

## 4 Exercise 4. NOCl Photodissociation

### 4.1 Determining the absorption spectrum for the photodissociation of NOCl

The photodissociation of NOCl is a simple photo-chemical reaction. After excitation from the ground to the first excited state,  $S_0 \rightarrow S_1$ , the chlorine atom dissociates on a femto-second time-scale. This results in a broad band for the absorption spectrum.

The calculation consists of two stages. First, the ground state wavefunction is generated by energy relaxation of an initial guess wavefunction on the ground state surface,  $S_0$ . The second stage then places this wavepacket on the excited state surface,  $S_1$ , leading to photodissociation.

1. Copy the files `$MCTDH_DIR/inputs/nocl0.inp` and `$MCTDH_DIR/inputs/nocl1.inp` to your tutorial directory, and create there the directories `nocl0` and `nocl1`.
2. To perform the ground state relaxation calculation, type

```
quantics nocl0
```

3. To perform the photo-dissociation calculation, type

```
quantics nocl1
```

The calculation can now be analysed. Move to the directory `nocl1` which contains all the data files from the propagation.

1. To watch the system dissociating, start the `showd1d` program

```
showd1d -inter
```

and follow the menu options to plot. First type 1. This gives a 3D plot of the wavepacket as a function of time. Next type 10 to change the plot task and choose 2 to plot time slices. Enter 1 to plot these. You can now make a movie by typing 280 and selecting 1 or 2. With option 1 you need to press return to go through the frames.

2. To plot the spectrum, type

```
autospec -inter
```

You now need to enter the required range for the spectrum, a damping time and a damping order. For the range enter 0.6 2.0 ev. For the damping time 0, for the damping order 1. To plot the spectrum type 1. The result is shown in Fig. 1. Note that the spectrum shown is the Fourier-transform of the autocorrelation function times the energy. Hence it is assumed that the ground state energy is at zero, such that energy equals excitation energy. If this is not the case, use option 802 to shift the energy scale.

Before the autocorrelation function is Fourier transformed, it gets modified. To reduce artifacts of the Gibbs phenomenon, the autocorrelation function is multiplied with  $\cos^n(\pi t/2T)$ , where  $n = 0, 1, 2$  and where  $T$  denotes the final time (plus one time step) of the autocorrelation function. Due to the

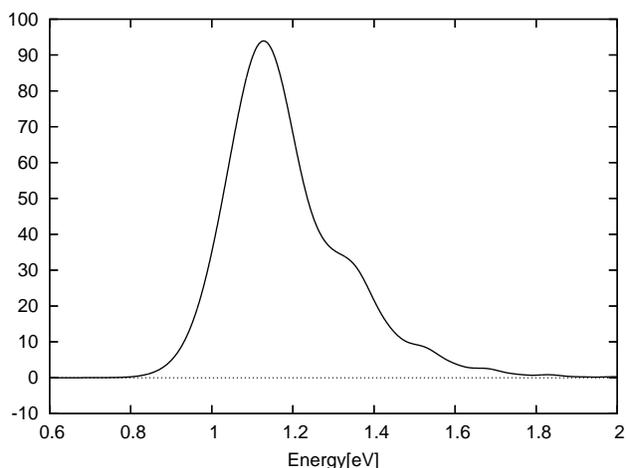


Figure 1: The absorption spectrum for the NOCl molecule on excitation to the  $S_1$  state.

$t/2$ -trick, see Eq. (167) of the MCTDH review, the propagation time is only  $T/2$ . The columns 2–4 of the `spectrum.pl` file list the results for the different  $n$ 's. To introduce a damping, i. e. a Lorentzian or Gaussian broadening, the autocorrelation function is further multiplied with  $\exp(-(|t|/\tau)^i)$  where  $\tau$  and  $i = 1, 2$  are the two last arguments of `autospec`. The exponential is ignored if  $\tau = 0$ . Finally the Fourier transform is multiplied with the photon energy  $\omega$  to arrive at an absorption spectrum.

