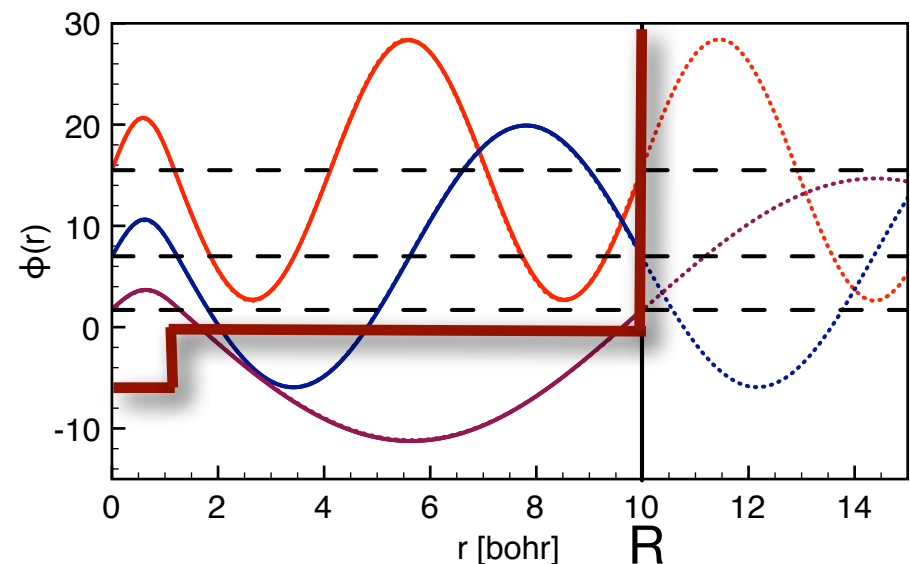
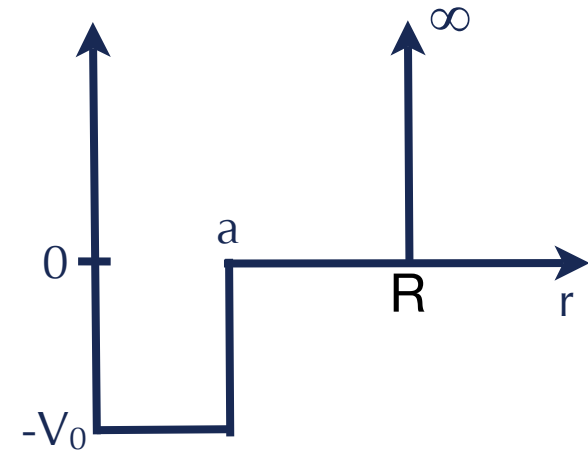


For very high energies we expect the potential to have less and less influence, the phase shift should go to zero



The square well potential in a box

- If we add an infinitely high wall at a distance R to the potential we discretize the continuum
- Only “continuum” states with a node at the wall are retained
- We place the wall well outside the range of the potential, i.e. $R \gg a$
- In the region $r > a$ we can study the “asymptotic” behavior of each state and obtain phase shifts like in the free case



The spherical potential well: $l=0$ in a box

- In the inner region the wave function must vanish at $r=0$

$$\begin{aligned}u(r) &= \sin(k'r) & r \leq a \\ &= A \sin(kr + \delta) & r > a\end{aligned}$$

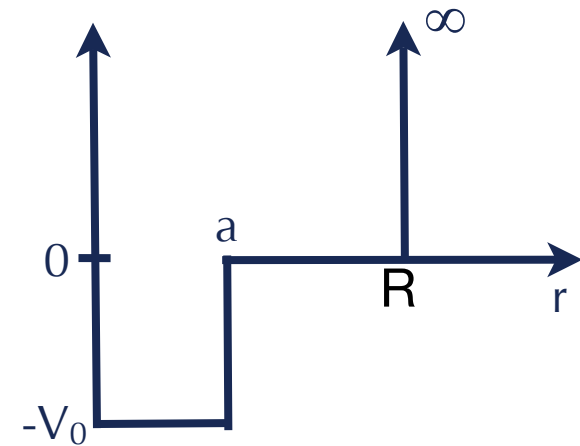
- The wave function must also vanish at $r=R$

$$\sin(kR + \delta) = 0$$

- For this case we instantly obtain an expression for the phase shifts in terms of the energies k :

$$\delta = -kR + n\pi$$

- We need to find the *discrete* energies k



- We again need to match the wave function and its derivative at a with the restriction that the wave function is 0 at $r=0$ and at $r=R$

$$\begin{aligned} u(r) &= \sin(k' r) & r \leq a \\ &= A \sin(kr - r) & r > a \end{aligned}$$

