Numerov's methods for H-Kr scattering

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Introduction

The exercise we are solving is based on the H-Kr scattering described in the article by J.P. Toennies, W. Welz, and G. Wolf, J. Chem. Phys. 71, 614 (1979).

We are modeling the interaction between the atoms with the Lennard-Jones potential:

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

with r being the interatomic H-Kr distance and the parameters $\epsilon = 5.9\,\text{meV}$ and $\sigma = 3.18\,\text{Å}$ taken by the article. We are computing the total cross section of the H-Kr scattering and comparing it with the results from the article.

In order to solve the assigned exercises we need to apply Numerov's method on different radial Schrödinger equations. We are going to implement both the matrix version and the "shooting" version of the algorithm.

The shooting approach consists in fixing an energy and computing the radial wave equation, approximating the second derivative in the kinetic part with a numerical three points formula, obtaining the following recursion relation for the radial wave function:

$$u_{i+1} = \frac{u_i(2 - \frac{5}{12}\Delta r^2 k_i^2) - u_{i-1}(2 - \frac{1}{12}\Delta r^2 k_{i-1}^2)}{1 + \frac{1}{12}\Delta r^2 k_{i+1}^2} \tag{2}$$

where $k_i^2 = E - V_i$. The shooting approach can be used to compute both bound states and scattering states, but it is mainly used for the scattering states. In fact in principle the bound state energy is not known a priori and further techniques are required to find the right values of the energies.

The matrix version consists in diagonalizing the Hamiltonian matrix formed again by approximating the second derivative presents in the kinetic part. The eigenvalue problem we have to solve will be:

$$Hu = \left(-\frac{1}{2}B^{-1}A + V\right)u = Eu \tag{3}$$

where:

$$A_{ij} = \frac{1}{\Delta r^2}\left(\delta_{i+1j} - 2\,\delta_{ij} + \delta_{i-1j}\right) \qquad B_{ij} = \frac{1}{12}\left(\delta_{i+1j} + 10\,\delta_{ij} + \delta_{i-1j}\right) \qquad V = \text{diag}(V_0, V_1, \ldots, V_{N-1})$$

where Δr it's the width of the spacial discretization, V_i is the effective potential (including the centrifugal part) calculated on the ith point of the spacial mesh. The matrix approach is suitable only for bound states, since the diagonalization will return a discrete spectrum.

1 One dimensional harmonic oscillator

The first task requires us to write a code solving the one dimensional Schrödinger equation for an harmonic potential. The Hamiltonian we consider is dimensionless:

$$-\frac{1}{2}\frac{d^2}{dx^2}+\frac{1}{2}x^2 \tag{4}$$

We solved the task by using the matrix form of the Numerov's method on a spacial mesh for $-5 < r < 5$. The results are presented in the graph below.

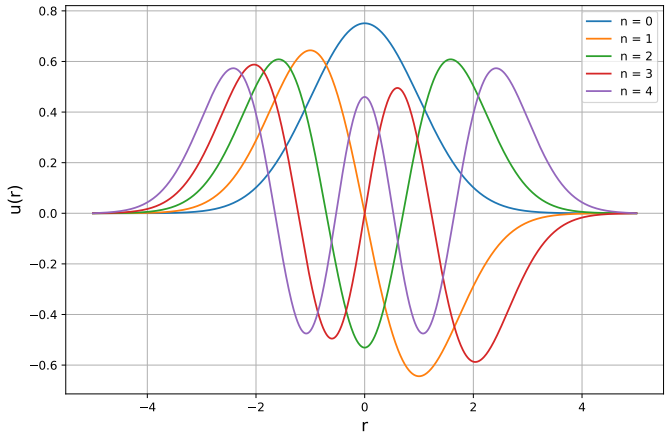


Figure 1: First 5 solutions for a 1D harmonic oscillator

Num	0.5005	1.5016	2.5027	3.5038	4.5049
Th	0.5	1.5	2.5	3.5	4.5

We are not able to perform an error estimation on the results of the diagonalization (the energies), but by rounding the results on the second decimal digit we obtain the correct results of $E_n = n + 0.5$.
In order to establish the correctness of our code we perform an analysis on the number of point of the spacial mesh. We obtain the result for the ground state energy for different number of points $N < 1000$ and we show them in the graph below.

