

# Quantum dynamics tutorial

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## I. INTRODUCTION

In this tutorial you will propagate a wave packet in two types of potential: a harmonic potential and a symmetric double-well potential. We will consider a particle with a mass  $m$  of 1 atomic mass unit ( $= 1g/mol = 1822.89m_e$ ) which is defined as one twelfth of the mass of a carbon atom. The box in which we propagate has a length of 5.12 Bohr. We use Hartree atomic units ( $\hbar = e = m_e = 1$ ) throughout unless stated otherwise.

## II. ACKNOWLEDGMENTS

The examples used in this tutorial were inspired by the following article: J. J. Tanner, J. Chem. Education 67, 917 (1990). The program you will use is a modified version of a program written by Anders Sandvik (<http://physics.bu.edu/py502/lectures4/examples/graphwavepacket.f90>).

## III. THEORY

### A. Fourier transformation

We use the following convention for the Fourier transforms:

$$\begin{aligned}\bar{f}(p) &= \int_{-\infty}^{\infty} dx f(x) e^{-ipx} & f(t) &= \int_{-\infty}^{\infty} dE \bar{f}(E) e^{-iEt} \quad (\text{forward transform}) \\ f(x) &= \frac{1}{2\pi} \int_{-\infty}^{\infty} dp \bar{f}(p) e^{ipx} & \bar{f}(E) &= \frac{1}{2\pi} \int_{-\infty}^{\infty} dt f(t) e^{iEt} \quad (\text{backward transform})\end{aligned}$$

### B. Gaussian wave packet

We will consider that our initial wave packet is a gaussian:

$$\Psi(x) = N e^{-\alpha x^2}, \quad (1)$$

where  $N$  is the normalisation constant and  $\alpha$  determines the width  $\Delta x = \sqrt{\langle x^2 \rangle}$  of the wave packet. One can demonstrate that  $\Delta x = \frac{1}{2\sqrt{\alpha}}$ . The Fourier transform of a Gaussian is also a Gaussian:

$$\bar{\Psi}(p) = FT[\Psi(x)](p) = N \int_{-\infty}^{\infty} dx \Psi(x) e^{-ipx} = \left( \frac{N}{\sqrt{2\alpha}} \right) e^{-\frac{p^2}{4\alpha}} \quad (2)$$

The width of this gaussian is  $\Delta p = \sqrt{\langle p^2 \rangle} = \sqrt{\alpha}$

#### 1. Heisenberg uncertainty principle

The Heisenberg uncertainty principle for position and momentum is given by

$$\sigma_x \sigma_p \geq \frac{1}{2} \quad (\hbar = 1) \quad (3)$$

where  $\sigma_x$  and  $\sigma_p$  are the uncertainties in position and momentum, respectively. They can be quantified in terms of standard deviations:

$$\sigma_x = \sqrt{\langle x^2 \rangle - \langle x \rangle^2} \quad (4)$$

$$\sigma_p = \sqrt{\langle p^2 \rangle - \langle p \rangle^2} \quad (5)$$

One can show that for a gaussian  $\langle x \rangle = \langle p \rangle = 0$ . We therefore have that  $\sigma_x = \Delta x = \frac{1}{2\sqrt{\alpha}}$  and  $\sigma_p = \Delta p = \sqrt{\alpha}$  and the Heisenberg relation for a gaussian is given by

$$\sigma_x \sigma_p = \frac{1}{2} \quad (\text{gaussian}) \quad (6)$$

In other words for a gaussian wave packet an increase (decrease) of  $\sigma_x$  means a decrease (increase) of  $\sigma_p$

### C. Time propagation

In one dimension the time-dependent Schrödinger equation is given by (in au)

$$i\partial_t \Psi(x, t) = \hat{H} \Psi(x, t) = [\hat{T} + \hat{V}] \Psi(x, t) \quad (7)$$

in which  $\hat{T}$  and  $\hat{V}$  are the kinetic and potential operators, respectively. If  $\hat{V}$  is time independent its formal solution is given by

$$\Psi(x, t) = e^{-i\hat{H}t} \Psi(x, t=0) = e^{-i[\hat{T} + \hat{V}]t} \Psi(x, t=0) \quad (8)$$