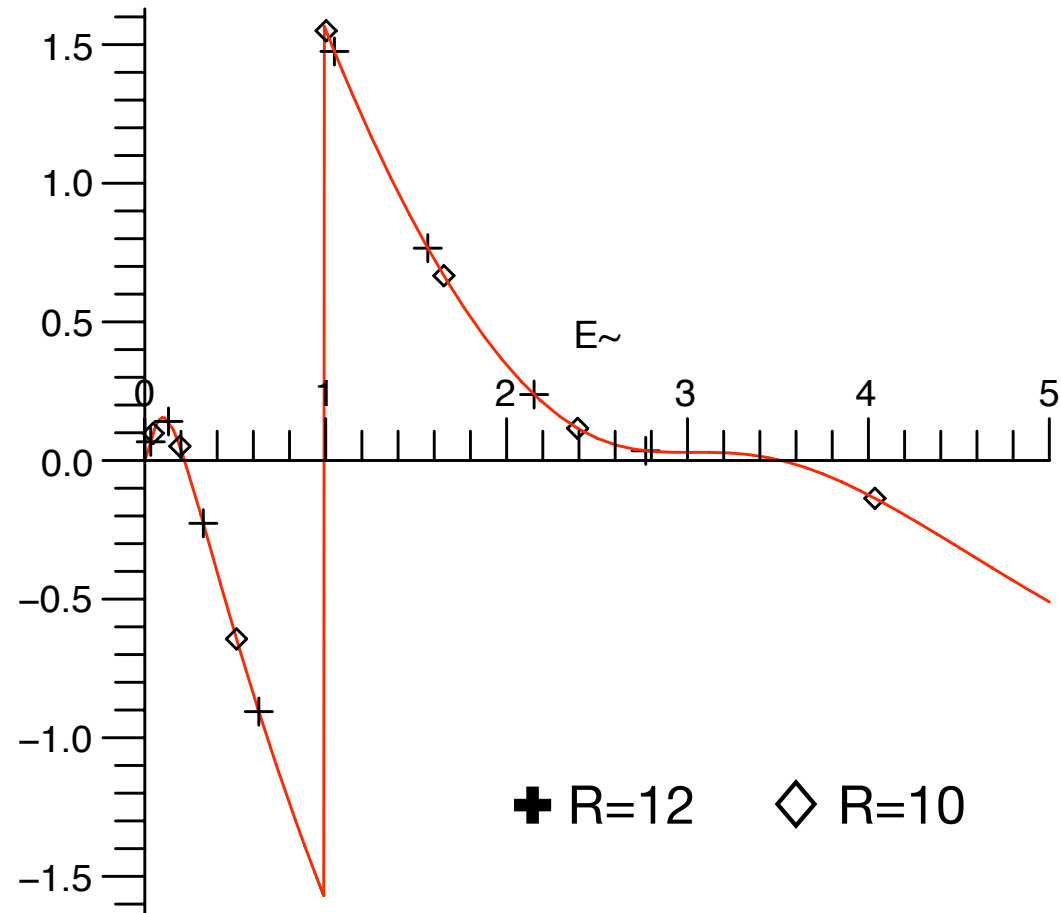
$$\begin{aligned} A \sin(k(R - a)) &= \sin(Ka) \\ -Ak \cos(k(R - a)) &= K \cos(Ka) \end{aligned}$$

- We can obtain the allowed values of k by solving the following equation:

$$-k \cot(k(R - a)) = K \cot(Ka)$$

- The coefficients A are given by: $A = \frac{\sin(Ka)}{\sin(k(R - a))}$

Phase shift: $a=3$ $V_0=3$



$$\left(-\frac{1}{2} \frac{d^2}{dr^2} + \frac{l(l+1)}{2r^2} + V(r) \right) \phi_l(r) = E \phi_l(r)$$

- The general solution for this equation when $V(r)$ is short ranged plus pure Coulomb:

$$u_s(r) = F_l(\eta, kr) \quad u_c(r) = G_l(\eta, kr)$$

$$\begin{aligned} u(r) &= Au_s(r) + Bu_c(r) \\ &= \sqrt{A^2 + B^2} \left[\frac{A}{\sqrt{A^2 + B^2}} u_s(r) + \frac{B}{\sqrt{A^2 + B^2}} u_c(r) \right] \\ &= \sqrt{A^2 + B^2} [\cos(\delta) u_s(r) + \sin(\delta) u_c(r)] \end{aligned}$$

- at $r=R$: $u(R) = A k R F_l(\eta, kR) + B k R G_l(\eta, kR) = 0$

$$\left(-\frac{1}{2} \frac{d^2}{dr^2} + \frac{l(l+1)}{2r^2} + V(r) \right) \phi_l(r) = E\phi_l(r)$$