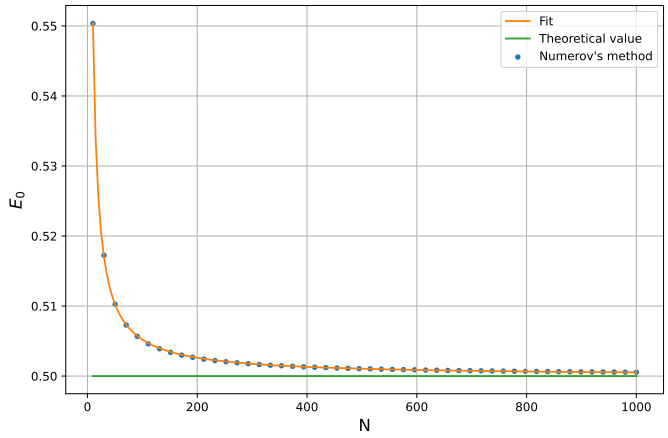


Figure 2: Ground state energy for different number of points in the spacial grid

As expected the accuracy of the method increases with the number of points of the grid since the error on every point of the radial function is of the order Δr^4. We estimate the ground state energy by fitting the energy on the number of the point with a function of the type

$$E(N) = \frac{a}{N^b} + c \tag{5}$$

where c will represent the value of E_0 for $N \to \infty$ and our estimate for the ground state energy. The fit result holds

$$E_0 = 0.49998 \pm 0.00001 \tag{6}$$

which is definitely compatible with the theoretical value.

2 Three dimensional harmonic oscillator

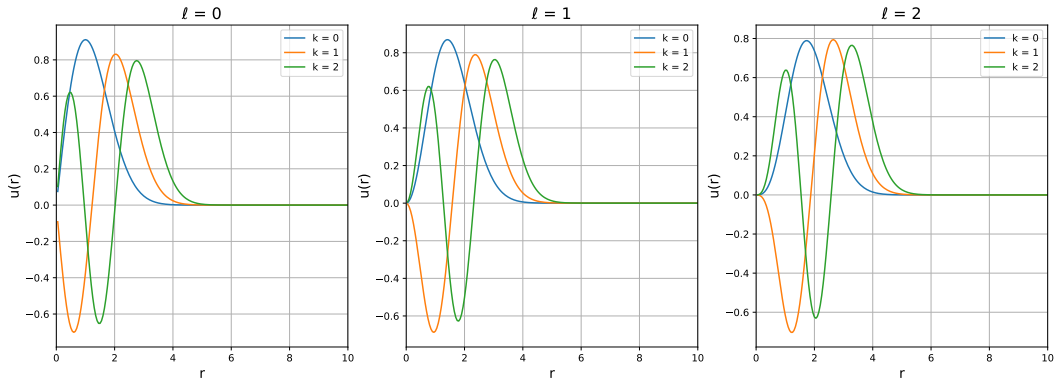
In this section we are going to solve the Schrödinger equation for a 3D harmonic oscillator.
The Hamiltonian for this system having set $\hbar = 1$ and $m = 1$ is:

$$H = -\frac{\nabla_r^2}{2} + \frac{1}{2} r^2 \tag{7}$$

then the radial Schrödinger equation is:

$$\left[-\frac{1}{2}\frac{d^2}{dr^2} + \frac{\ell(\ell+1)}{2r^2} + \left(\frac{1}{2} r^2 - E \right) \right] u(r) = 0 \tag{8}$$

The solution of this equation can be obtained via Numerov's method in matrix form.
We present our results in the following graphs.



The resulting eigenvalues are:

ℓ	Num	Th
$\ell = 0$	1.4999	1.5
	3.4999	3.5
	5.4999	5.5

ℓ	Num	Th
$\ell = 2$	3.4999	3.5
	5.4999	5.5
	7.4999	7.5

ℓ	Num	Th
$\ell = 1$	2.4999	2.5
	4.4999	2.5
	6.4999	6.5

We conclude that the results are in accordance with the theoretical prediction.

