Scattering of H atoms on a Kr atom

Advanced Computational Physics - Exercise 1

Vincenzo Zimbardo, Teresa Dalle Nogare, Alexander Ferraro

March 29, 2022

Abstract

In this project we implemented using the C language the Numerov's algorithm to solve two types of problems: find the bound states and find the cross-section of a scattering process. Fistly, we found the bound states for a 1D harmonic oscillator, then we switched to a 3D harmonic system and compared the results with the analytical theory. Regarding the scattering problem, we implemented a program which produces the right Bessel functions; these were properly compared to the ones computed exploiting the GSL library. Then, we computed the cross section of an H atom on a Kr atom and compared the result with the J.P.Toennies' article.

1 1D HARMONIC OSCILLATOR: BOUND STATES

1.1 Theory 1D harmonic oscillator

The problem of finding the first 5 eigenvalues for a 1D quantum harmonic oscillator has been solved by considering the action $\hbar$, mass m and frequency ω as natural units.
The derived units have been expressed in terms of the fundamental ones as:

- Energy : $E_0 = \hbar\omega$
- Length : $x_0 = \sqrt{\frac{\hbar}{m\omega}}$

Given the Hamiltonian for a 1D harmonic oscillator, the Schrödinger equation for a generic wave function $\psi(x)$ is given by:

$$\frac{d^2}{dx^2}\psi(x) = F(x)\psi(x), \tag{1}$$

with $F(x) = (-2E + x^2)$, that is in the appropriate form to apply the Numerov algorithm.
For this system, analytical results for the spectrum of energies and for the corresponding eigenfunctions can be determined according to:

$$E_n = n + \frac{1}{2}, \qquad n = 0, 1, 2, ... \tag{2}$$

$$\psi_n(x) = \frac{1}{\sqrt{2^n n!}}\pi^{-1/4}\exp\{-x^2/2\}H_n(x) \tag{3}$$

where $H_n(x)$ are the Hermite polynomials.

1.2 Problem setup and result discussion

A numerical procedure for determining the wave function, solution of the equation (1), has been obtained exploiting the Numerov's algorithm.

In the first part of the project, a set of parameters has been fixed. A value for the interval length `L = 6.0` and for the spatial increment `h = 1e-3` have been properly chosen so that the `n = 5` eigenvalues are held within the potential.

The procedure implemented to find the bound states is based on the regular behaviour of the wave function. In particular, we know that it has to have a continuous logarithmic derivative and this is true only for that functions that satisfy the equation, *i.e.* only when we consider the correct energy.
To exploit this fact numerically, we run the Numerov's algorithm twice for every value of E, one from the left-hand side, obtaining $\psi_L(x)$, and one from the right-hand side, for $\psi_R(x)$. Then we impose separately the continuity (adjusting the normalization of one of the two functions) and the continuity of the derivative at one point x_0, using the relation:

$$\begin{aligned}\Delta(E) &= \psi'_L(x_0) - \psi'_R(x_0) \\ &= \frac{\psi_L(x_0 - h) + \psi_R(x_0 + h) - [2 + h^2 F(x_0)]\psi_L(x_0)}{h}\end{aligned}$$

The point x_0 has to be chosen inside the classical allowed region. Accordingly, we chose it in proximity of the classical inversion point, that is $x_0 = \sqrt{2E}$. This is because outside the classical allowed region, if we consider the incorrect energy the wave function diverges exponentially and this could cause numerical problems. Moreover it is better not to choose this point in the minimum of the potential, because at the end we would calculate the zeros of the function $\Delta(E)$, and if x_0 is the minimum of the potential, from symmetry considerations also the wave function would have a zero derivative. Therefore we would calculate differences of very small numbers, and also this could cause numerical problems. In order to compute the zeros of $\Delta(E)$ we consider the following algorithm:

- Start from E_{min} and calculate $\Delta(E_{min})$
- Slightly increase the energy and calculate the corresponding $\Delta(E)$, until $\Delta(E_{min})\Delta(E) < 0$.
- At this point we are able to find an appropriate interval in which use the bisection algorithm.
- Update E_{min} and restart for the excited states

Another thing to say is about the initial conditions. The differential equation we have to solve is (1). We can

consider the asymptotic behaviour, for $|x| >> 1$:

$$\psi''(x) \sim x^2\psi(x) \tag{4}$$

The only normalizable solution of this equation goes asymptotically like a gaussian. Moreover we know that for the excited states the sign of the function at the edge of the domain depends on the principal quantum number. So, in order to take all of these into account we set as initial conditions:

```
#initial condition 1D_ho
/* wave function */
psi[0]=pow(x[0]/fabs(x[0]),n)*exp(-x[0]*x[0]/2.0);
psi[1]=pow(x[1]/fabs(x[1]),n)*exp(-x[1]*x[1]/2.0);
```

In this way we are able to take into account the different values of `psiL[0]` and `psiR[0]` according to the value of `xL[0]` and `xR[0]`.

