Below are a set of example calculations to introduce the basic ideas of quantum dynamics calculations and how they are performed using the Quantics program. The information given is reduced as the examples progress and looking back to earlier examples should give the answer as to how something should be done. Further information is to be found in the on-line documentation, where detailed information on keywords available etc. are present. If $MCTDH_DIR is the root directory of the Quantics installation, the documentation is to be found at $MCTDH_DIR/doc/index.html

1 Exercise 1. One-Dimensional Oscillator

1.1 First Calculations: The Harmonic Oscillator

The Hamiltonian for a 1D harmonic oscillator is

$$H = -\frac{1}{2m}\frac{\partial^2}{\partial q^2} + \tfrac{1}{2}m\omega^2 q^2 \tag{1}$$

where m is the mass and ω the frequency. Note that we are using atomic units in which $\hbar = 1$ so it can be omitted.

To specify a Hamiltonian, you need an *operator file*. The operator file "ho1.op" codes the Harmonic oscillator Hamiltonian above. You will see there are 3 SECTIONS.

The OP_DEFINE-SECTION contains a title that will be printed in output.

The HAMILTONIAN-SECTION defines the operator. The line beginning "modes" defines the fact there is a single coordinate, labelled "x". The 2 lines between the dashes (these are not required for the operator, only to help readability) define 2 terms that can be related to the Hamiltonian 1.

The PARAMETER-SECTION defines the mass and frequency. Values of a proton mass with a frequency close to 3500 cm^{-1} are given. This is an approximate C–H stretch.

To run a calculation you need an input file. Look at ho1.inp. Again there are various SECTIONs.

The OPERATOR-SECTION defines the file containing the operator - here "ho1.op".

The PRIMITIVE-BASIS-SECTION defines the "primitive basis set" - a grid of points on which the wavepacket will be propagated. Here 121 points between $x = -2$ au and $x = 2$ au are defined. ($1au \sim 0.5\text{Å}$).

The SPF-BASIS-SECTION defines the number of "single-particle" basis functions that will be used to describe the evolving wavepacket. For a 1D problem only 1 function is required.

The INIT_WF-SECTION defines the initial wavefunction. A Harmonic oscillator ground-state eigenfunction is specified here for mode x. The 4 parameters specify the centre of the wavepacket, its momentum, and the frequency and mass of the harmonic oscillator. Notice that the oscillator has been displaced to $x = 0.5au$.

Finally, the RUN-SECTION defines what will be calculated. Here we are running a propagation that will last for 20 fs with output written ever 0.5 fs. Output will be written to a directory "ho1".

1. Set-up the directory and run the calculation

- `mkdir ho1`

- `quantics ho1`

It should finish in a few seconds.

2. Move into the directory and list the contents

- `cd ho1`

- `ls`

There will be a number of files including `psi and pes`.

1.2 Analysing the Results

3. Plot the potential surface and wavepacket motion using the `showsys` program. This is driven by a simple menu. Type the number to activate the desired option and follow the instructions. You might have to type enter a number of times to be able to enter an option. To start type

- `showsys`

A menu will appear. Look at item 10, the plot task. Type

- `10`

A menu will appear with the possible plot tasks. Select

- `2 plot pes`

Now type 1. This activates "plot to screen" and a plot of the potential surface will be shown. This should be a quadratic curve. Try changing the energy units using option `90` to cm^{-}1 by using the keyword `cm-1`. Try changing the range over which the PES is plotted using options 30 (to change x-axis) and 70 (to change y-axis).

4. Now plot the wavepacket motion. From option 10 choose

- `7 plot reduced density`

The density is Ψ^2, i.e. the probability density for the particle. Reduced density means that the density has been integrated over any other degrees of freedom to allow the 1D plot to be made. Now type 1 to produce a plot of the wavepacket. By typing return repeatedly the wavepacket will move and the time shown at the top of the plot will be incremented. The plots should be 0.5 fs apart - the value of `tpsi` in the RUN-SECTION. If this was given a different value the snapshots would be at this new value.

Try option `280`. Selecting

- `2 = movie`

followed by `1` will provide a movie of the motion.

6. Plot the trajectory of the centre of the wavepacket. The easiest way to do this is to use another program that will extract the expectation value of the coordinates stored in the file `check`. Type

- `rdcheck -g`

Answer `1` in response to both `state = ?`   and `mode = ?`   as we are looking at the first mode of the first electronic state (that is all we have). This will produce a file `qdq.pl`. The option `-g` meant that this file is ready to be plotted using the `gnuplot` program. Type

- `gnuplot`

A prompt `gnuplot>` appears. To plot column 1 against 2 of the data using a line plot, type

- `plot "qdq.pl" u 1:2 w l`

This is the expectation value of the coordinate, which can be interpreted as the centre of the wavepacket. It should oscillate from 0.5 to -0.5, and should agree with what you saw as the wavepacket motion.