3 Bessel and Neumann spherical functions

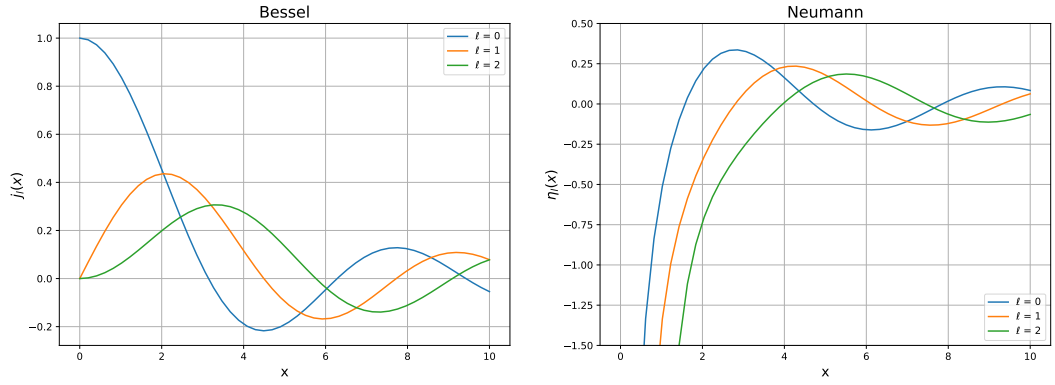
Spherical Bessel functions and spherical Neumann's functions are used to describe the radial wave function of a free particle in spherical coordinates:

$$u(r) = A_l r j_l(kr) + B_l r \eta_l(kr) \tag{9}$$

There will be useful later since when the Hydrogen atom is sufficiently far from the Krypton target we can use this wave functions to describe it. We have written a program that computes iteratively these functions as follows:

$$\begin{cases} j_{-1}(x) = \dfrac{\cos(x)}{x} \\ \eta_{-1}(x) = \dfrac{\sin(x)}{x} \\ j_0(x) = \dfrac{\sin(x)}{x} \\ \eta_0(x) = -\dfrac{\cos(x)}{x} \end{cases} \Longrightarrow s_{\ell+1}(x) = \frac{2\ell+1}{x} s_\ell(x) - s_{\ell-1}(x) \tag{10}$$

The results for the $\ell = 0, 1, 2$ are presented below.



We did not plot the exact results available from the functions in Python scientific libraries since the recursive formula it's exact and the two plots would perfectly correspond. From now on, in order to speed up the calculation, we will use the functions included in the Python libraries, which are definitely faster since they are not defined in a recursive way.

4 Natural units of the problem

In the following sections we are going to analyze the relative problem of an Hydrogen-Krypton collision using the Lennard-Jones potential which depends on the depth of the potential ε and the interatomic distance σ at which the interatomic potential. In order to rescale the radial Schrödinger equation in the natural units of the problem we are interested in calculating the value of $\frac{\hbar^2}{2\mu}$ in respect to the typical physical quantities of the problem, i.e. ε and σ. The calculation is straightforward once we consider the reduced mass $\mu = \frac{m_H m_{Kr}}{m_H + m_{Kr}}$:

$$\frac{\hbar^2}{2\mu} = \frac{\hbar^2}{2\mu} \cdot \frac{1}{\varepsilon\sigma^2} [\varepsilon][\sigma^2] = 0.0352 [\varepsilon][\sigma^2] \tag{11}$$

5 Solution of the radial equation for $r \to 0$

We are now interested in the determination of the boundary conditions for the scattering problem between an Hydrogen atom and a Krypton atom. The process is described by the following Hamiltonian in $\sigma - \epsilon$ units:

$$H = -\frac{\hbar^2}{2\mu}\frac{d^2}{dr^2} + \frac{\hbar^2 \ell(\ell+1)}{2\mu r^2} + 4\left[\left(\frac{1}{r}\right)^{12} - \left(\frac{1}{r}\right)^{6}\right] \tag{12}$$

We make the ansatz that for $r \to 0$ the solution of the radial problem is of the following form

$$v(r) = A \exp\left[-\left(\frac{b}{r}\right)^5\right] \tag{13}$$

We are now going to prove this and find the parameter b. Let's recall the radial Schrödinger equation and consider it in the $r \to 0$ limit:

$$\left[-\frac{\hbar^2}{2\mu}\frac{d^2}{dr^2} + \frac{\hbar^2 \ell(\ell+1)}{2\mu r^2} + 4\left(\frac{1}{r}\right)^{12} - 4\left(\frac{1}{r}\right)^{6}\right] v(r) = E v(r) \Longrightarrow \frac{d^2 v(r)}{dr^2} + \frac{2\mu}{\hbar}\frac{u(r)}{r^{12}} = 0 \tag{14}$$