Save the spectrum to a gnuplot file using option `4` = save plot to a gnuplot file (use after 1 or 2). Give the name `spectrum1.pl`. This file contains the data and commands to plot using `gnuplot spectrum1.pl`

The program `showsys` is a powerful tool for plotting 1D and in particular 2D views on wavepackets and potentials. Type

```
showsys
```

A menu appears which allows various options to be set. Go to menu point 10 (type 10), and change the plot task to `2 = plot pes` (type 2). Next input a 1 three times and a 2D cut through the surface (with theta fixed to 1.545 radians) will pop up. Now use menu point `20 = change coordinate section`, i.e. chose another cut. If one gives  $x$  and two numbers, a 1D plot will appear. After you have played around enough, go back to menu point 20 and input

```
x y 2.1
```

Then use menu point 5. You will be asked for a file name. Chose any convenient name, e. g. `xyz`. The plot data is then written to the file `xyz` for later use.

Next we want to inspect the wavefunction. Go to menu point 10 and chose `5 = plot reduced density`. The density, i.e  $|\Psi|^2$  integrated over all coordinates, except those specified by  $x$  and  $y$  (that is integrated over all angles in the present case), will be shown. Input a 1 three times and you will see the initial density. Pressing RETURN will display the density propagated by one time step, and so on. After you have returned to the menu, chose point `400 = Overlay plots` and then `410 = File for overlay` and enter the file name (`xyz`). Turn off the key using option 240.

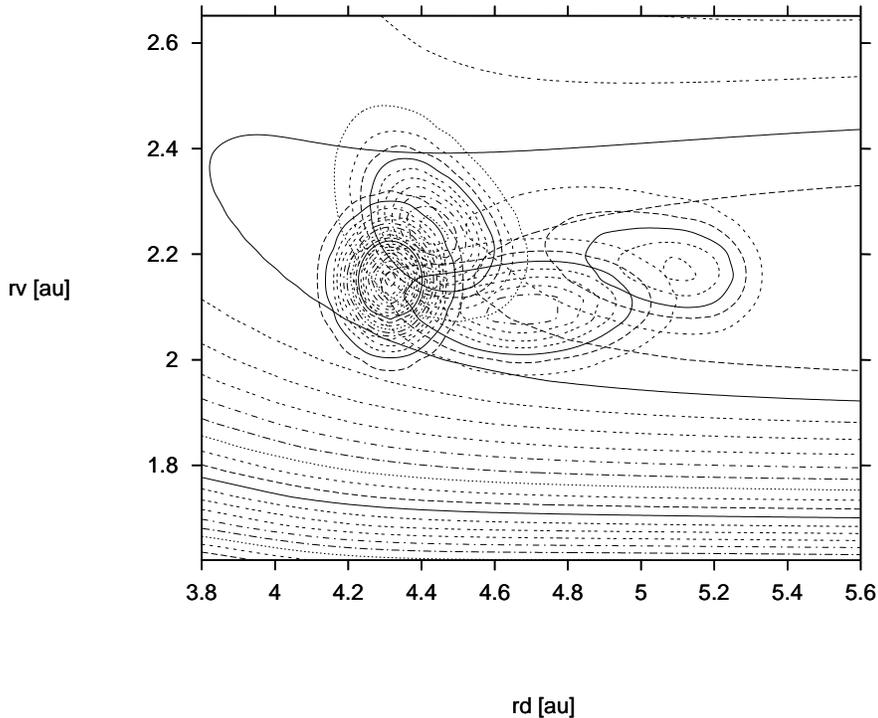


Figure 2: Overlay plot, wavepacket on potential. The Wavepacket density is shown for the times  $t = 0, 10, 20, 30$  fs. The density is obtained by integrating  $|\Psi|^2$  over all angles, whereas the potential contour lines are obtained by fixing the angle to 2.1 rad.

After inputting 1's you will now see an overlay plot, i. e. the wavepacket on top of the contour lines of the potential.

With menu points 240 and 245 one may switch off the legend (or keys) and the title. Menu point 285 allows to take larger time steps and with point 280 one may switch to different plot forms, e. g. to plot all time slices at once. Such a plot is shown in Fig. 2.

Inspect the ASCII files of the name directories, in particular `output`, `log`, and `timing`. The file `input` contains a copy of the input file, the options, and the operator file. Thus, it tells you exactly what you have been doing. Since an NOCI run is so fast, NOCI is ideally suited for testing. Just play around with it! You may e. g. change the numbers of single particle functions or alter the integrator accuracies. You also may try the options, e. g. to start a continuation run type:

```
quantics -c -tfinal 50 nocl1
```

Type `quantics -h` to obtain the list of options.