This expression can be approximated by splitting the operators according to

$$\Psi(x, n\Delta t) \approx \left[ e^{-i\hat{T}\Delta t} e^{-i\hat{V}\Delta t} \right]^n \Psi(x, t=0) \quad (9)$$

where we discretized the equation by writing  $t = n\Delta t$ . The error due to the splitting of the operators is of the order  $(\Delta t)^2$  and therefore the value for  $\Delta t$  should be small to obtain reliable results. For example, for  $n = 1$  we obtain

$$\Psi(x, \Delta t) \approx e^{-i\hat{T}\Delta t} e^{-i\hat{V}\Delta t} \Psi(x, t=0). \quad (10)$$

Here we will consider two potentials, the harmonic potential and a double-well potential. In position space their expressions are given by

$$\hat{V}_{\text{harmonic}} = \frac{1}{2} m \omega^2 x^2 \quad (11)$$

$$\hat{V}_{\text{doublewell}} = E_{\text{barrier}} (16x^4 - 8x^2 + 1) \quad (12)$$

where  $\omega$  is the angular frequency and  $E_{\text{barrier}}$  is the height of the barrier separating the two wells. The kinetic potential in position space is given by

$$\hat{T} = -\frac{1}{2m} \frac{\partial^2}{\partial x^2} \quad (\text{position space}) \quad (13)$$

While the potential operators are simple multiplicative operators the kinetic operator is a differential operator. The opposite is true in momentum space in which the kinetic operator is a multiplicative factor:

$$\hat{T} = \frac{p^2}{2m} \quad (\text{momentum space}) \quad (14)$$

Therefore, if we go back and forth between position and momentum space using Fourier transformations we can calculate Eq. (9) just by multiplying. For example, we can rewrite Eq. (10) according to

$$\Psi(x, \Delta t) \approx FT^{-1} \left[ e^{-i\hat{T}\Delta t} FT \left[ e^{-i\hat{V}\Delta t} \Psi(x, t=0) \right] \right] \quad (15)$$

where  $FT$  and  $FT^{-1}$  denotes a forward and backward Fourier transformation, respectively. The wave packet at larger times can be obtained in a similar way, for example  $\Psi(x, 2\Delta t)$  can be calculated from

$$\Psi(x, 2\Delta t) \approx FT^{-1} \left[ e^{-i\hat{T}\Delta t} FT \left[ e^{-i\hat{V}\Delta t} \Psi(x, \Delta t) \right] \right] \quad (16)$$

$$\approx FT^{-1} \left[ e^{-i\hat{T}\Delta t} FT \left[ e^{-i\hat{V}\Delta t} FT^{-1} \left[ e^{-i\hat{T}\Delta t} FT \left[ e^{-i\hat{V}\Delta t} \Psi(x, t=0) \right] \right] \right] \right] \quad (17)$$

## D. Eigenvalue spectrum

The initial wave packet can be expressed as a linear combination of stationary states of the Hamiltonian.

$$\Psi(x, t = 0) = \sum_n c_n \Phi_n(x) \quad (18)$$

where  $\Phi_n(x)$  are the stationary states and  $c_n$  the coefficients. Substitution of the above expression into the solution of the time-dependent Schrödinger equation given in Eq. (8) leads to

$$\Psi(x, t) = e^{-i\hat{H}t} \sum_n c_n \Phi_n(x) = \sum_n c_n e^{-i\hat{H}t} \Phi_n(x) = \sum_n c_n e^{-iE_n t} \Phi_n(x) \quad (19)$$

where  $E_n$  are the eigenenergies. To perform the last step remember that the exponential function is defined as  $e^X = \sum_{n=0}^{\infty} \frac{X^n}{n!}$ . We will now give some illustrative examples.