In order to find the first 5 eigenvalues, the zeroes of the function $\Delta(E)$ have been determined exploiting the bisection method. The obtained eigenvalues have been collected in the vector `E_bound[n]` and the corresponding eigenfunctions have been generated by performing the Numerov's method for these values of energy.

Furthermore, we noticed that the algorithm is already stable for `h=1e-3`. From the theory we know that the Numerov's algorithm error goes like h^4, so reducing the step theoretically we would get a bigger precision. Nevertheless, the resolution of our code is less than h^4, hence by shrinking the step the results doesn't change meaning that the algorithm is already stable for our resolution scale.

The obtained values computed for the eigenvalues are reported in table (1),

`n`	`E_bound[n]`	E^{th}_{bound}
n = 0	0.500	0.500
n = 1	1.500	1.500
n = 2	2.500	2.500
n = 3	3.500	3.500
n = 4	4.500	4.500

Table 1: First 5 eigenvalues obtained through the Numerov algorithm,`E_bound[n]`, and theoretical results obtained through eq.(2), E^{th}_{bound}.

As an example, the eigenfunctions corresponding to $n = 0$ and $n = 4$ are reported in Figure (1) and Figure (2) respectively.

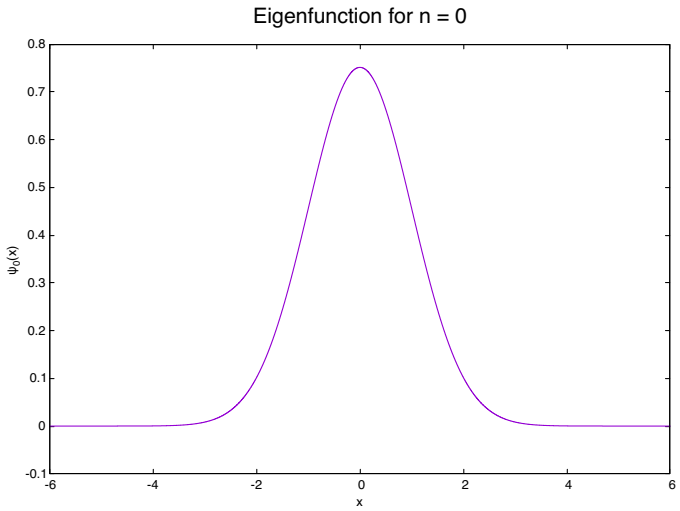

Figure 1: The picture shows the eigenfunction for $n = 0$ computed with Numerov. We used as increment step $h = 10e - 3$.

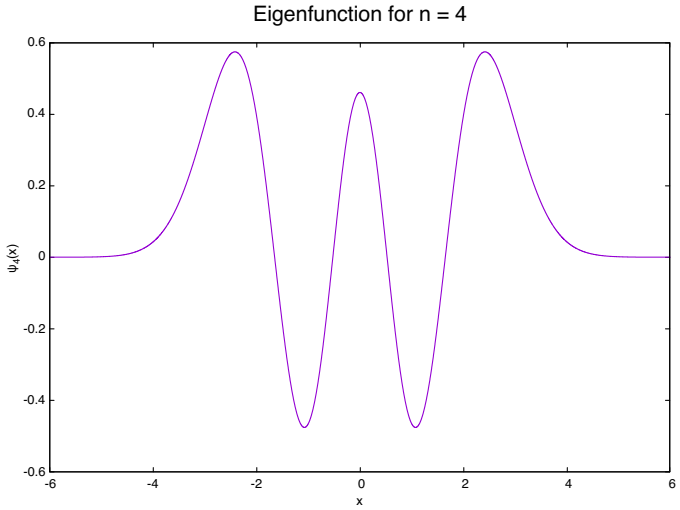

Figure 2: The picture shows the eigenfunction for $n = 4$ computed with Numerov. We used as increment step $h = 10e - 3$

