Advanced Computational Physics - Exercise I

Leonardo Chiesa

Scattering of H atoms on a Kr atom

The aim of this numerical exercise is to compute the total cross section of a H-Kr scattering process and justify in this way the experimental results described in the paper by J.P.Toennies, W.Welz and G.Wolf, J. Chem. Phys. 71, 614 (1979). We assume that the interaction between the two atoms is modelled by a Lennard-Jones potential:

$$v(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] \tag{1}$$

where $\varepsilon = 5.9$ meV and $\sigma = 3.18$ Å.
The cross section will be computed by finding the phase shifts from the radial solution of the Schrödinger equation. The latter will be built by implementing the Numerov algorithm for the solution of differential equations. But before doing that, one should first consider a simpler case (like the harmonic oscillator in one dimension) in order to check that its code is working well.

1 1D Harmonic Oscillator

The stationary Schrödinger equation for the one dimensional harmonic oscillator is:

$$H_{1D}\phi_n(x) = E_n\phi_n(x)$$

where the dimensionless Hamiltonian ($\hbar = m = \omega = 1$) is given by:

$$H_{1D} = -\frac{1}{2}\frac{d^2}{dx^2} + \frac{1}{2}x^2 \tag{2}$$

So the full equation is:

$$-\frac{1}{2}\frac{d^2}{dx^2}\phi_n(x) + \frac{1}{2}x^2\phi_n(x) = E_n\,\phi_n(r)$$

and can be rewritten in a suitable form for the application of the Numerov method in the following way:

$$\frac{d^2}{dx^2}\phi_n(x) + k^2(x)\phi_n(x) = 0 \qquad\qquad k^2(x) = 2\left(E_n - \frac{1}{2}x^2\right) \tag{3}$$

This algorithm is able to solve a differential equation by computing the solution at a certain point of the mesh starting from the values in the previous two points (since the equation is of the second order):

$$y_{i+1} = \frac{y_i(2 - 5/6\,h^2k_i^2) - y_{i-1}(1 + h^2/12\,k_{i-1}^2)}{1 + h^2/12\,k_{i+1}^2} \tag{4}$$

In the code the solution was propagated from a minimum position $x_{min} = 0$ to a maximum position $x_{max} = 10$ with a number of steps equal to $n_{step} = 10000$. The initial conditions have been calculated from the analytic solution of the equation in the limit of $x \to 0$:

$$\frac{d^2}{dx^2}\phi_n(x) + 2E_n\phi_n(x) \simeq 0 \qquad \phi_n = A_n \sin(\sqrt{2E}x) + B_n \cos(\sqrt{2E}x)$$

In particular one knows that the harmonic oscillator eigenfunctions are odd for a odd value of the principal quantum number n and therefore the solution must go to zero in the origin (and then the coefficient B_n has to be zero). On the other hand the eigenfunctions labelled by an even n are even and so in this case we can have a value of B_n different from zero.
The propagation has been implemented in a function that returns the value of the solution in x_{max}:

```
double k(double r, double E) {
  return 2*E-r*r;
}

double findzeros(double E, int n) {
  double x, xmin = 0, xmax = 10;
  int nstep = 10000;
  double h = (xmax-xmin) / (double) nstep;
  double k0, k1, k2, y0, y1, y2;
```

```
    k0 = k(xmin, E);
    k1 = k(xmin + h, E);

    if(n%2==0){
        y0 = 1;
        y1 = cos(sqrt(2*E)*(xmin+h));
    } else {
        y0 = 0;
        y1 = sin(sqrt(2*E)*(xmin+h));
    }

    for(x=xmin;x<xmax;x+=h) {
        k2 = k(x+2*h, E);
        y2 = (double) (y1*(2.-5./6.*h*h*k1)-y0*(1.+1./12.*h*h*k0)) /
            / (1.+1./12.*h*h*k2);
        y0 = y1;
        y1 = y2;
        k0 = k1;
        k1 = k2;
    }

  return y2;
}
```