### 1. Two-state superposition

Let us consider a wave packet that is a superposition of two states:

$$\Psi(x, t) = c_1 e^{-iE_1 t} \Psi_1(x) + c_2 e^{-iE_2 t} \Psi_2(x) \quad (20)$$

and calculate its probability density (for simplicity we assume  $\Psi_1, \Psi_2, c_1, c_2$  real):

$$|\Psi(x, t)|^2 = [c_1 e^{iE_1 t} \Psi_1(x) + c_2 e^{iE_2 t} \Psi_2(x)] [c_1 e^{-iE_1 t} \Psi_1(x) + c_2 e^{-iE_2 t} \Psi_2(x)] \quad (21)$$

$$= c_1^2 \Psi_1^2(x) + c_2^2 \Psi_2^2(x) + c_1 c_2 \Psi_1(x) \Psi_2(x) \left( e^{i(E_1 - E_2)t} + e^{-i(E_1 - E_2)t} \right) \quad (22)$$

$$= c_1^2 \Psi_1^2(x) + c_2^2 \Psi_2^2(x) + 2c_1 c_2 \Psi_1(x) \Psi_2(x) \cos[(E_2 - E_1)t] \quad (23)$$

We conclude that the probability density varies with time and that this variation is periodic and has a period

$$T = \frac{2\pi}{E_2 - E_1} \quad (24)$$

The energy difference of two levels can be expressed in terms of the wavenumber  $\bar{\nu}$  according to

$$E_2 - E_1 = \frac{2\pi}{T} = 2\pi\nu = 2\pi c\bar{\nu} \quad (25)$$

In spectroscopy energies are often expressed in  $\text{cm}^{-1}$ . These units are not true energy units but units proportional to energies. Indeed, we see that the energy difference between two levels is proportional to  $\bar{\nu}$  (which has units  $\text{cm}^{-1}$ ), the prefactor  $2\pi c$  being constant. “Energies“ expressed in  $\text{cm}^{-1}$  can be calculated from the period  $T$  according to

$$\bar{\nu} = \frac{1}{cT} \quad (26)$$

### 2. Harmonic potential

Let us now consider a wave packet that is a linear combination of several states that is governed by a Hamiltonian in which the potential is harmonic. The eigenenergies of such a Hamiltonian are  $E_n = \omega(n + \frac{1}{2})$  where  $\omega$  is the angular frequency. We can rewrite these eigenenergies according to  $E_n = \frac{2\pi}{T}(n + \frac{1}{2})$  where  $T$  is the period of the classical oscillator. We will now show that the probability density of the wave packet has the same period. Since the eigenenergies are equidistant we can write the wave packet at  $t = mT$  as

$$\Psi(x, mT) = \sum_n c_n e^{-iE_n mT} \Phi_n(x) = \sum_n c_n e^{-i2\pi(n+\frac{1}{2})m} \Phi_n(x) \quad (27)$$

$$= \sum_n c_n e^{-i2\pi n m} e^{-i\pi m} \Phi_n(x) = \sum_n c_n (e^{-i2\pi})^{nm} (e^{-i\pi})^m \Phi_n(x) \quad (28)$$

$$= (-1)^m \sum_n c_n \Phi_n(x) = (-1)^m \Psi(x, t = 0) \quad (29)$$

As a result the probability density at  $t = mT$  is the same as the probability density at  $t = 0$ :

$$|\Psi(x, mT)|^2 = (-1)^{2m} |\Psi(x, t = 0)|^2 = |\Psi(x, t = 0)|^2 \quad (30)$$

This shows that indeed the probability density has the same period as that of the classical oscillator. Note that the wave packet itself has a period of  $2T$ .