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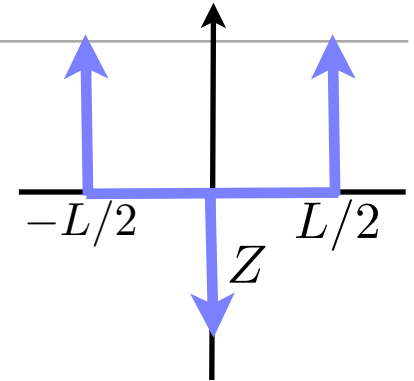
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- at $r=R$: $u(R) = A k R F_l(\eta, kR) + B k R G_l(\eta, kR) = 0$

$$\tan \delta_l = -\frac{F_l(\eta, kR)}{G_l(\eta, kR)}$$

Using DFT: delta potential well

$$\Psi(x) \rightarrow \begin{cases} \psi_L(x) = A_o \sin k_n x + A_e \cos k_n x & x < 0 \\ \psi_R(x) = B_o \sin k_n x + B_e \cos k_n x & x > 0 \end{cases}$$



The right and left functions need to be zero at $L/2$ and $-L/2$ respectively:

Even solution:

$$\psi_L^+(x) = \frac{A_o}{\cos\left(\frac{1}{2}k_n^+ L\right)} \sin\left(k_n^+ x + \frac{1}{2}k_n^+ L\right)$$

$$\psi_R^+(x) = \frac{B_o}{\cos\left(\frac{1}{2}k_n^+ L\right)} \sin\left(k_n^+ x - \frac{1}{2}k_n^+ L\right)$$

Odd solution:

$$\psi_L^-(x) = A_0 \sin(k_n^- x)$$

$$\psi_R^-(x) = B_0 \sin(k_n^- x)$$

$$k_n^- = \frac{2n\pi}{L}$$

For the even functions: continuity of function and derivative at zero....

Continuity

- Integrating the SE in an interval around $x=0$ going from a^- to a^+ and letting this interval go to zero will give the desired results.

$$\begin{aligned}\int_{a^-}^{a^+} \left[-\frac{1}{2} \frac{d^2}{dx^2} - \lambda \delta(x-0) \right] \Psi(x) dx &= E \int_{a^-}^{a^+} \Psi(x) dx \\ -\frac{1}{2} \int_{a^-}^{a^+} \Psi''(x) dx - \lambda \int_{a^-}^{a^+} \delta(x-0) \Psi(x) dx &= E \int_{a^-}^{a^+} \Psi(x) dx \\ -\frac{1}{2} \Psi'(x) \Big|_{a^-}^{a^+} - \lambda \Psi(0) &= 0 \\ \Psi'(x) \Big|_{a^+} - \Psi'(x) \Big|_{a^-} &= -2\lambda \Psi(0)\end{aligned}$$

- Using this continuity condition we get

$$\begin{aligned}\frac{d}{dx} \psi_R(x) \Big|_{x=0} &= \frac{d}{dx} \psi_L(x) \Big|_{x=0} - 2\lambda \Psi(0) \\ \frac{d}{dx} \psi_R(x) \Big|_{x=0} &= \frac{d}{dx} \psi_L(x) \Big|_{x=0} - 2\lambda \psi_L(0)\end{aligned}$$

Potential scattering in a box: Even

Continuity of function at $x=0$: $A_o = -B_o$

Continuity of derivative at $x=0$:

$$\left. \frac{d}{dx} \psi_R(x) \right|_{x=0} = \left. \frac{d}{dx} \psi_L(x) \right|_{x=0} - 2Z\Psi(0) \Rightarrow B_o k_n^+ = A_o k_n^+ - 2Z A_o \frac{\sin\left(\frac{1}{2} k_n^+ L\right)}{\cos\left(\frac{1}{2} k_n^+ L\right)}$$

$$-k_n^+ \cos\left(\frac{1}{2} k_n^+ L\right) = k_n^+ \cos\left(\frac{1}{2} k_n^+ L\right) - 2Z \sin\left(\frac{1}{2} k_n^+ L\right)$$

$$k_n^+ = Z \tan\left(\frac{1}{2} k_n^+ L\right)$$

$$\frac{k_n^+}{Z} = \tan\left(\frac{1}{2} k_n^+ L\right) \Rightarrow \frac{Z}{k_n^+} = \cot\left(\frac{1}{2} k_n^+ L\right)$$

Obtaining the phase shift

- We compare the odd and even functions for the delta well in a box with free odd and even functions at the same energy k_n

Odd: $\phi_{\text{free}}^-(x) = F_o \sin(k_n^- x)$

$$\psi_R^-(x) = B_o \sin(k_n^- x)$$

Even: $\phi_{\text{free}}^+(x) = F_e \cos(k_n^+ x)$

$$\begin{aligned}\psi_R^+(x) &= B' \sin\left(\frac{1}{2}k_n^+ L - k_n^+ x\right) \\ &= B' \cos\left(k_n^+ x + \left[\frac{\pi}{2} - \frac{1}{2}k_n^+ L\right]\right)\end{aligned}$$

$$\delta^+ = \frac{\pi}{2} - \frac{1}{2}k_n^+ L$$

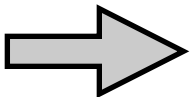
$$\tan \delta^+ = \tan\left(\frac{\pi}{2} - \frac{1}{2}k_n^+ L\right)$$

$$= \cot\left(\frac{1}{2}k_n^+ L\right)$$

Free:

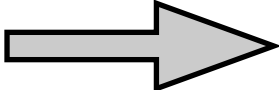
$$\delta^- = 0$$

$$\tan \delta^+ = \frac{Z}{k}$$



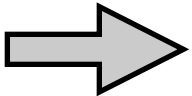
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Free:
 $\delta^- = 0$
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 $\tan \delta^+ = \tan\left(\frac{\pi}{2} - \frac{1}{2}k_n^+ L\right)$
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Obtaining the phase shift

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 $\delta^- = 0$
 $\tan \delta^+ = \frac{Z}{k}$

\longrightarrow $\delta^+ = \frac{\pi}{2} - \frac{1}{2}k_n^+ L$
 $\tan \delta^+ = \tan\left(\frac{\pi}{2} - \frac{1}{2}k_n^+ L\right)$ \longrightarrow $\tan \delta^+ = \frac{Z}{k_n^+}$
 $= \cot\left(\frac{1}{2}k_n^+ L\right)$

Scattering from a delta potential well: (TD)DFT

- Scattering with TDDFT: start with the N+1 electron system, then excite electron into the continuum
- We only have one electron. The KS potential is given by:

$$v_{\text{KS}}(x) = v_{\text{ext}}(x) + v_{\text{Hxc}}(x)$$

- For 1 electron: $v_{\text{x}}(x) = -v_{\text{H}}(x) \quad v_{\text{c}}(x) = 0$

- TDDFT corrections to KS are a result from xc-kernel

- Again for one electron: $v_{\text{Hxc}}(x, t) = 0 \longrightarrow f_{\text{Hxc}}(x, x', \omega) = 0$

- TDDFT case is equal to the exact case, i.e. box case = free case

DFT: 2 electrons in delta well in a box

- The KS potential is exponentially decaying and non-zero everywhere

$$v_s(x) = -Z\delta(x) + \lambda Z e^{-2Z|x|}$$

assume:
 $L \gg 1/Z$

- If we choose $L \gg 1/Z$ we can still use this potential within the box (we make an exponentially small error)
- To calculate the transmission coefficient we use that

$$t = e^{i(\delta^+ + \delta^-)} \cos(\delta^+ - \delta^-)$$

$$\delta^\pm = \frac{\pi}{4} - \frac{k_n^\pm L}{2} \pm \frac{\pi}{4}$$

- We need to find the energies k_n in the box

Free solution:

$$t_{\text{sing}} = t^0 \left(1 - \frac{2i\lambda k}{Z^2 + k^2} \right)$$

$$t_{\text{trip}} = t^0 = \frac{1}{1 + Z/ik}$$

DFT: 2 electrons in delta well in a box

- We treat the interaction potential as a perturbation
- The energies of the scattering states in the box:

$$\varepsilon_n = \varepsilon_n^0 + \delta\varepsilon_n$$

$$\delta\varepsilon_n = \langle n | \delta v | n \rangle = \lambda Z \int_{-L/2}^{L/2} dx e^{-2Z|x|} |\phi_n^0(x)|^2$$

- Inserting the orbitals for the delta well in a box, using $L \gg 1/Z$ and integrating, we obtain,

$$\delta\varepsilon_n = \frac{\lambda}{L} \cdot \frac{1}{1 + Z^2 / (k_n^0)^2}$$

- For either odd or even states

DFT: 2 electrons in delta well in a box

$$\delta\varepsilon_n = \frac{\lambda}{L} \cdot \frac{1}{1 + Z^2/(k_n^0)^2}$$

Remember that we are looking for an expression for k_n

$$\varepsilon_n = \varepsilon_n^0 + \delta\varepsilon_n$$

$$2\varepsilon_n = 2\varepsilon_n^0 + 2\delta\varepsilon_n$$

$$k_n^2 = (k_n^0)^2 + 2\delta\varepsilon_n$$

$$k^2 = 2\varepsilon$$

$$k_n = k_n^0 \sqrt{1 + 2 \frac{\delta\varepsilon_n}{(k_n^0)^2}} \approx k_n^0 + \frac{\delta\varepsilon_n}{k_n^0} = k_n^0 + \delta k_n$$

$$\delta k_n = \frac{\delta\varepsilon_n}{k_n^0}$$

DFT: 2 electrons in delta well in a box

$$\delta\varepsilon_n = \frac{\lambda}{L} \cdot \frac{1}{1 + Z^2/(k_n^0)^2}$$

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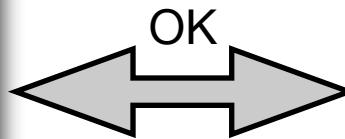
$$L\delta k_n = \frac{\lambda}{k_n^0} \cdot \frac{1}{1 + Z^2/(k_n^0)^2}$$

$$\delta^\pm = \frac{\pi}{4} - \frac{Lk_n^\pm}{2} \pm \frac{\pi}{4} = \frac{\pi}{4} - \frac{Lk_n^0}{2} - \frac{L\delta k_n}{2} \pm \frac{\pi}{4}$$

$$t = e^{i(\delta^+ + \delta^-)} \cos(\delta^+ - \delta^-)$$

- We finally obtain for the KS transmission in a box:

$$\begin{aligned} t_s &= t^0 e^{-i\lambda/k_n(1+Z^2/k_n^2)} \\ &= t^0 \left(1 - \frac{i\lambda k_n}{Z^2 + k_n^2} \right) \end{aligned}$$