Since the condition for E_n to be an eigenvalue of the Hamiltonian is that it has to lead to a square integrable solution, by looking at the sign changes of the function in the final point of the mesh one can identify some energy intervals that contain the eigenvalues E_n. This was done with a scan of the function "findzeros()" in the energy range $E \in [0, 5]$ with a number of steps equal to 1000. Then, for each energy range found, in an arbitrarely chosen middle point ($x_{mid} = 0.5$) the secant method was applied in order to find the zero of the difference of the logarithmic derivatives of the forward and backward propagations (this is possible since the Numerov algorithm is reversible). In particular the leftward solution was computed starting from x_{max} with two initial values sufficiently close to zero.
Here are the results found for the first 5 solutions (eigenvalues and eigenfunctions). The functions can be easily extended to the negative x semiaxis just by considering their symmetry properties: they are odd functions when n is odd whereas they are even when n is even (n is the quantum number that corresponds to the number of nodes of the solution). Moreover they have been normalized through the division by the square root of their integral,

computed with the Simpson rule.

n	E_n
0	0.50000
1	1.50113
2	2.50056
3	3.50169
4	4.50085

Table 1: First 5 eigenvalues of the 1D dimensionless harmonic oscillator ($n_{step} = 10000$)

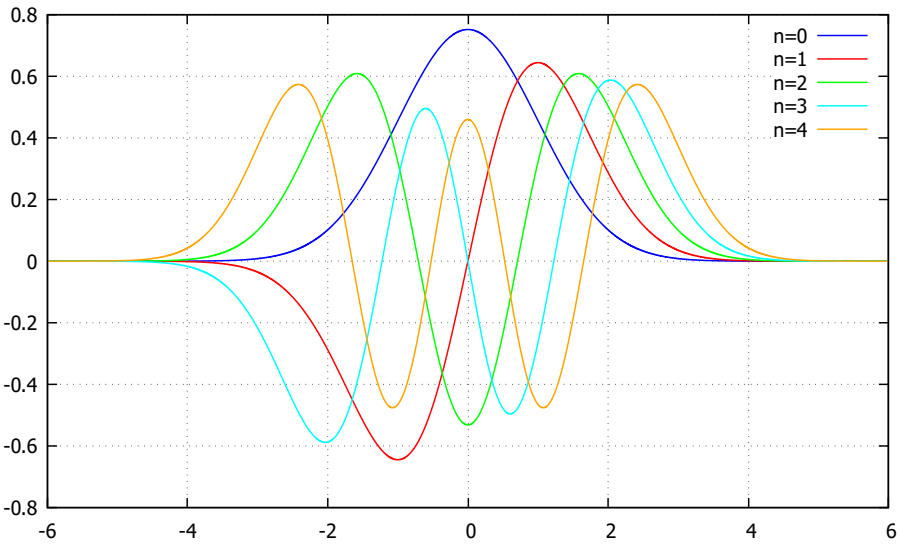

Figure 1: First 5 eigenfunctions of the 1D dimensionless harmonic oscillator

The obtained results agree with the theoretical prediction ($E_n = n + 1/2$) with an error smaller than 1%. The accuracy gets better by increasing the number of points of the mesh to the detriment of the running time. On the other hand if we make the grid less dense the error gets worse, for example with a number of steps in the propagation equal to 100 the energies are:

n	E_n
0	0.49995
1	1.63010
2	2.55741
3	3.69265
4	4.58564

Table 2: First 5 eigenvalues of the 1D dimensionless harmonic oscillator ($n_{step} = 100$)

2 3D harmonic oscillator

The procedure described in the last section can be easily generalized for the solution of the Schrödinger equation for a 3-dimensional isotropic harmonic oscillator:

$$H_{3D}\phi_{nl}(\vec{r}) = E_{nl}\phi_{nl}(\vec{r})$$

Indeed if we use spherical coordinates the radial equation (still in dimensionless units) becomes:

$$u_{nl}(r) \equiv r\, R_{nl}(r)$$

$$\frac{d^2}{dr^2}u_{nl}(r) + k^2(r)u_{nl}(r) = 0 \qquad k^2(r) = 2\left(E_{nl} - \frac{l(l+1)}{2r^2} - \frac{1}{2}r^2\right) \tag{5}$$