2 3D HARMONIC OSCILLATOR: BOUND STATES

2.1 Theory 3D harmonic oscillator

The 3D quantum harmonic oscillator has no further complexity with respect to the 1D problem, other than the dimension. The problem of finding the eigenvalues and eigenfunctions can be stated by starting from the time independent Schrödinger equation in spherical coordinates:

$$\left(-\frac{\hbar^2}{2mr}\frac{\partial^2}{\partial r^2}r + \frac{L^2}{2mr^2} + \frac{1}{2}m\omega^2 r^2\right)\psi(\mathbf{r}) = E\psi(\mathbf{r}) \tag{5}$$

It is worth noticing that both operators L^2 and L_z commute with the Hamiltonian because of the radial symmetry of the potential. Accordingly, the total wave function describing the system can be separated into its radial and angular part:

$$\psi_{nlm}(r,\theta,\phi) = R_n(r)Y_{lm}(\theta,\phi) \tag{6}$$

where $Y_{lm}(\theta,\phi)$ are the well known spherical harmonics. This yields to a purely radial Schrödinger equation:

$$-\frac{\hbar^2}{2m}\frac{d^2u(r)}{dr^2} + \left(\frac{\hbar^2 l(l+1)}{2mr^2} + V(r)\right)u(r) = Eu(r) \tag{7}$$

in which the reduced wave function

$$u(r) = rR(r) \tag{8}$$

has been introduced.
Analogously to the 1D case, the action $\hbar$, mass m and angular frequency ω have been considered as natural units. With this choice, the dimensionless Schrödinger equation is given by:

$$\frac{d^2}{dr^2}u(r) = \underbrace{\left(r^2 + \frac{l(l+1)}{r^2} - 2E\right)}_{F(r)}u(r) \tag{9}$$

Since the radial problem is equivalent to solve the 1D harmonic oscillator problem with an effective potential $V_{\text{eff}}(r) = r^2 + \frac{l(l+1)}{r^2}$, the Numerov's algorithm can be used.
Lastly, the eigenvalue problem yields to the energy values of the bound states:

$$E_{kl} = \hbar\omega(\underbrace{2k+l}_{n}+\frac{3}{2}) \tag{10}$$

which are labelled by 2 quantum numbers, namely a non negative integer k and l.

2.2 Problem Setup and results

In the first part of the project, the spatial interval has been chosen to be limited in the range `[h:L]`, spanned with a step `h = 1e-3`. It is worth mentioning that starting from exactly zero would have led us to severe divergences in our code.
From the theory one knows that the asymptotic behavior of the reduced wave function is

$$u(r) \sim \begin{cases} r^{l+1}, & r \to 0 \\ \exp\left\{-\frac{r^2}{2}\right\}, & r \to \infty \end{cases} \tag{11}$$

These again can be found analyzing the asymptotic equations. So the initial conditions for the Numerov's method can be set up

```
#initial_condition_3ho
/* position */
  xL[0] = h;
  xL[1] = xL[0] + h;

  xR[0] = L;
  xR[1] = xR[0] - h;

  /* wave function */
  psiL[0] = pow(xL[0],l+1);
  psiL[1] = pow(xL[1],l+1);

  psiR[0] = exp(-xR[0] * xR[0] / 2.0);
  psiR[1] = exp(-xR[1] * xR[1] / 2.0);
```

By using the same algorithm of the 1D harmonic oscillator we solved equation (9) for 3 different value of l, more precisely $l = 0, 1, 2$.

The obtained values of the bound states energies for different l are reported in Table (2):

l	k	`E_bound[n]`	E^{th}_{bound}	acc. ratio
0	0	1.500	1.5	10e-3
0	1	3.500	3.5	10e-3
0	2	5.500	5.5	10e-3
1	0	2.500	2.5	10e-3
1	1	4.500	4.5	10e-3
1	2	6.499	6.5	10e-3
2	0	3.499	3.5	10e-3
2	1	5.499	5.5	10e-3
2	2	7.499	7.5	10e-3

Table 2: The table reports the results of the computed energies for each l and k. These are compared with the analytical value.

Once the right energy eigenvalues are calculated with certain precision ϵ, that we initially set to $\epsilon = 10e-3$, we calculated the correspondent radial eigenfunction $u(r)$.
Some of the radial wave function $u(r)$ are shown in figure (3),(4) and (5).