Then after some simple calculations we obtain

$$\frac{25b^{10} - \frac{8m}{\hbar^2}}{r^{12}} = 0 \Longrightarrow b = \left(\frac{8m}{25\hbar^2}\right)^{1/10} = 1.1636 \tag{15}$$

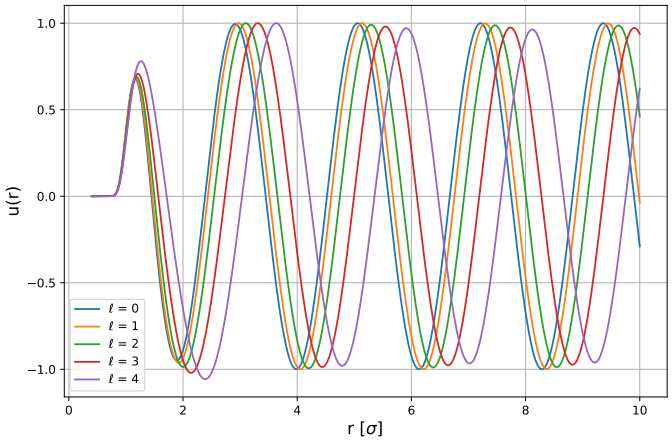
where we have used the value for $\frac{\hbar^2}{2\mu}$ computed in eq. 11. In the following chapter we can finally compute the scattering process by using $v(r)$ to set the boundary conditions for the Numerov's method.

6 Numerov's method on the interatomic potential

In this section we use the "shooting" approach described in the introduction to solve the Schrödinger equation for the complete interatomic potential of eq. 1 for a fixed energy $E = 0.3\ [\epsilon]$.

Since for $r \to 0$ the solution is independent from ℓ, due to the fact that the Lennard-Jones contribution is much larger than the centrifugal one, the boundary conditions are set by the function of the previous section $v(r)$ at some point r_{low}, such that $0 < r_{low} < 1\ [\sigma]$ for every ℓ value.

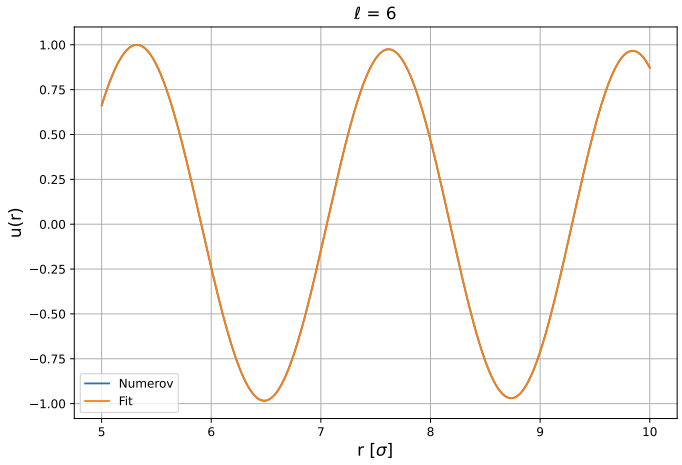
We show the radial wave functions obtained for different value of ℓ in the graph below. Since these are scattering state, their are non normalizable states and the amplitude of the wave can be arbitrary, so we divided every function by its maximum.



Once we have computed the solutions of the SE we can fit them after $r_{max} = 5$ with the radial function of a free particle:

$$u_\ell(r) = C_\ell \left(\cos\delta_\ell j_\ell(kr) - \sin\delta_\ell \eta_\ell(kr)\right) \tag{16}$$

obtaining the phase shifts δ_ℓ for $\ell = 0, 1, 2, 3, 4, 5, 6$. An example of the fit can be seen in the following figure:



The resulting phase shifts are:

ℓ	0	1	2	3	4	5	6
$\delta_\ell\ [rad]$	2.502	0.641	1.621	2.277	2.571	2.122	0.360

We are now interested on the variation of the results against small variations of r_{low} and r_{max}.
In order to view the effect of small variations of r_{low} we compute the total cross section varying r_{low} from 0 to 1, this means that we repeat the previous procedure by varying the point in which the wave function is initialized, and every time we compute the total cross section as:

$$\sigma = \sum_{\ell=0}^{\infty} \sigma_\ell = \frac{4\pi}{k^2} \sum_{\ell=0}^{\infty} (2\ell + 1) \sin^2 \delta_\ell \tag{17}$$

which in this case will be approximated by the same sum truncated at $\ell = 6$. We will discuss in the next section why this is a good approximation for $E \leq 0.3[\varepsilon]$.
We show the total cross section as a function of r_{low} in the graph below:

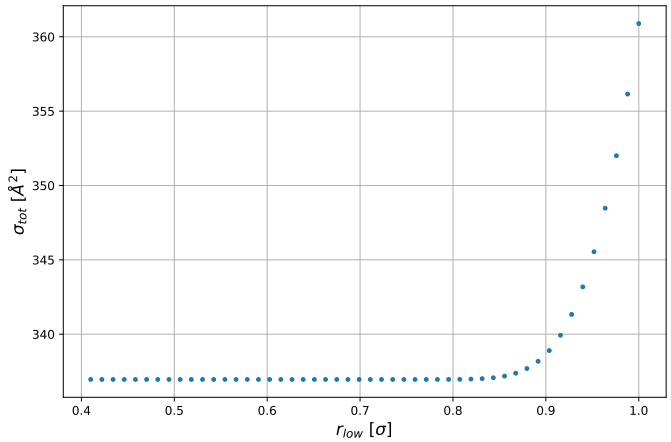


Figure 3: Cross section dependence on r_{low}

Note that we couldn't use an $r_{low} < 0.4$ since due to computational limitations the values of $v(r)$ for $r < 0.4$ were computed as zero.
However we can see from the graph that for $r_{low} \to 0$ the results are constant, while for $r_{low} \to 1$ the total cross section tends to diverge, this is due to the fact that $v(r)$ is a good boundary condition only for $r \to 0$.
This means that we should initialize our wave function at the first viable point, that is $r_{low} = 0.4$

Finally we study the dependence on r_{max} by varying it from 1 to 9 and calculating at every step the relative error on the total cross section. The result can be seen in the following graph:

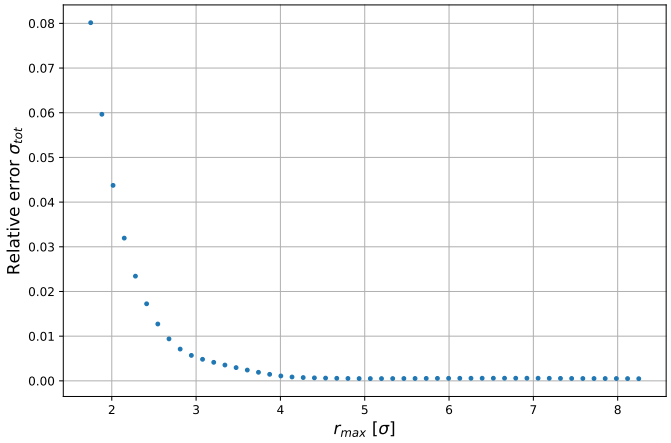
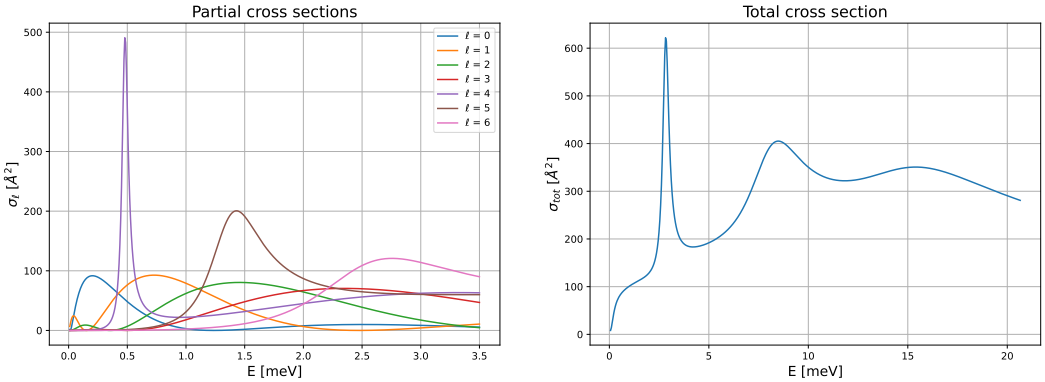


Figure 4: Cross section dependence on r_{max}

We note that for $r_{max} < 5$ the results tend to get worse, this is due to the fact that the approximation of free particle is not valid in that range of r_{max}. On the other hand for $r > 5$ the relative error is less than 1%, the best value of r_{max} would then be the maximum possible, we fix it to 5 in order to have the necessary points to fit the wave functions.