This equation is analog to the one for the 1D case except for the additional presence in k^2 of the centrifugal term depending on l (quantum number relative to the angular momentum of the oscillator). This requests a modification of the function k in the code:

```
double k(double r, int l, double E) {
  return 2*E-l*(l+1)/(r*r)-r*r;
}
```

Another difference is that now the analytic solution in the limit $r \to 0$ is different because of the predominance of the centrifugal potential:

$$k^2(r) \simeq -\frac{l(l+1)}{r^2} \qquad\qquad u_{nl}(r) \propto r^{l+1}$$

so the initial conditions were implemented in the following way:

```
y0 = pow(xmin, l+1);
y1 = pow(xmin+h, l+1);
```

This time the value of x_{min} was chosen slightly different from zero in order to avoid the divergence of the l-dependent term.
The solutions were computed in the same way that was mentioned before: first the energy intervals containing the values of E_{nl} were found by looking at the change of sign of $u_{rl}(r_{max})$, then the eigenvalues and the normalized eigenfunctions were constructed by putting the difference of the logarithmic derivatives in x_{mid} equal to zero. This time the maximum energy considered in the scanning of the "findzeros()" function was $E_{max} = 8$, in order to include the values of the first three eigenstates for $l = 0, 1, 2$. Indeed the energy levels of an adimensional 3D harmonic oscillator are given by $E_{nl} = 2n + l + 3/2$, where n is still the number of nodes of the solution. For the sake of brevity only the plot of the s-wave eigenfunctions is reported.

$l = 0$	
n	E_{n0}
0	1.50000
1	3.50000
2	5.50000

$l = 1$	
n	E_{n1}
0	2.50000
1	4.50000
2	6.50000

$l = 2$	
n	E_{n2}
0	3.50000
1	5.50000
2	7.50000

Table 3: First 3 eigenvalues of the 3D dimensionless harmonic oscillator for $l = 0, 1, 2$

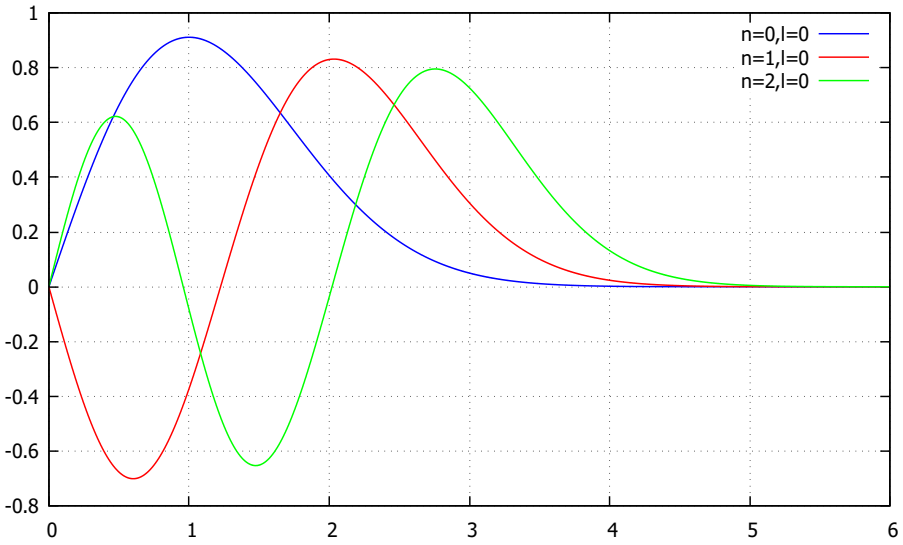

Figure 2: First 3 radial solutions $u_{n0}(r)$ for the 3D dimensionless harmonic oscillator (l=0)