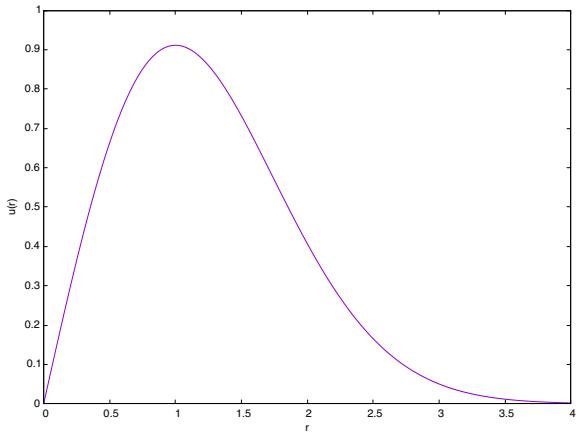

Figure 3: This figure shows $u(r)$ that has been computed for the first eigenvalue $E_{00} = 1.5$ - $k = 0$ and $l = 0$ - exploiting the Numerov's method. The eigeinfuction is reported over a mesh from `h` to `4.0`, taking as step `h = 1e-3`

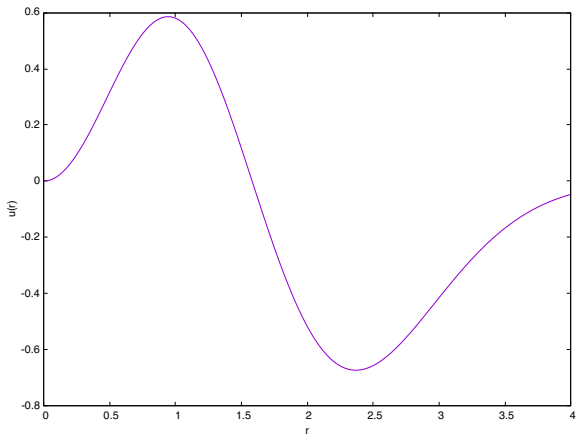

Figure 4: This figure shows $u(r)$ that has been computed for the first eigenvalue $E_{11} = 4.5$ - $k = 1$ and $l = 1$ - exploiting the Numerov's method. The eigeinfuction is reported over a mesh from `h` to `4.0`, taking as step `h = 1e-3`

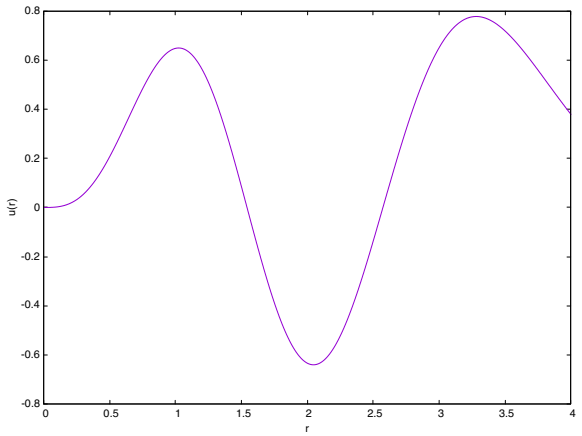

Figure 5: This figure shows $u(r)$ that has been computed for the first eigenvalue $E_{22} = 7.5$ - $k = 2$ and $l = 2$ - exploiting the Numerov's method. The eigeinfuction is reported over a mesh from `h` to `4.0`, taking as step `h = 1e-3`

3 SCATTERING OF H ATOMS ON A Kr ATOM

3.1 Theory

The aim of this part of the project is to determine the total scattering cross section deriving from the interaction of H atoms with a Kr atom. The problem has been formulated in terms of reduced units in which the typical length $\sigma = 3.18$ Å and energy $\epsilon = 5.9$ meV have been chosen as fundamental units.
The interaction between particle is well described by a reduced Lennard-Jones potential given by the expression

$$v(r) = 4\ (r^{-12} - r^{-6}) \tag{12}$$

Because of the radial symmetry of the potential, the Schrödinger equation for the total wave function $\psi(r, \theta, \phi) = R(r)\ \mathcal{Y}_{lm}(\theta, \phi)$ is restricted to a one dimensional equation for the radial part $u(r) = rR(r)$

$$-\frac{\hbar^2}{2\mu}\frac{d^2}{dr^2}u(r) + \left(v(r) + \frac{\hbar^2 l(l+1)}{2\mu r^2}\right)\ u(r) = E\ u(r)$$

in which μ represents the reduced mass of the system. By introducing the dimensionless parameter

$$\xi = \frac{\hbar^2}{2\mu\sigma^2\epsilon}$$

the radial Schrödinger equation can be reformulated as :

$$\frac{d^2}{dr^2}u(r) = \frac{1}{\xi}\left(v(r) + \frac{\xi l(l+1)}{r^2} - E\right)u(r) \tag{13}$$