## 4.2 Computing excitation and reaction probabilities

The analysis of scattering processes, i. e. the computation of excitation and reaction probabilities, is performed by evaluating the quantum flux going into a particular channel. The quantum flux is determined by the interaction of the time-dependent wavepacket with a CAP. The program `flux` performs the necessary analysis. The `psi` file is read and the energy resolved flux is computed and written to the `flux` file. Additionally this flux is divided by the energy distribution of the initial wavepacket to obtain the transition or reaction probabilities. The latter step requires in general that the `quantics` program has computed the energy distribution of the initial wavepacket and has written it to the `enerd` file. (NB: The file `enerd` is called `adwkb`

in older versions). Besides the `flux` file, `flux` creates the files `flux.log`, `gtau` and `wtt`. When the file `gtau` is present the flux program skips the time consuming evaluation of the integrals  $\langle \Psi(t)|W|\Psi(t + \tau) \rangle$  but reads the function  $g(\tau)$  from the `gtau` file. (See the MCTDH review, section 8.6.3, Eq.(199), for more details). This allows to re-do the Fourier integrals for another energy interval very quickly. The option `-w` enforces the re-calculation of  $g(\tau)$ .

The file `wtt` contains the expectation values  $W_{tt} = \langle \Psi(t)|W|\Psi(t) \rangle$ . This information is useful for checking that the absorption process has finished. The shell script `plwtt` visualises the function  $W_{tt}$ , while `plflux` and `plflux -r` visualise the flux and the transition probability, respectively.

The program `flux` cannot only determine the total energy resolved flux going into a particular arrangement channel (i. e. going into a particular CAP) but can also determine the flux which is projected onto final quantum states or which is weighted by an operator. This is probably best demonstrated by an example. We also want to plot the flux as a function of time so want to calculate the expectation value of the flux operator in the dissociation channel.

Copy the file `nocl1.op` to your tutorial directory and add the following lines to this operator file to define the NO vibrational Hamiltonian and the flux operator.

```
HAMILTONIAN-SECTION_vib
usediag
-----
modes      | rd      | rv      | theta
-----
1.0         | 1       | KE      | 1
1.0         | 1       | v:NO    | 1
-----
end-hamiltonian-section

HAMILTONIAN-SECTION_flux
-----
modes      | rd      | rv      | theta
-----
1.0         | flux    | 1       | 1
-----
end-hamiltonian-section
```

Define the flux operator to start just before the CAP by adding a definition to the LABELS-SECTION so that it reads

```
LABELS-SECTION
V = srffile {nocl1um, default}
flux = flux[4.8,1]
end-labels-section
```

Then edit the input file `nocl1.inp` and set the propagation time to `tfinal=100.0` as the propagation has to be run until all the wavefunction passes through the dividing surface defined by the flux operator. Add the keyword `expect = flux` to evaluate the expectation of the flux operator and re-run.

To analyse the result, move into the directory `nocl1`. First plot the flux as a function of time. This is contained in the file `expectation`. Start up `gnuplot` and type

```
plot "expectation" u 1:2 w l
```

This plots the norm which is close to 0 at the end of the propagation.

```
plot "expectation" u 1:3 w l
```

plots the flux. There is a set of peaks, dominated by a first, fast component and a second, slower component.

Next evaluate the total flux as a function of energy and save it in the file `flux.0`

```
flux -w 0.61 2.0 ev rd  
mv flux flux.0
```

To display it, type

```
plflux -f flux.0
```

As you will notice, the plot looks very similar to the absorption spectrum calculated above (and shown in figure 1). It is not identical, though, as the definition of an absorption spectrum contains a factor  $\omega$ , the energy of the absorbed photon. This multiplication is omitted when **autospec** is run with the `-FT` option. Do this

```
autospec -FT 0.61 2.0 ev 0 1
```

Now the spectra are identical as one observes when typing

```
plflux -G -f flux.0 -d spectrum.pl
```

This shows the flux and the Fourier transform of the autocorrelation function on top of each other.