3 Bessel functions

In order to compute the values of the phase shift one should be able to evaluate the spherical Bessel functions of the first kind (j_l) and of the second kind (n_l) in an arbitrary point of the mesh. A smart way to do this is to exploit the following recursive formula (valid for both the functions):

$$\begin{cases} j_{-1}(x) = \frac{\cos x}{x} \\ j_0(x) = \frac{\sin x}{x} \end{cases} \qquad \begin{cases} n_{-1}(x) = \frac{\sin x}{x} \\ n_0(x) = -\frac{\cos x}{x} \end{cases}$$

$$s_{l+1}(x) = \frac{2l+1}{x} s_l(x) - s_{l-1}(x) \tag{6}$$

which was implemented in the code through the definition of the following function:

```
double bessel(double x, int l, int sphorder){
int i;
double s0,s1,s2;

if(sphorder == 1){
```

```
    s0 = cos(x)/x;
    s1 = sin(x)/x;
  }else{
    s0 = sin(x)/x;
    s1 = -cos(x)/x;
  }

  s2 = s1;

  for(i=0;i<l;i++){
    s2 = (2*i+1)*s1/x - s0;
    s0 = s1;
    s1 = s2;
  }

  return s2;
}
```

where the integer *sphorder* is exploited to distinguish the two different spherical functions.
The correctness of this implementation was checked by computing the difference between the output values of "bessel()" and of the GNU GSL functions "gsl_sf_bessel_jl()" for $j_l(x)$ and "gsl_sf_bessel_yl()" for $n_l(x)$. The differences have been calculated in some points within the range $x \in [0.5, 25]$. In all the cases for both the spherical functions the differences found were smaller than 10^{-9} when l=0,1,2,3,4,5,6.

4 Natural units of the problem

If we choose as "natural" units of the problem $\varepsilon = \sigma = 1$, the Lennard-Jones potential of Eq. (1) can be rewritten as:

$$v(r) = 4\left[\left(\frac{1}{r}\right)^{12} - \left(\frac{1}{r}\right)^{6}\right]$$

The reduced mass μ, given the hydrogen mass ($m_H = 938.8 \times 10^6$ eV/c^2) and the kriptum mass ($m_{Kr} = 78057.4 \times 10^6$ eV/c^2), is equal to:

$$\mu = \frac{m_H\, m_{Kr}}{m_H + m_{Kr}} = 927.6 \times 10^6\ eV/c^2$$

The constant $\hbar^2/(2\mu)$, which enters in the function $k^2(r)$ in the Numerov algorithm, in this units is equal to:

$$\frac{\hbar^2}{2\mu} = \frac{\hbar^2}{2\mu\varepsilon\sigma^2} = \frac{4.332 \times 10^{-31}\, eV^2 s^2\ c^2}{2 \cdot 927.6 \times 10^6\, eV \cdot 0.0059\, eV \cdot (3.18 \times 10^{-10}\, m)^2} =$$

$$= 3.91 \times 10^{-19}\, \frac{s^2}{m^2} \cdot c^2 = 3.91 \times 10^{-19}\, \frac{s^2}{m^2} \cdot \left(2.99 \times 10^8\, \frac{m}{s}\right)^2 \simeq 0.035$$

5 Solution in the limit $r \to 0$

The Schrödinger equation of the H-Kr system is:

$$\frac{d^2}{dr^2} u_l(r) + k^2(r) u_l(r) = 0 \tag{7}$$

$$k^2(r) = \frac{2\mu}{\hbar^2}\left(E_l - \frac{\hbar^2}{2\mu}\frac{l(l+1)}{r^2} - 4\left[\left(\frac{1}{r}\right)^{12} - \left(\frac{1}{r}\right)^{6}\right]\right)$$

In the limit for $r \to 0$ this equation can be approximated as:

$$\frac{d^2}{dr^2} u_l(r) \simeq \frac{2\mu}{\hbar^2}\frac{4}{r^{12}} u_l(r)$$

Now one can do the following ansatz:

$$u_l(r) = A \exp\left[-\left(\frac{b}{r}\right)^5\right]$$

and calculate its second derivative:

$$\frac{d^2}{dr^2} u_l(r) = 5Ab^5 \frac{d}{dr}\left(\frac{1}{r^6} \exp\left[-\left(\frac{b}{r}\right)^5\right]\right) =$$

$$= 5Ab^5 \left(\frac{5b^5}{r^{12}} \exp\left[-\left(\frac{b}{r}\right)^5\right] - \frac{6}{r^7} \exp\left[-\left(\frac{b}{r}\right)^5\right]\right) =$$

$$= 5Ab^5 \exp\left[-\left(\frac{b}{r}\right)^5\right]\left\{\frac{5b^5}{r^{12}} - \frac{6}{r^7}\right\} \simeq \frac{25Ab^{10}}{r^{12}} \exp\left[-\left(\frac{b}{r}\right)^5\right]$$