The period of the probability density can be calculated from the angular frequency or, equivalently, from the energy difference between adjacent levels:

$$T = \frac{2\pi}{\omega} = \frac{2\pi}{E_n - E_{n-1}} \quad (31)$$

This result is therefore equivalent to that obtained for the case of a superposition of two states. The energy difference of two adjacent levels can therefore be expressed in terms of the wavenumber  $\bar{\nu}$  in a similar way as well:

$$E_n - E_{n-1} = \omega = \frac{2\pi}{T} = 2\pi\nu = 2\pi c\bar{\nu} \quad (32)$$

“Energies“ expressed in  $cm^{-1}$  can be calculated from the period  $T$  according to

$$\bar{\nu} = \frac{1}{cT} \quad (33)$$

### 3. Autocorrelation function

The autocorrelation function  $C(t)$  is the overlap of the wave packet at time  $t$  with the wave packet at  $t = 0$ . It is defined by

$$C(t) = \langle \Psi(t = 0) | \Psi(t) \rangle \quad (34)$$

and can be used to find repeating patterns in the wave packet.

The Fourier transform of the autocorrelation function is the energy eigenvalue spectrum  $\bar{C}(E)$ .

*Proof:*

$$\bar{C}(E) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dt C(t) e^{iEt} = \frac{1}{2\pi} \int_{-\infty}^{\infty} dt \langle \Psi(t = 0) | \Psi(t) \rangle e^{iEt} \quad (35)$$

$$= \frac{1}{2\pi} \int_{-\infty}^{\infty} dt \int_{-\infty}^{\infty} dx \Psi^*(x, t = 0) \Psi(x, t) e^{iEt} \quad (36)$$

$$= \frac{1}{2\pi} \int_{-\infty}^{\infty} dt \int_{-\infty}^{\infty} dx \sum_m c_m^* \Phi_m^*(x) \sum_n c_n e^{-iE_n t} \Phi_n(x) e^{iEt} \quad (37)$$

$$= \frac{1}{2\pi} \sum_{mn} c_m^* c_n \int_{-\infty}^{\infty} dx \Phi_m^*(x) \Phi_n(x) \int_{-\infty}^{\infty} dt e^{i(E - E_n)t} \quad (38)$$

$$= \sum_{mn} c_m^* c_n \delta_{mn} \delta(E - E_n) \quad (39)$$

$$= \sum_n |c_n|^2 \delta(E - E_n) \quad (40)$$

where we used the fact that the eigenfunctions of the Hamiltonian are orthonormal. We see that the eigenvalue spectrum  $\bar{C}(E)$  will have peaks at the eigenenergies of the Hamiltonian except if  $c_n = 0$  which means that the stationary state  $\Phi_n$  is absent in the wave packet.

#### IV. DESCRIPTION OF THE PROGRAM

The program with which we will perform the propagation consists of three files:

- **propagate.f90**: The main file containing the program **propagate** and several other subroutines needed to propagate the wave packet.
- **dfft.f**: Auxiliary file containing the subroutines to perform fast-Fourier transformations.
- **graphics.f90**: Auxiliary file containing subroutines to create snapshots at selected times during the propagation. The snapshots are stored in postscript files.

There is a fourth file called **analysis.f90** which we will discuss later. Now edit the file **propagate.f90** using your favorite text editor, **vim** for example:

**vim propagate.f90**

You will see that the first part of the file is a module containing some parameters and conversion factors that will be needed in the program. Let us now look at the main program **propagate** just below. The first thing the program does is read two input files:

- **wavepacket**: contains information on the initial wave packet (initial position and width) as well as information on the time step, the number of grid points and the frequency at which snapshots are taken.
- **potential**: contains information on the type of potential (harmonic or doublewell) and the angular frequency  $\omega$  of the harmonic potential and the barrier height of the double-well potential.

Two input file templates with default values are provided. Have a look at them.

##### *Questions:*

1. What is the distance between adjacent grid points? (The length of the box is 5.12 Bohr)
2. What is the initial position of the centre of the wave packet?
3. What is the total propagation time?
4. At which interval are the snapshots taken?
5. What is the period  $T$  of the probability density of the harmonic oscillator?
6. What is the energy of the barrier in the double-well potential?

After the input has been read the initial wave packet **psi0** is calculated in the subroutine **initpsi**. Have a look at this subroutine and see if you can understand how it is calculated. Note that for negative  $x$  the corresponding values of **psi0** are stored after the values for positive  $x$ .