Free answer:

$$t_s = t^0 \left(1 - \frac{i\lambda k}{Z^2 + k^2} \right)$$

TDDFT: 2 electrons in delta well in a box

- Singlet case:
- We make the small matrix approximation (SMA) to obtain the Omega matrix of Casida's equations:

$$\Omega^S = \omega_{0,n} + \langle 0, n | f_{\text{Hx}} | 0, n \rangle \rightarrow \begin{aligned} \varepsilon_n &= \varepsilon_n^s + \langle 0, n | f_{\text{Hx}} | 0, n \rangle \\ &= \varepsilon_n^0 + \langle n | \delta v | n \rangle + \langle 0, n | f_{\text{Hx}} | 0, n \rangle \end{aligned}$$

$$\langle 0, n | f_{\text{Hx}} | 0, n \rangle = 2\lambda Z \int_0^{L/2} e^{-2Z|x|} |\phi_n(x)|^2 dx = \langle n | \delta v | n \rangle$$

$$t_{\text{sing}} = t^0 \left(1 - \frac{2i\lambda k_n}{Z^2 + k_n^2} \right)$$

- Triplet case:

- $f_{\text{Hx}}=0 \rightarrow t_{\text{trip}} = t^0$

Exact:

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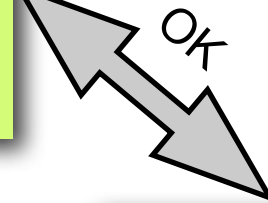
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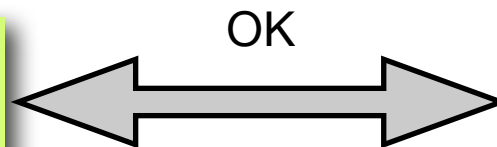
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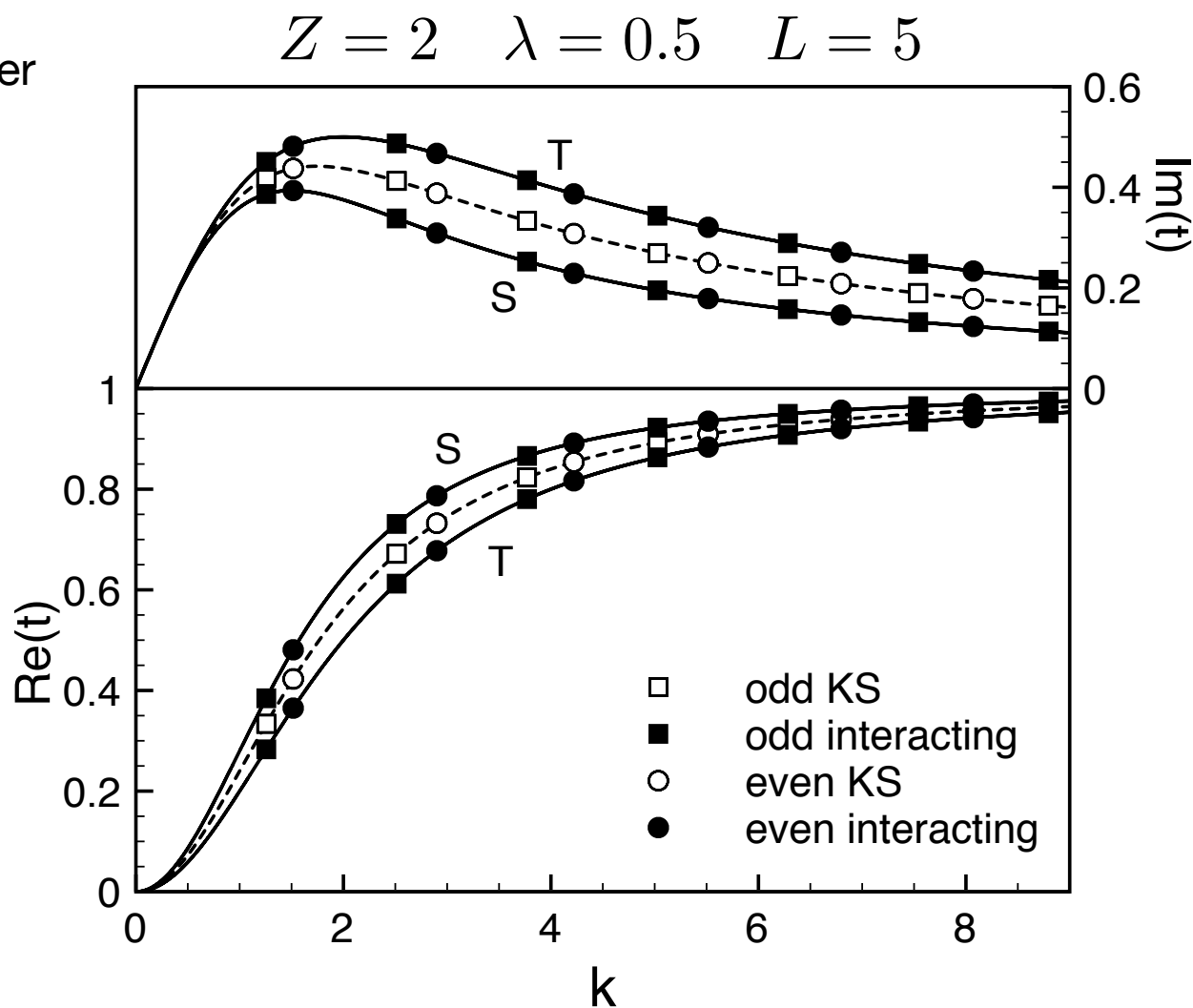
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(TD)DFT: 2 electrons in delta well in a box