Next we modify the flux by letting the operator of the vibrational energy act on it.

```
flux -w -0 vib -u 200. 0.61 2.0 ev rd  
mv flux flux.op
```

To view this

```
plflux -G -f flux.0 -d flux.op
```

and you will see the total flux in comparison with the vibrational energy weighted flux. It is now clear that the structures in the spectrum are due to vibrational excitation of the NO fragment. By the way, via the option `-u 200` the modified flux was multiplied by the factor 200. This was done to make it comparable with the total flux. Usually the option `-u` is followed by an energy keyword, e.g. `-u ev`, to transform the weighted flux from a.u. to a desired energy unit.

One may divide the weighted flux by the total flux to observe the vibrational energy content by using the option `-ed flux.0`

```
flux -ed flux.0 -0 vib -u ev 0.61 2.0 ev rd  
mv flux flux.op_r
```

To visualise the quotient weighted-flux/total-flux, which is related to the reaction probability, type

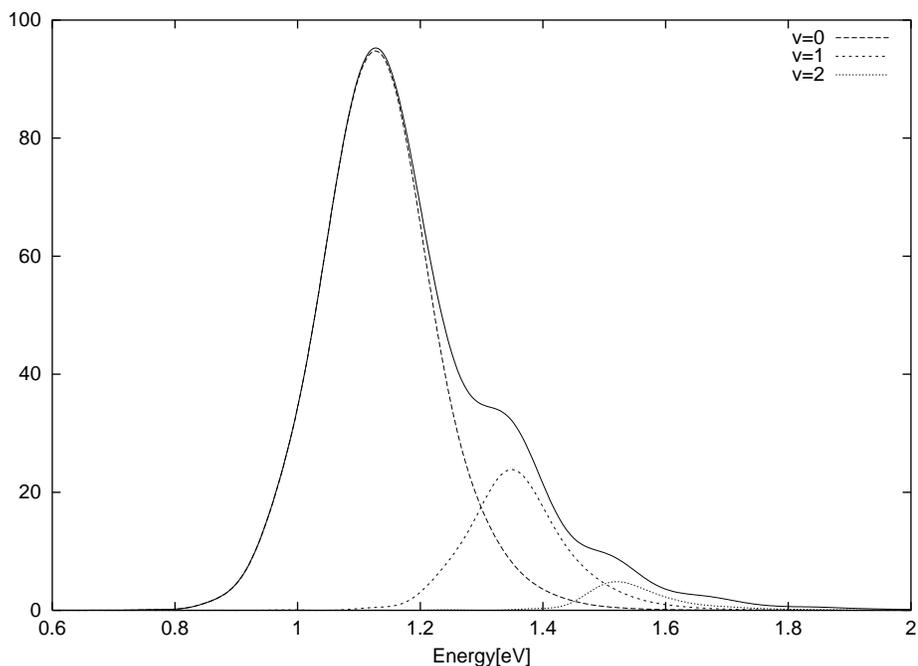


Figure 3: The total (full line) and projected flux of dissociating NOCl. The projection is on the vibrational states of the NO fragment,  $v=0$ ,  $v=1$ , and  $v=2$ , respectively.

```
plflux -G -r -f flux.op_r
```

The structures below 0.8 eV are numerical noise because one divides a very small number by another very small number. Obviously, the higher the energy of the absorbed photon, the larger is the vibrational energy of the NO fragment and the higher the chance of dissociation.

Finally we demonstrate the use of projectors. To project onto the lowest 3 vibrational eigenfunctions of the NO Hamiltonian, type

```
flux -w -P 2 eigenf vib 1 % 0.61 2.0 ev rd
mv flux flux.1
flux -w -P 2 eigenf vib 2 % 0.61 2.0 ev rd
mv flux flux.2
flux -w -P 2 eigenf vib 3 % 0.61 2.0 ev rd
mv flux flux.3
```

To display the results type

```
plflux -G -f flux.0 -d flux.1 -e flux.2
plflux -G -a 1.0 -y 25. -f flux.0 -d flux.2 -e flux.3
```

The first plot shows the flux projected onto the vibrational ground state and the first excited state, respectively, in comparison with the total flux. The second plot is similar, but shows the flux projected onto the first and second excited state, respectively. The Fig. 3 displays the total and projected projected flux, similarly to the plots generated above.