EM-TCCM (September 2023)

COURSE: THE TIME-DEPENDENT WAVEPACKET APPROACH, OBTAINING SCATTERING INFORMATION (Manuel Lara Garrido)

HOMEWORK

Before starting…

During the course, you got a code to propagate a 1D wavepacket interacting with an Eckart-potential. ***In case you do not have it yet****, please follow the following instructions:*

-You need to connect to login.g100.cineca.it

If you connect from a linux computer use:

ssh -Y username@login.g100.cineca.it

If you connect from windows, use putty *(for example) to connect through SSH to login.g100.cineca.it (do not forget to enable X11 in case you also want to plot afterwards).*

-Enter your home directory and use the following command to copy all the files you will need:

cp /g100/home/userexternal/mlaragar/PROGRAMDEFNEW/ .*

-You will find the files of the code (barreritafluxexpenmomchebcontabsmod.f , locales.parameter.h and locales.common.h), the file to initialize the propagation (cont.data) and a few files to create animations using the output (extension ".gnu"). Besides, I have included some videos with extension ".gif", that were included in the class powerpoint.

-You can enter the file that contains the main program using "vi" editor, or similar:

vi barreritafluxexpenmomchebcontabsmod.f

-Read carefully the head of the file, and follow the instructions that you will find there to run the code.

-In brief, load the module corresponding to the library:

module load fftw/3.3.10--gcc--10.2.0

-Then compile using:

gfortran barreritafluxexpenmomchebcontabsmod.f -lfftw3

-The following command will execute and you will get a lot of files…

./a.out>sal &

-You can plot the output files using "gnuplot", but first load the module:

module load gnuplot

- There are sections at the head of the program called "IMPORTANT NOTES", "OUTPUT FILES", "IMPORTANT VARIABLES" and "IMPORTANT PARAMETERS"; they will help you to understand the information needed and provided by the program and their corresponding units. These sections may be useful if you need to modify the program.

-As you know, the program has many functionalities and this homework only requires you to use very few of them. In principle, you will only have to modify a few parameters (you do not even have to understand well how the whole program works). Note that a significant change in the value of the parameters (number of points, average kinetic energy, mass…) may have unexpected consequences on issues like the absorption or the accuracy of the propagator. My piece of advice: think what you want from the program, scroll the OUTPUT FILES section to find out where the information that you are looking for is written, and search for the very few things that you may want to modify in the sections IMPORTANT PARAMETERS or IMPORTANT VARIABLES.

- The .pdf with the class notes (in Moodle) is going to be very helpful. Remember that you can find inside many labels which were added to the text to allow you to find more easily the meaning of the parameters and the output. The labels of the IMPORTANT PARAMETERS have been typed in "bright green" and the OUTPUT FILES in "indigo" color. The labels of IMPORTANT VARIABLES are in "orange".

-Please, find the homework on the next page.

INSTRUCTIONS: The answer to each exercise should NOT occupy more than two pages (considering both sides), which would be already too much. They should only include text (with detailed explanations and description of changes in the parameters or variables in the code) equations and figures (with clear information about axis, units…), but not pieces of the code.
Please, besides uploading them, send me your answers by email, to manuel.lara@uam.es, stating clearly in the "subject": "ANSWERS TO THE EXERCISES BY (NAME…)"
Please, do not hesitate to contact me in case of questions or doubts about the homework.
Final comment: the exercises are supposed to be straightforward and very simple: don´t look for complicate answers.

EXERCISES:

1. (5 points) During the course, we discussed the meaning of the Fourier Transform and, particularized to Quantum Mechanics, the importance of the momentum representation. In this context, the Heisenberg's uncertainty principle, $\Delta_\psi X \cdot \Delta_\psi P_x \geq \hbar/2$ is simply a particular case of a general property, which links a function ψ with its Fourier Transform $\hat{\psi}$.

Let's consider a particular state of the system, $|\psi\rangle$. We use $\psi(x)$ to name the corresponding wavefunction in the position representation and $\widehat{\psi(p)}$ to name the wavefunction in the momentum representation.

a) Explain the meaning of $|\psi(x)|^2 dx$ in Quantum Mechanics.

b) Write down the mathematical relation which allows to calculate $\psi(x)$ starting from $\widehat{\psi(p)}$.

c) Explain the precise meaning of $\Delta_\psi P_x$ in Quantum Mechanics and give a mathematical expression to calculate it.

d) How do you calculate $< X >_\psi$ using the function $\psi(x)$?

e) Considering the gaussian which is programmed in the code,

$$\psi(x) = \left(\frac{2}{\pi\Gamma^2}\right)^{1/4} e^{-\frac{(x-X_0)^2}{\Gamma^2}} e^{\,ik_0(x-X_0)}$$

obtain analitically $\widehat{\psi(p)}$.