After initializing the FFT subroutine **fourier** the kinetic and potential operators are calculated in the subroutine **operators**. The kinetic operator is calculated in momentum space according to Eq. (14) and the potential operator is calculated in position space according to Eq. (11) or (12). Have a look at this subroutine and see if you can recognize these expressions. In the same subroutine the exponential is taken of both operators which we need for the time propagation (see Eq. (10)). Note that  $(0,1)$  is the imaginary unit  $i$ .

We have calculated the initial wave packet  $\Psi(x, t = 0)$  as well as  $e^{-i\hat{T}\Delta t}$  and  $e^{-i\hat{V}\Delta t}$ . Therefore, we can now start the time-propagation loop. Have a look at the first part of this loop (the last part is just for producing the snapshots). Do you understand that one cycle corresponds to Eq. (15) and two cycles to Eq. (17), etc?

We are now ready to compile the source code and run the program

## V. COMPILING THE SOURCE CODE AND RUNNING THE PROGRAM

Go to the appropriate working directory and compile the source code with gfortran using

```
gfortran propagate.f90 graphics.f90 dfft.f -o propagate
```

which creates the executable **propagate**

### A. Harmonic potential

Let us first propagate the wave packet in the harmonic potential. Create a directory in which you will run the program, for example:

```
mkdir harmonic
```

Change directory to **harmonic** and copy the input files **wavepacket** and **potential**. Now run the program

```
../propagate
```

The program produces **psi\*\*\*.ps** files with snapshots at various times during the propagation.

Considering that  $\Psi(x, t)$  represents a physical wave packet, what should the area under the curve  $(\int_{-\infty}^{\infty} |\Psi(x, t)|^2 dx)$  be equal to at any time  $t$ ? Now look at the snapshot of  $|\Psi(x, t = 0)|^2$  at  $t = 0$  which is plotted in **psi000.ps** and make a rough estimate of the area under the curve.

You have discovered a bug in the program!

#### *Exercise 1:*

Edit the file **propagate.f90** and scroll down to the subroutine **initpsi**. Implement the code necessary to calculate numerically the normalisation constant  $N$ . Then multiply the initial wave packet  $\Psi(x, t = 0)$  with  $N$  to obtain a normalized wave packet.

*Hint:* numerically an integral is calculated as a sum of small areas:

$$\int_{-\infty}^{\infty} |\Psi(x, t = 0)|^2 dx \rightarrow \Delta x \sum_{i=1}^{N_{points}} |\Psi(x_i, t = 0)|^2 \quad (41)$$

Now that the bug is fixed we can recompile (gfortran ...) and rerun the program.

You can convert the .ps files to an animated .gif file using Imagemagick:

```
convert -set dispose previous -delay 20 psi*.ps harmonic.gif
```

The option “-set dispose previous” indicates that when a new image is shown the previous one should be disposed of (to avoid that images at different times overlap) and the option “-delay 20” indicates that the time delay between subsequent images is 20/100 seconds. The creation of the animated .gif might take a couple of minutes. You can view the animated .gif with any web browser. For example, with **chrome**:

```
google-chrome harmonic.gif
```

#### *Questions*

1. From the animation make an estimate of the period  $T$ ? Does it correspond to the one calculated from the angular frequency?
2. Use the period  $T$  to calculate the energy difference between two stationary states in  $\text{cm}^{-1}$ ? ( $c = 2.99792458 \times 10^8 \text{ m/s}$ )
3. The width of the wave packet in position space is smallest at the turning points and largest at the centre of the potential. What does that tell you about the width of the wave packet in momentum space at the turning points and at the centre?

## B. Symmetric double-well potential

Let us now propagate the wave packet in the double-well potential. Create a directory in which you will run the program, for example:

```
mkdir doublewell
```

Change directory to **doublewell** and copy the input files **wavepacket** and **potential**. Make sure that in the input file **potential** the type of potential is set to **doublewell**. For the double well it might be useful to increase the total time of the propagation to 160 fs (without changing the time step). It is a good idea to also quadruple the snapshot frequency in order to have the same number of snapshots. Now run the program and create the animated .gif which you could call **doublewell.gif** for example.