The time-period of a harmonic oscillator is given by

$$T = \frac{2\pi}{\omega}$$

If T is in fs and ω in cm^{-1}, then using the appropriate conversions factors

$$T = \frac{33356}{\omega}$$

For the system above what is the time period? Is that what is seen?

Column 3 contains the width of the wavepacket, defined as the standard deviation $\sqrt{<x^2> - <x>^2}$. This is plotted using

- `plot "qdq.pl" u 1:3 w l`

It also oscillates, but looking at the values is nearly constant.

1.3   Changing the system

To run a similar, but altered calculation move back up to the starting directory and copy the operator and input files.

- `cd ..`
- `cp ho1.op ho2.op`
- `cp ho1.inp ho2.inp`

Change the frequency of the oscillator in `ho2.op` to give a time period of 35 fs (change the parameter in the operator file). Run a propagation of 70 fs (2 time periods) by changing `tfinal` in the new input file. Also change the value of the `name` variable so that all the results are written to a directory `ho2`. Now make the new directory and run the new calculation

- `mkdir ho2`

- `quantics ho2`

Change into `ho2` and use `showsys` to plot the potential surface and wavepacket motion as before. Is it what you expect?

Try different starting points. To do this change the centre of the initial wavepacket in ho2.inp (the first parameter in the line defining the initial wavepacket in the INIT_WF-SECTION). Also try different initial widths (change the frequency, the third parameter in the line defining the initial wavepacket in the INIT_WF-SECTION).

Points to note:

- The time period does not depend on the initial displacement.

- If the frequency defining the initial wavepacket width matches the frequency of the potential function the wavepacket remains the same width at all times.

1.4   Harmonic Oscillator: Simple form

By transforming to dimensionless coordinates,

$$Q = \sqrt{\frac{m\omega}{\hbar}}\, x$$

(the square-root term has dimension length^{-1}) the Hamiltonian for a harmonic oscillator takes the neater form

$$H = \frac{\hbar\omega}{2}\left(-\frac{\partial^2}{\partial Q^2} + Q^2\right)$$

The operator file `ho.op` is for this form. Take it and the related input file `ho.inp`. Run the calculation in the same way as the first exercise and look at the results. Are they the same? The files are contained in the directory `ho`. The value of the coordinate has changed due to the scaling

$$Q = \sqrt{m[amu] \times \omega[cm^{-1}] \times 0.0083}$$

but the time period, the total energy (look in the file `output` at the value of "E-tot") and the behaviour of the wavepacket should all be the same (to a few significant figures at least).

1.5   Extension to anharmonicity: Quartic Oscillator

Some vibrations are better described by adding a quartic term to account for loss of harmonicity at large amplitudes

$$H = \frac{\omega}{2}\left(-\frac{\partial^2}{\partial Q^2} + Q^2\right) + \gamma Q^4$$

Copy `ho.op` and `ho.inp` to `quart.op` and `quart.inp`. Now edit the operator `quart.op` to add the quartic term. Add the parameter

- gamma = 20, cm-1

to the PARAMETER-SECTION and the quartic term by adding the line

- gamma | q^4

below the quadratic term in the HAMILTONIAN-SECTION

Edit `quart.inp` to read the operator file `quart.op` and write the information to a directory `quart`. Run the calculation and again analyse the results. Note that even though the potential does not look that different it has changed the period and regularity of the dynamics.

1.6 Double Well Minima

Copy `quart.op` and `quart.inp` to `dble.op` and `dble.inp`. In the new operator file change the sign in front of the quadratic term so that the HAMILTONIAN-SECTION now reads

```
-0.5*omega        | dq^2
-0.5*omega         | q^2
gamma              | q^4
```

Change the value of `gamma` to 40 cm$^-$1.

In `dble.inp` change not only the operator and the output directory but start the wavepacket centred at $Q = -5$. Run the propagation as before.

On plotting the potential you will see that is has a "double-well" structure. This is typical of coordinates which involve 2 symmetrical minima separated by a barrier, e.g. proton transfer. The starting position chosen is fairly low in energy and in general the wavepacket stays in the one well.

Repeat the calculation starting with the wavepacket centred at 5.5, 6.0, 6.5. The behaviour changes as the energy approaches the top of the barrier (tunnelling occurs) and then exceeds it.

1.7 Advanced anharmonicity: The Morse Oscillator

Finally we shall change the harmonic oscillator to a Morse oscillator. To replace the harmonic potential with a Morse function. involves replacing the $\frac{1}{2}\omega Q^2$ with a label such as V and defining the Morse operator in a LABELS-SECTION. This has been done in `mo.op`. Note that this is based on the full x-coordinate system rather than the dimenless one.

Using the input file `mo.inp` run and look at the dynamics. Note that it looks much like the harmonic systems. Now move the initial wavepacket out, first to be centred at -0.2 and then -0.3. Notice the effects of the anharmonicity.