HINT: the following integral might be useful:

$\int_{-\infty}^{+\infty} e^{-a^2u^2/2} e^{ibu} du = \frac{\sqrt{2\pi}}{a} e^{-\frac{b^2}{2a^2}}$ (with Re(a^2)>0)

f) Remember that, using the code, you can generate the momentum representation of different Gaussians. Show, by plotting the position representation and the momentum representation associated to different Gaussian functions, that the uncertainty relation ($\Delta_\psi X \cdot \Delta_\psi P_x \geq \hbar/2$) holds, explaining its meaning. If you change any parameters in the code, please indicate which. (NOTE: you could also build these functions by yourself, without using the code; however, the code is ready to do that)

2. (5 points) When using time-dependent methods to simulate reactive scattering, the initial wavefunction (usually a Gaussian) is chosen to contain the particular range of energies that one is trying to explore. Let's assume **a free propagation** (*V=0*) for a system with mass μ, and let´s consider the Gaussian that is programmed in the code:

$$\psi(x) = \left(\frac{2}{\pi\Gamma^2}\right)^{1/4} e^{-\frac{(x-X_0)^2}{\Gamma^2}} e^{\,ik_0(x-X_0)}$$

i) Imagine that the mass of the particle is 80 u and we want to explore energies in the range (700 cm^{-1}, 900 cm^{-1}). Assuming that the TD method only provides accurate results for those energies in the Gaussian within the range $\langle T \rangle_\psi \pm \Delta_\psi T$, which numerical values of k_0 and Γ would you use (include units)? Use the code to generate this function and plot its modulus square.

ii) As we discussed, the mean value of the kinetic energy of this Gaussian is approximately given by $\langle T \rangle_\psi \approx \frac{\hbar^2 k_0^2}{2\mu}$ (accurate enough for our purposes). Obtain analytically (by integration) the **exact** expression of $\langle T \rangle_\psi$ as a function of μ, Γ, k_0 . This can be found in many text-books.
(HINTS: one way to do it is to use the momentum representation,
as the plane waves are eigenfunctions of the kinetic energy operator; the following integrals might be useful:

$\int_{-\infty}^{+\infty} e^{-ax^2} dx = \sqrt{\frac{\pi}{a}}$, with $a \in \mathbb{R}, a > 0$

$\int_{-\infty}^{+\infty} x^{2n} e^{-ax^2} dx = \frac{1 \cdot 3 \cdot 5 \cdot \ldots \cdot (2n-1)}{2^n a^n} \sqrt{\frac{\pi}{a}}$ (even integrand), with $a \in \mathbb{R}, a > 0, n \geq 1$

$\int_{-\infty}^{+\infty} x^{2n+1} e^{-ax^2} dx = 0$ (odd integrand), with $a \in \mathbb{R}, a > 0, n \geq 0$)

iii) Using a gaussian with parameters ecol=500.d0*conve1 and deltae=ecol/3.2d0, and the same mass that was initially in the program, generate using the code, the wavepackets $\psi(x)$ corresponding to various times of propagation, t_i. Compare them by plotting $|\psi(x)|^2$. From the graphs, and analyzing the change of the position of the center of the Gaussian with time, extract an approximate velocity for the wavepacket; relate it numerically to the mean momentum of the initial Gaussian using *Ehrenfest theorems* (be careful with units).

RUBRIC:

The total mark of the homework is equivalent to 10 points (100%). Any mark below 5 will be considered as "unsatisfactory"; from 5-7 as "satisfactory"; from 7-9 as "good" and from 9-10 as "excellent". The following evaluation criteria will be considered:

-Delivery: if the homework is not delivered on time, a penalty of 1.5 point will be applied to the final mark of the exercises.

-Grammar and document organization: a maximum penalty of 1.5 point will be applied to the final mark of the exercises if the homework shows grammar errors, misspellings or is not well organized.

-Solutions to the exercises: each exercise has an associated mark of 5 points. To reach the maximum mark, answers to the questions have to be *correct*, and the explanations sufficient; please *detail the integrals and calculations.* In figures, *axes should be labelled (not only explained in the caption)* with the corresponding magnitudes with their units. Any change of the parameters or variables in the code should be noted. Text-books or external sources of information should be referred.