### Questions:

1. After a certain amount of time the wave packet is almost the same (but not exactly) as the wave packet at  $t = 0$ . We can consider this time to be a pseudoperiod  $\tilde{T}$  of the probability density. Make an estimate of  $\tilde{T}$ . (If the animation is too fast, note that you can slow it down by increasing the delay.)
2. The initial wave packet can be expressed as a linear combination of stationary states (Eq. (18)). Let us now assume that this linear combination is dominated by the first two states, i.e., all the coefficients are small except those of state 1 and 2. Using the pseudoperiod  $\tilde{T}$  what do you expect that energy difference between these two states would be?

## VI. ANALYSIS

We will now calculate some properties that can be obtained from the wave-packet propagation. In particular, we will calculate the eigenvalue spectrum. To obtain it we will need to propagate for a longer time than we have done so far; we will use a total time of 5000 fs. With a time step equal to 0.01 fs the propagation might take quite long. We should therefore increase the time step but we must be careful not to choose a value that is too big such that the errors in the propagated wave packet become too big. Since our main interest is the calculation of the eigenvalue spectrum we should in principle calculate this spectrum for different time steps until the spectrum is converged (See exercise 7).

However, an indication of the stability of the time propagation can be obtained by verifying that some exact constraints remain satisfied during the time propagation. We will test two such constraints: conservation of the norm and conservation of the total energy. It turns out that for the chosen propagation scheme conservation of the norm is satisfied by construction for any time step. Nevertheless, it remains a good exercise to also check the conservation of the norm.

We will use the file **analysis.f90** which is a copy of **propagate.f90** but without the graphics part which we no longer need. (You might also want to clean up the directory /harmonic and /doublewell by removing the psi\*.ps files which we also no longer need). In the following you will create or complete several subroutines needed to verify the exact constraints and to calculate the spectra.

Edit the file **analysis.f90** and have a look at the program **propagate**. It is similar as before but we have added calls to several subroutines which you will find at the bottom of the file. You will now complete these subroutines.

### A. Norm conservation

#### Exercise 2:

In the program **analysis.f90** uncomment the call to **calcnorm**. Now write the subroutine **calcnorm** such that it calculates the norm  $\langle \Psi(x, t) | \Psi(x, t) \rangle$  for all times  $t$  of the propagation and such that it writes the results (the norm as a function of time) to file. You might call this file **norm**, for example.

*Hint:* Writing to file is very similar to reading from file; instead of **read** use **write**.

When you have finished to implement the calculation of the norm compile the program:

```
gfortran analysis.f90 dfft.f -o analysis
```

which creates the executable **analysis**. Now go to the directory **harmonic** and run the program using a time step of 1 fs.

**../analysis**

Now plot the norm as a function of time for the harmonic potential using, for example, gnuplot. Is the norm conserved?

Do the same for the double-well potential.

## B. Energy conservation

### Exercise 3:

In the program **propagate** uncomment the call to **calcenergy**. Now complete the subroutine **calcenergy** such that it calculates the energy  $E(t) = \langle \Psi(x, t) | \hat{H}(x) | \Psi(x, t) \rangle = \langle \Psi(x, t) | \hat{T}(x) | \Psi(x, t) \rangle + \langle \Psi(x, t) | \hat{V}(x) | \Psi(x, t) \rangle$  for all times  $t$  of the propagation and such that it writes  $E(t)$  to file. You might call this file **energy**, for example.

*Hint:* Remember that  $\hat{T}(x) | \Psi(x, t) \rangle$  is best calculated in momentum space. Also, when you use the wave packet **psi** in the subroutine **calcenergy** you should be careful not to modify it.

Then recompile the program. Now go to the directory **harmonic** and run the program using the time steps 1 fs, 0.5 fs, and 0.1 fs.