- The box values at a finite number of k_n values, correspond to the continuum values



General spherical systems

$$\left(-\frac{1}{2} \frac{d^2}{dr^2} + \frac{l(l+1)}{2r^2} + V(r) \right) \phi_l(r) = E \phi_l(r)$$

- The general solution for this equation when $V(r)$ is short ranged:

$$u_s(r) = kr j_l(kr) \quad u_c(r) = kr n_l(kr)$$

$$\begin{aligned} u(r) &= Au_s(r) + Bu_c(r) \\ &= \sqrt{A^2 + B^2} \left[\frac{A}{\sqrt{A^2 + B^2}} u_s(r) + \frac{B}{\sqrt{A^2 + B^2}} u_c(r) \right] \\ &= \sqrt{A^2 + B^2} [\cos(\delta) u_s(r) + \sin(\delta) u_c(r)] \end{aligned}$$

- at $r=R$: $u(R) = A k R j_l(kR) + B k R n_l(kR) = 0$

k can be obtained
from (TD)DFT
calculation in a box

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$$\tan \delta_l = \frac{\sin \delta}{\cos \delta} = \frac{B}{A} = -\frac{j_l(kR)}{n_l(kR)}$$

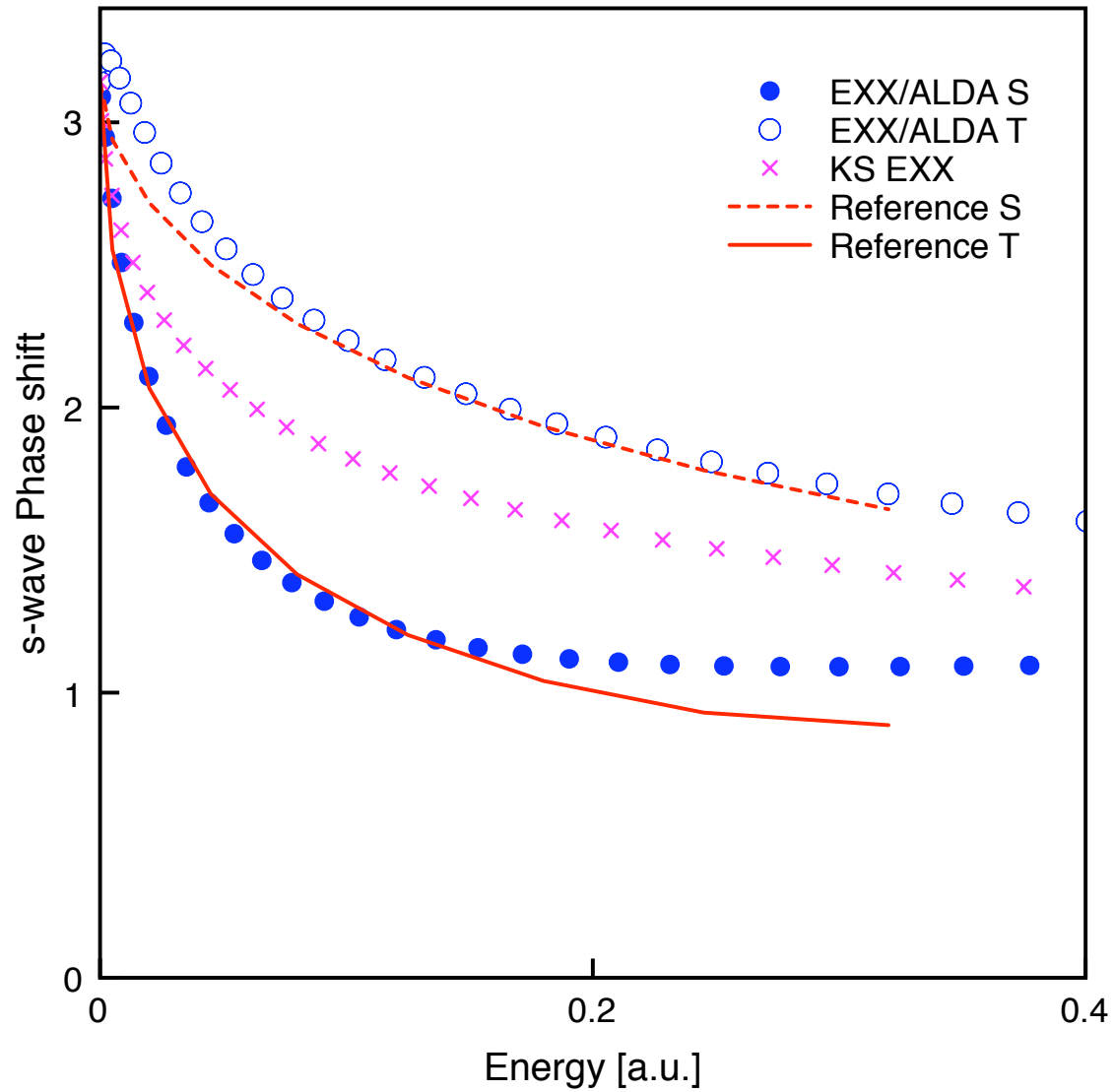
k can be obtained
from (TD)DFT
calculation in a box