This equation can be numerically integrated through the Numerov's method and the value of $u(r)$ can be obtained for various values of l. Then, the total cross section $\sigma_{tot}(E)$ can be obtained as a function of the energy by

$$\sigma(E) = \sum_l \frac{4\pi}{k^2}(2l+1)\sin{\delta_l}^2, \quad k = \sqrt{\frac{E}{\xi}} \tag{14}$$

The values for the phase shifts δ_l are determined through the expression

$$\tan\delta_l = \frac{j_l(kr_2) - Kj_l(kr_1)}{n_l(kr_2) - Kn_l(kr_1)}, \quad K = \frac{u(r_1)}{r_1}\frac{r_2}{u(r_2)} \tag{15}$$

in which the Bessel functions $j_l(kr)$ and Neumann functions $n_l(kr)$ are evaluated in two positions r_1 and r_2 where the potential is approximately zero.

3.2 Problem setup and result discussion

3.2.1 Bessel functions

In order to compute the Bessel functions we implement an algorithm that uses the recursive following formula:

$$s_{\ell+1}(x) = \frac{2\ell+1}{x}s_\ell(x) - s_{\ell-1}(x) \tag{16}$$

in which s_l could be either a j_l or a n_l. The recursion formula is defined, since we know the initial functions:

$$j_{-1}(x) = \frac{cos(x)}{x} \qquad j_0(x) = \frac{sin(x)}{x} \tag{17}$$

$$n_{-1}(x) = \frac{sin(x)}{x} \qquad n_0(x) = -\frac{cos(x)}{x} \tag{18}$$

We implement a function to use this recursive formula, then we compare the obtained functions with the ones calculated with the GSL library, and they result the same, as it is possible to see from the following graphs:
As we can appreciate from figure (6) and figure (7) we

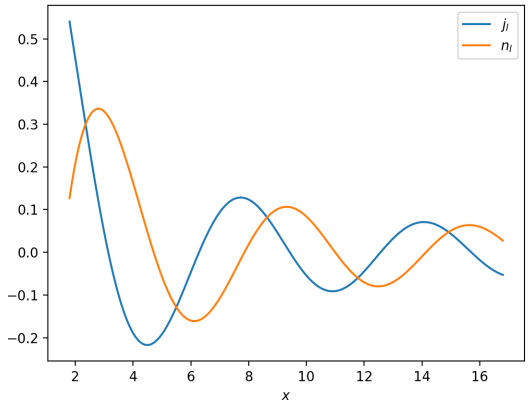

Figure 6: This figure shows the theoretical Bessel's functions taken from the GSL library

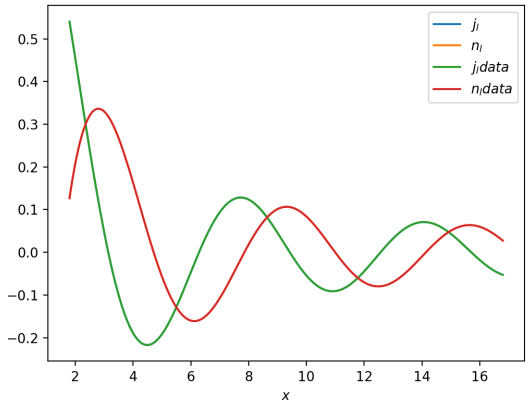

Figure 7: This figure instead shows the computed Bessel's functions over the theoretical ones

see that with the implemented algorithm we get the same theoretical Bessel's functions. In the following programs we used the functions from the GSL library.

3.2.2 Natural units

The Schrodinger equation with the Lennard-Jones potential suggest a choice of "natural" units, in particular it suggests to use as a fundamental units the action $S_0 = \hbar$, the length $\ell_0 = \sigma$ and the energy $E_0 = \varepsilon$. With these choices other parameters, for example the mass, is not a fundamental units but a derived one, in particular the mass scale is defined by $m_0 = S_0^2/(E_0\ell_0^2) = \hbar^2/\varepsilon\sigma^2$. Therefore, the parameter $\hbar^2/2m$ in natural units is:

$$\frac{\hbar^2}{2m^* m_0} = \frac{\varepsilon\sigma^2}{2m}$$

Where m^* is the reduced mass, *i.e.* the (adimensional) mass in reduced units. We can also notice that the parameter ξ that appears in the Schrodinger is $1/2m$ in reduced units.