**../analysis**

Now plot the energies for these time steps as a function of time for the harmonic potential and zoom in on the range 0-100 fs. For a time step of 0.1 fs the energy should be conserved to within 0.1 kcal/mol at all times  $t$ , i.e.  $E(t) - E(t = 0) < 0.1$  kcal/mol for all  $t$ .

Do the same for the double-well potential. Also here the energy should be conserved to within 0.1 kcal/mol at all times  $t$  for a time step of 0.1 fs. We will now use this time step for the calculation of the autocorrelation function and the eigenvalue spectrum.

## C. Autocorrelation function

### Exercise 4:

In the program **propagate** uncomment the call to **autocorrelation**. Now write the subroutine **autocorrelation** such that it calculates the autocorrelation function  $C(t) = \langle \Psi(x, t = 0) | \Psi(x, t) \rangle$  for all times  $t$  of the propagation. Since the autocorrelation function is complex also calculate the square of its absolute value which is the survival probability:  $S(t) = |C(t)|^2$  which is easier to visualize. Write the survival probability to file. You might call this file **survival**, for example. Recompile the program, go to the directory **harmonic** and run the program

**../analysis**

Now plot the survival probability as a function of time for the harmonic potential and zoom in on the range 0-100 fs.

### Questions:

1. What does the probability density look like when the survival probability is equal to 1?
2. Can you deduce its period  $T$  from the survival probability? Does it correspond to the period calculated before?

Now calculate and plot the survival probability as a function of time for the double-well potential. Zoom in on the range 0-600 fs.

### Question:

1. Can you deduce the pseudoperiod  $\tilde{T}$  from the survival probability? Does it correspond to the pseudoperiod obtained before?



## D. Eigenvalue spectra

### Exercise 5:

We are now ready to calculate the eigenvalue spectra. In the subroutine **propagate** uncomment the call to **spectrum**. Now write the subroutine **spectrum** such that it calculates the eigenvalue spectrum  $\bar{C}(E)$ ,

$$\bar{C}(E) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dt C(t) e^{iEt}, \quad (42)$$

in both  $\text{cm}^{-1}$  and  $\text{kcal/mol}$ . Note that the energy step is defined in a similar way as the momentum step, i.e.,  $dE = \frac{2\pi}{t_{max}}$ .

Recompile the program, go to the directory **harmonic** and run the program

**../analysis**

Now plot the spectrum as a function of the energy in  $\text{cm}^{-1}$  for the harmonic potential and zoom in on the range 0-15000  $\text{cm}^{-1}$ .

### Questions:

1. What is the energy difference between two eigenvalues? Does it correspond to the value calculated before?
2. What do the values of the peaks correspond to? Which stationary states contribute to the wave packet?

Now calculate the eigenvalue spectrum for the double-well potential and plot the spectrum as a function of the energy in  $\text{cm}^{-1}$  for the harmonic potential and zoom in on the range 0-5000  $\text{cm}^{-1}$ .

### Questions:

1. Which stationary states contribute the most to the wave packet?
2. What is the energy difference between the first two eigenvalues? Does it correspond to the approximate value calculated before?

Finally, plot the spectrum as a function of the energy in  $\text{kcal/mol}$  for the harmonic potential and zoom in on 0-15  $\text{kcal/mol}$ .

### Question:

1. Which stationary states have an energy that are lower than the barrier between the two wells?

## VII. EXTRA EXERCISES

### Exercise 6:

For the harmonic potential centre the initial wave packet at  $x = 0.0$  and interpret the results (survival probability, eigenvalue spectrum).

### Exercise 7:

Calculate the kinetic and potential energy separately and plot them together with the total energy. When is the kinetic energy largest? and when is the potential energy largest?

### Exercise 8:

Check the convergence of the positions of the peaks in the eigenvalue spectra with respect to the time step. Use, for example, time steps of 1 fs, 0.1 fs, and 0.01 fs.

You can also check the convergence of the positions of the peaks in the eigenvalue spectra with respect to the total propagation time. Use, for example, propagation times of 1000 fs, 5000 fs, and 10000 fs.