Real-life examples: atoms

- Do a ground state DFT calculation for the (N+1)-electron system
- Obtain KS phase shifts from KS orbital energy differences: $k_n^{\text{KS}} = \sqrt{2\varepsilon_n} - \sqrt{2\varepsilon_0}$
- Do a TDDFT calculation, exciting one electron into the continuum
- Obtain the TDDFT phase shifts from the excitation energies
- Examples: e-H (start from H⁻) and e-He⁺ (start from He)

- Used a grid code that solves the radial KS equations

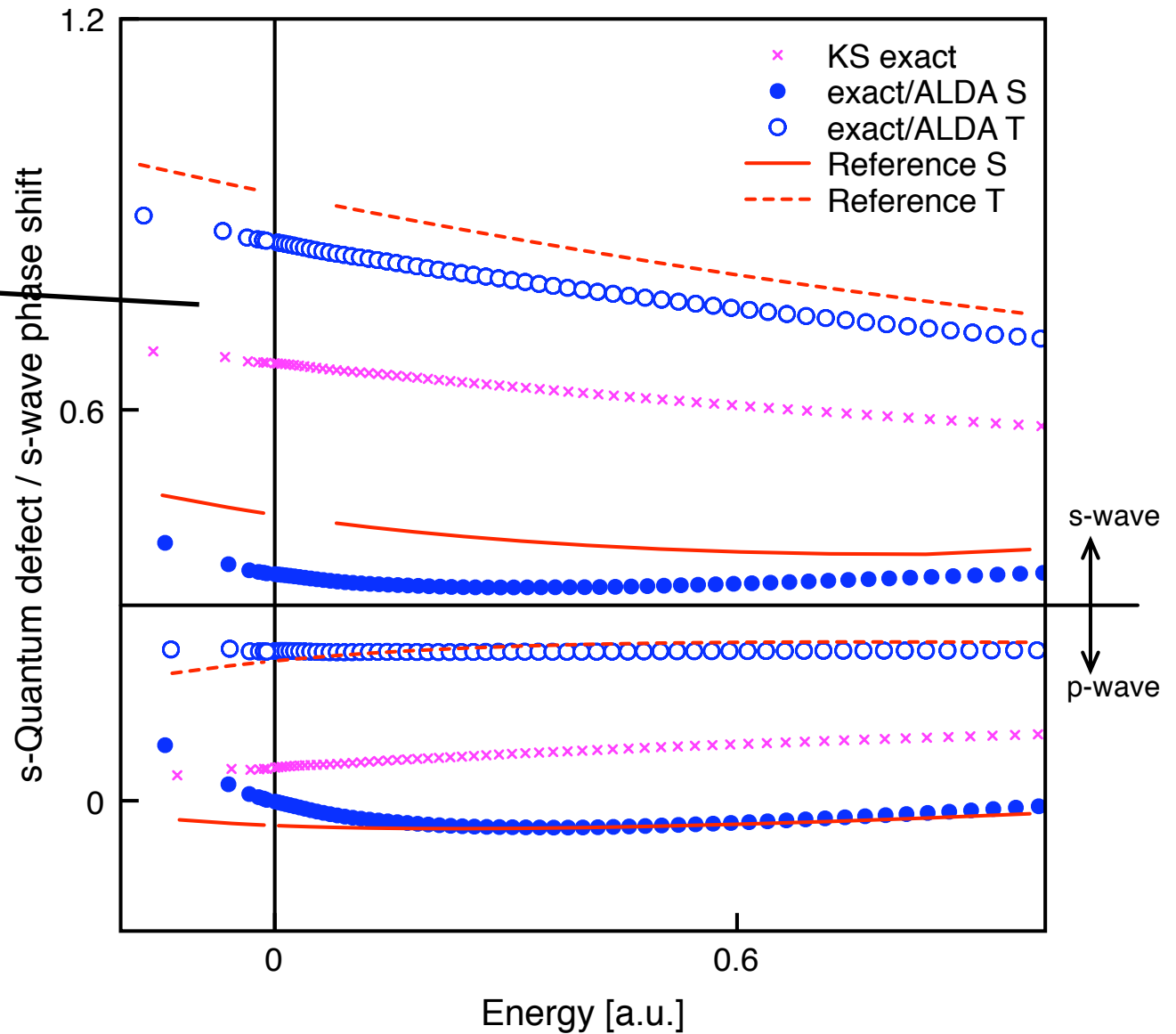
e-H scattering



e-He+ scattering

$$\omega_n = I - \frac{1}{2(n - \mu_{nl})^2}$$

Seaton's theorem:
Smooth transition from quantum defect to phase shift



Towards molecules with TDDFT: basis sets

- Grid code can be used for atoms
- For efficient calculation of molecules most codes use basis sets (Gaussians)
- Want to use ADF code: how to include a wall?
- Adapt the STO basis set

Towards molecules....