By inserting it in the approximated Schrödinger equation we find out that it is the correct analytic solution in the limit $r \to 0$ and in addition we can fix the value of the constant b:

$$\frac{25Ab^{10}}{r^{12}} \exp\left[-\left(\frac{b}{r}\right)^5\right] = \frac{2\mu}{\hbar^2}\frac{4}{r^{12}} A \exp\left[-\left(\frac{b}{r}\right)^5\right]$$

$$b^5 = \frac{2}{5}\sqrt{\frac{2\mu}{\hbar^2}} \tag{8}$$

6 Phase shift calculation

The calculation of the phase shift for a given l starts from the evaluation of the ratio C which is defined as:

$$C = \frac{u_l(r_1)\, r_2}{u_l(r_2)\, r_1} \tag{9}$$

where r_1,r_2 are two points of the mesh larger than $r_{max} = 5\sigma$ (in the code they have been set equal to $r_1 = r_{max} + 0.1$ and $r_2 = r_{max} + 0.2$). The solution in these two points was propagated using the Numerov code for the 3D harmonic oscillator where the harmonic potential was substituted with the Lennard-Jones one. In both cases the propagation (with a number of steps equal to 10000) started from $r_{min} = 0.5$ with the initial conditions defined by the analytic solution of the previous section. Note that the value of the parameter A is irrelevant since it cancels out in the ratio.
Once calculated this ratio, it is possible to find the value of the phase shift from the arctangent of the following expression:

$$\tan\delta_l = \frac{C\, j_l(kr_2) - j_l(kr_1)}{C\, n_l(kr_2) - n_l(kr_1)} \tag{10}$$

where k is the relative momentum between the two atoms and depends on the relative energy E (fixed to $E = 0.3$ in this section):

$$k = \sqrt{\frac{2\mu E}{\hbar^2}}$$

The spherical Bessel functions have been calculated with the help of the "bessel()" function described in section 3. Here are presented the results:

l	δ_l
0	-0.6327
1	0.6466
2	-1.5178
3	-0.8609
4	-0.5623
5	-1.0140
6	0.3631

Table 4: Phase shift values (in radiants) for a relative energy of E=0.3

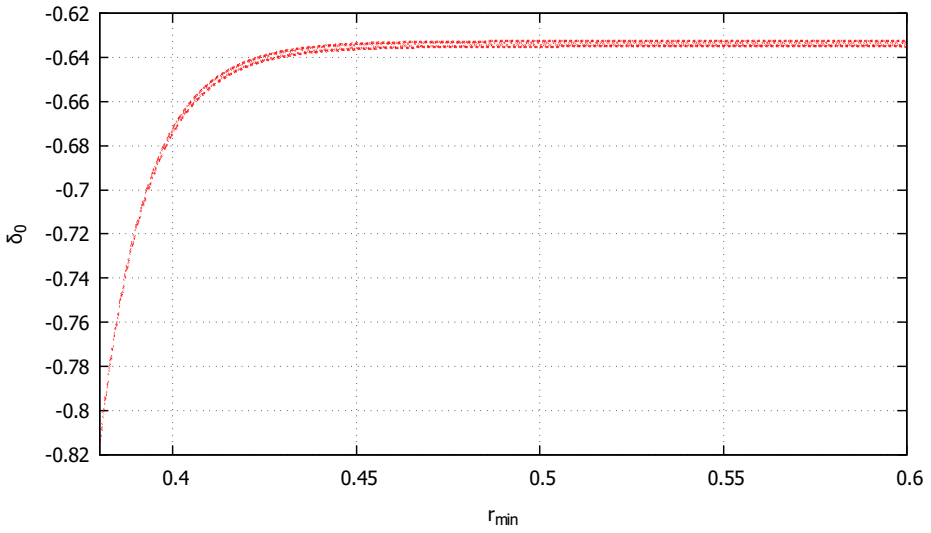

Figure 3: Value of δ_0 (phase shift for $l = 0$) depending on the starting point of the propagation

By changing the parameters that enter in the propagation one can analyze how the phase shift is affected by these variations. An example is the check of the δ_l dependence on the starting point of the solution. From Fig. 3 we can notice that, moving from the right to the left, the value of δ_0 remains constant until $r_{min} \simeq 0.45$ (actually there is an oscillation of the order of 0.003 radiants) and then it starts to change more and more as r_{min} becomes smaller and smaller, until a certain point where the code is no longer able to compute it because of the divergence of the potential. One can check that this behaviour is valid for each value of $l \in [0, 6]$.