7 Total integral cross section of H-Kr scattering

In order to compute the total cross section of the process we iterate the procedure used in the previous section for different energies $0 < E < 0.6$ [ϵ] corresponding to $0 < E < 3.5$ [meV] for $\ell \leq 6$. We plot the obtained results in the graphs below:



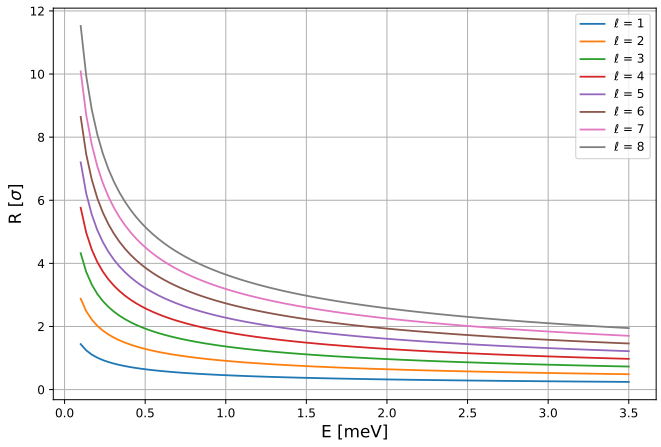
The figures are in good accordance with the ones in figure 3 of the original article, but in order to give a more quantitative comparison we compare the resonant energies for $\ell = 4, 5, 6$ with the one presented in table 3 of the article. Our results are:

ℓ	E_{res}
4	(0.479 ± 0.007) meV
5	(1.430 ± 0.007) meV
6	(2.759 ± 0.007) meV

which are all compatible with the respective center of mass resonance energy presented in the table of the article.

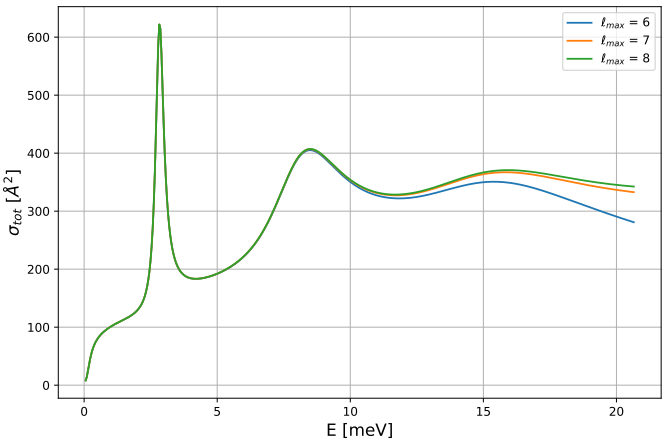
In order to justify the truncation of the sum in the total cross section formula we note that a particle with momentum $p = \hbar k$ and angular momentum $\hbar\ell$ at the nearest possible point of interaction will be at $R = \ell/k$. For low energy and high angular momentum, R is such that the particle won't feel the potential, the phase shift will be negligible then resulting in no contribution in the total cross section.

We show the values of R for $\ell \leq 8$ in the range of energy considered in the cross section study.



We note that in the higher bound of the energy range the values of R for $\ell > 6$ become comparable with the ones

for $\ell < 6$. Then the partial cross sections for $\ell > 6$ will have a relevant contribution in the total cross section. In order to appreciate this behaviour we plot in the following graph the total cross section for $\ell_{\max} = 6, 7, 8$.



As it results from the graph, for $E > 2\,\text{meV}$ the contribution due to the partial wave for $\ell = 7$ is not negligible, while the one from $\ell = 8$ continue to be negligible for these energy values.
A better result would then be obtained by truncating the sum at $\ell = 10$, but this is out of the aim of this exercise.