- If all basis functions are 0 at the wall radius R and beyond, than any linear combination of them (i.e. AOs and MOs) must also be 0: we implicitly include a wall

$$\phi_{nlm}^{\text{BSTO}}(r, \theta, \phi) = N f(r; R) \phi_{nlm}^{\text{STO}}(r, \theta, \phi)$$

$$f(r; R) = \begin{cases} \left(1 - \frac{r}{R}\right) & r \leq R \\ 0 & r > R \end{cases}$$

$$\phi_{nlm}^{\text{STO}}(r, \theta, \phi) = r^{n-1} e^{-\alpha r} Y_{lm}(\theta, \phi)$$

- A smaller wall distance R limits the number of functions necessary but it must be outside of the range of the density and/or the range of the occupied orbitals.

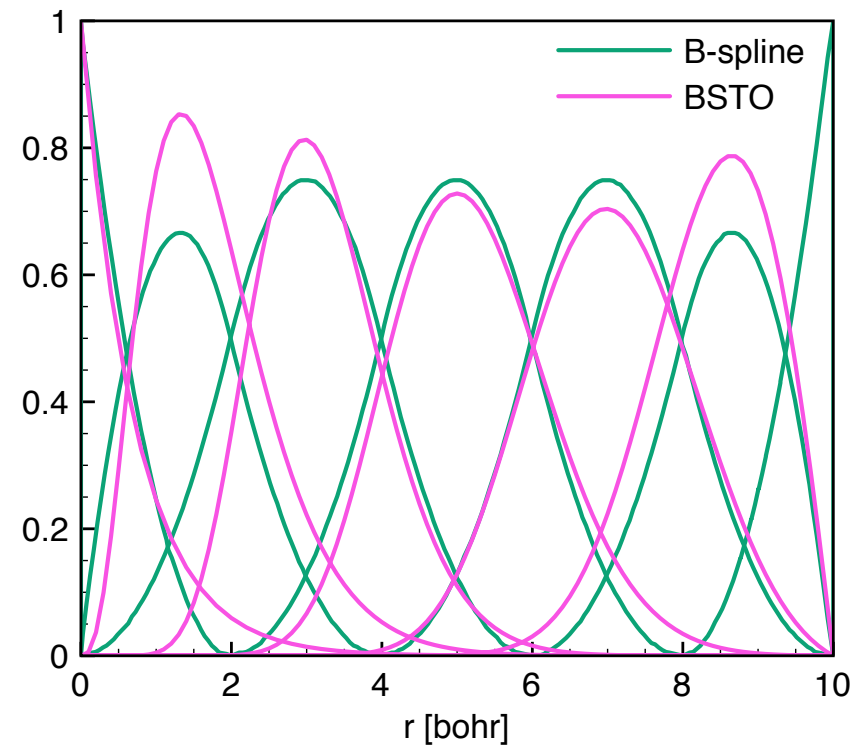
Towards molecules....

- If we choose the parameters n and α in a smart way, we can generate a basis set that is suitable for describing oscillating functions

- At a BSTO function maximum ($n > 1$) we have the relation

$$\alpha = \frac{r + n(r - R)}{r(r - R)}$$

- The maxima are distributed evenly and n determines the “width” of the functions (n is chosen, α determined by n and R)



Towards molecules.....