An analog test can be done also for the dependence on the final points of the propagation. In particular one can set $r_1 = r_{max} + 0.01$, $r_2 = r_{max} + 0.02$ (so that their relative distance remains constant) and see how the phase shift behaves due to a variation of r_{max}. Fig. 4 clearly shows the phenomenon of

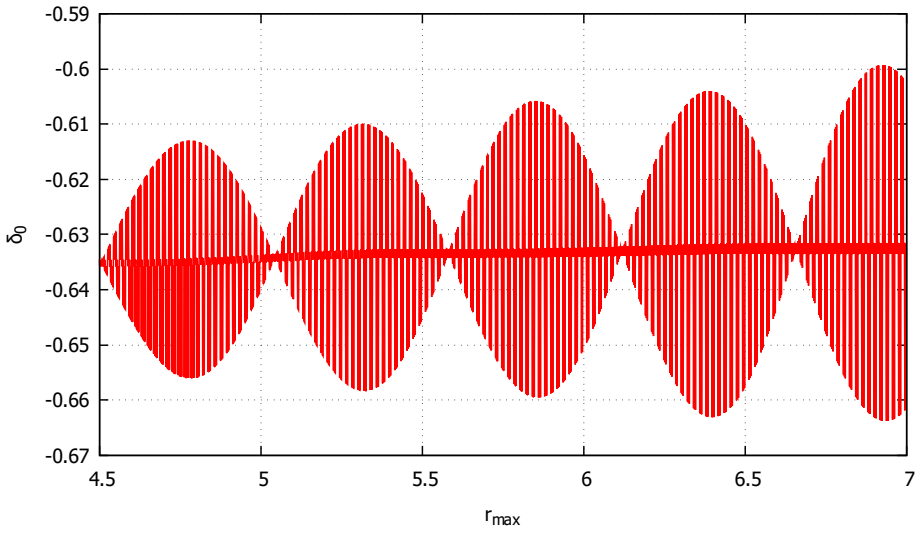

Figure 4: Value of δ_0 (phase shift for $l = 0$) depending on the final points of the propagation

beats, which is probably due to the sinusoidal behaviour of the solution when we are outside the potential range. Again, the dependence is qualitatively the same for every value of $l \in [0, 6]$.

7 Total cross section

Starting from the phase shift calculation, we can also compute the total cross section of the elastic H-Kr scattering event as a function of the relative energy between the two nuclei. Indeed, differently from the harmonic oscillator case, now we are looking to the scattering states and therefore the energy is not restricted to discrete values but can vary in a continuous way. In particular the energy range we are interesting in is $E \in [0, 3.5]$ meV.

The expression from which we can derive the total cross section is:

$$\sigma_{tot} = \frac{4\pi}{k^2} \sum_{l=0}^{\infty} (2l+1) \sin^2 \delta_l \tag{11}$$

Obviously, for a practical reason it is not possible to sum up infinite contributes, therefore the sum will be truncated at some finite value of l, chosen equal to 6.

$$\sigma_{tot} \simeq \frac{4\pi}{k^2} \sum_{l=0}^{6} (2l+1) \sin^2 \delta_l \tag{12}$$

This is still a good approximation since what is expected is that the contributions from higher l become important only at energies which are larger than the considered range. This argument can be demonstrated graphically:

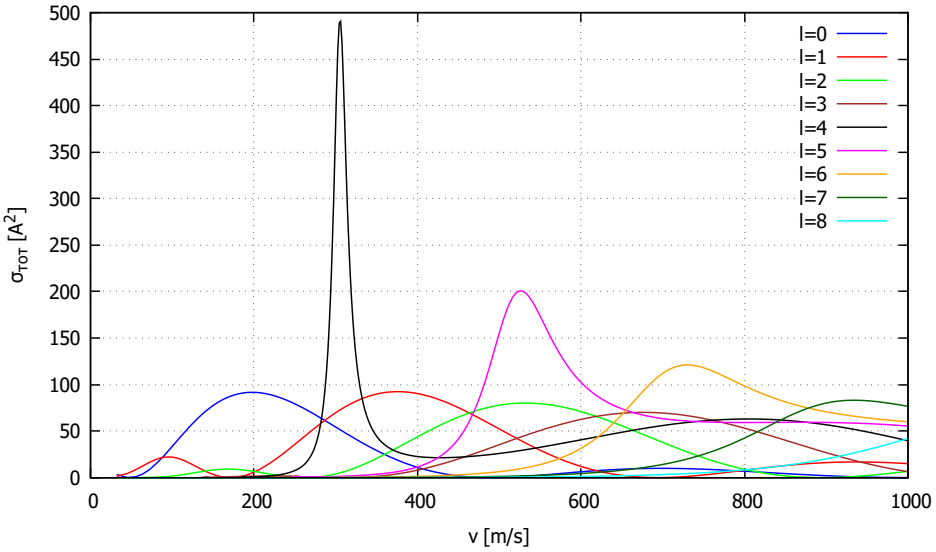

Figure 5: Contribution to the total cross section from different values of l

Fig. 5 shows that in the energy range of interest (up to a relative velocity of $v \simeq 800$ m/s), it is not so wrong to consider only the partial waves until $l = 6$, indeed the successive contribution ($l = 7$, dark-green colour) becomes important at higher energies (between $\simeq 800$ and 1000 m/s).
Here is the result for the total cross section, computed with Eq. (12):

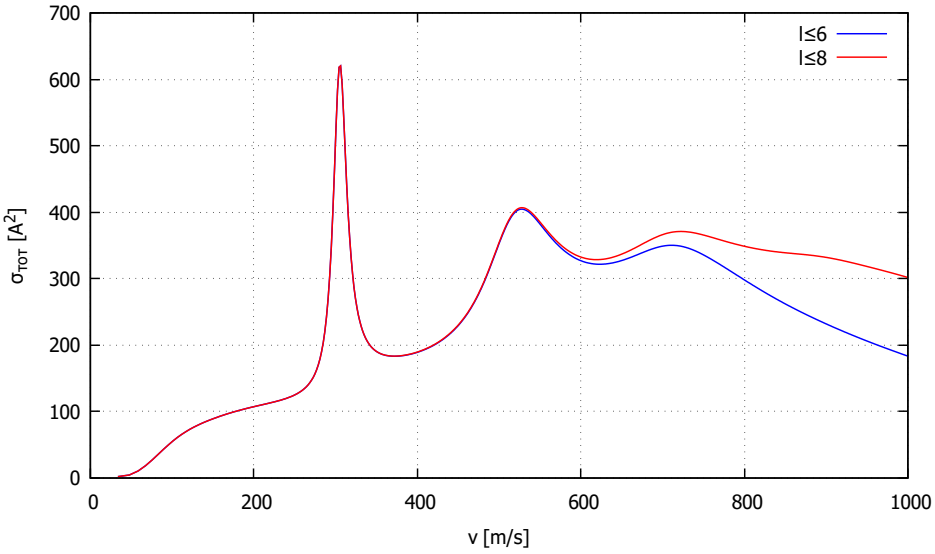

Figure 6: Total cross section of H-Kr scattering as a function of the relative velocity v

The theoretical results derived with the Lennard-Jones potential are in good agreement with the experimental ones since Fig. 6 is very similar to the plot showed in Fig. 3d at page 318 of the reference paper. In particular one can see that there are three resonances which are respectively due to the contribution of the partial waves $l = 4, 5, 6$, as shown in Fig. 5. Another important observation is that if we extend the energy range of interest up to a relative velocity of $v = 1000$ m/s ($\simeq 5.2$ eV) also the contributions to the total cross section from $l = 7$ and $l = 8$ become significant, then we should include also these terms in the sum (red curve) instead than truncating it at $l = 6$ (blue curve) in order to get a slope at high energy which is more similar to the plot in the paper.