3.2.3 Asymptotic solution

If we consider the asymptotic limit of (13) for $r \to 0^+$ we obtain the following equation:

$$u''(r) = \frac{4}{\xi}\frac{u}{r^{12}}$$

This equation can be rewritten as:

$$\left(\frac{u'}{u}\right)^2 + \frac{d}{dr}\left(\frac{u'}{u}\right) = \frac{4}{\xi}\frac{1}{r^{12}}$$

In the $r \to 0$ limit, since we consider only the normalizable solutions, we can neglect the second term in the left hand side of the equation, and therefore the wavefunction is approximately equal to the solution of

$$\frac{u'}{u} = \sqrt{\frac{4}{\xi}} r^{-6} \tag{19}$$

that is

$$u \simeq \exp\left[-\sqrt{\frac{4}{25\xi}} r^{-5}\right] \tag{20}$$

That is indeed in the form $u \simeq A\exp\{-(b/r)^5\}$. In the numerical implementation, we noticed that this initial condition yields to very small numbers, so to avoid possible numerical problems we have considered a large value for A (we have the freedom to choose it, since the Schrodinger equation is linear, so we can choose the normalization we want, and possibly normalize again at the end).

In the first part of the project, we calculate the dimensionless parameter ξ using the numerical value of the parameter of the Lennard-Jones potential and the resulting value is $\xi = 0.0352$.
A vector describing the spatial coordinates `r[dim]` has been initialized with a step of `dr = 0.01`, fixing the initial value to `r[0] = 0.5`. The initial conditions are chosen according to (20). Two points at the end of the vector `r[dim]` have been chosen to be in the region in which the contribution of the potential is approximately negligible. Thus, a series of wave functions have been generated for $l < l_{max}$ by exploiting the Numerov's algorithm. The relative phase shifts δ_l have been calculated making use of the function

```
double phase_shift(double r1, double r2, double u1,
    double u2, double k, int l, FuncBessel *f1,
    FuncBessel *f2)
```

Finally, the value of the total cross section has been calculated according to equation (14). This procedure has been performed for values of energy between `E_start = 0.1` and `E_end = 3.5`.

3.2.4 Small variation of r_{low} and r_{max}

We modified our Numerov code to verify how the effect of small variations on r_{low} or on the two points after r_{max} influence the phase shifts. The result of simulations are showed in Table (3). We notice that there are no relevant changes in the phase shifts after a small variation on the two points or r_{low}.

3.2.5 Total cross section

The resulting total cross section as a function of energy is shown in Figure (8). In order to compare the computed cross section with the one in the article, we plot the cross section in units of $Å^2$.

	no variation $r_{low} = 0.5$ $r_{1,2} = 5.75, 5.95$	r_{low} var $r_{low} = 0.4$ $r_{1,2} = 5.75, 5.95$	$r_{1,2} > r_{max} = 5\sigma$ var $r_{low} = 0.5$ $r_{1,2} = 5.52, 5.90$
δ_0	-0.6349	-0.6350	-0.6350
δ_1	0.6454	0.6454	0.6454
δ_2	-1.5167	-1.5168	-1.5168
δ_3	-0.8599	-0.8599	-0.8599
δ_4	-0.5656	-0.5656	-0.5656
δ_5	-1.0122	-1.0122	-1.0122
δ_6	0.3645	0.3645	0.3645

Table 3: This table shows how the phase shifts change for small variation of r_{low} and small variation of the two point after r_{max}, namely $r_{1,2}$.

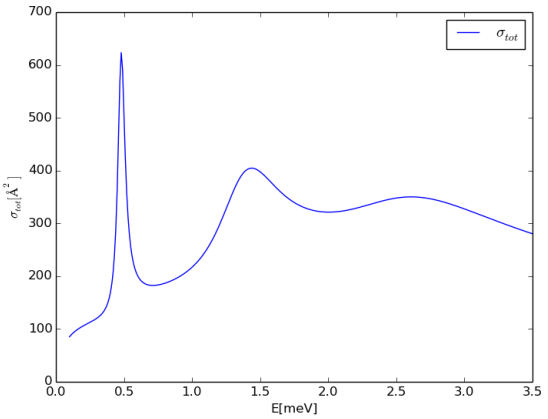

Figure 8: Total cross section as a function of energy $0 < E < 3.5meV$, and the cross section is given in $Å^2$.

Lastly, we compared the total cross section with the one in the J.P.Toennies' article. We obtained the same number of peaks as in the article, and also the heights reach the same values.