

2 Exercise 2. Spectroscopy

2.1 Absorption Spectrum

An absorption spectrum is calculated from the “Fourier Transform of an autocorrelation function”, i.e.

$$I(\omega) \propto \int_{-\infty}^{\infty} dt C(t) e^{i\omega t}$$

where

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

Assuming a *vertical excitation*, like that in Fig. 1, we can simply propagate the ground-state wavefunction place “vertically” onto the excited state.

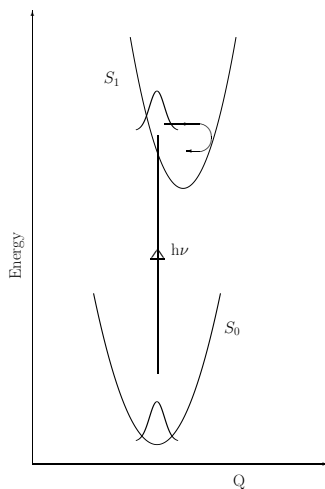


Figure 1: Schematic diagram of vertical excitation from S_0 into S_1

The simplest model of a bound excited state is a harmonic oscillator that is shifted and changed in frequency relative to the ground state. This is the case in `ho_ex.op`. Take this operator and the input file `ho_ex.inp` and first plot the PES by setting up the appropriate directory for the results, run

- `quantics -t ho_ex`

before moving into the directory and plotting the surface using `showsys`. The `-t` option is a test calculation that stops after setting up the calculation and calculating the initial energy. The minimum is not at $Q = 0$ and the energy of the minimum is now also not at 0. If you look in the operator file the new terms

```
E1          | 1
kappa       | q
```

are responsible for shifting the curve up and across.

Now run the dynamics. Note that in the input file the keyword `auto` has been set to create the autocorrelation file. As for the harmonic oscillator examples of exercise 1, the dynamics are run from the main directory (where the input file is) using

- `quantics -w ho_ex &`

You will need the `-w` option as the output directory is not empty due to the creation of files during the initial test calculation. The `&` puts the calculation into the background and you can get on with other work while it is running.

2.1.1 Plotting the results: autocorrelation function and spectrum

When it has finished, move into the output directory and look at the dynamics of the wavepacket. It should much the same as the ground-state harmonic oscillator. Now plot the autocorrelation function. To do this we need the program `rdauto`. Type

- `rdauto -inter`

A menu will appear (`-inter` is an argument that provides this). Plot the absolute value of the autocorrelation function. This is the default plot task and so this can be done by simply typing `1`. This is a periodic function with the time period of the harmonic motion that starts with a value of 1 (complete overlap) and falls to 0.8 as the wavepacket moves away.

To plot the spectrum, type

- `autospec -inter`

You will be asked to enter `E-min`, `E-max`, `unit =?` (e.g: `2.`, `5.`, `ev`), i.e. the energy bounds for the spectrum and the units. Enter `3 7 ev`. In response to `tau =?` (damping time in fs) respond with `100` and for `iexp =?` (damping order) enter `1`.

2.2 Further calculations

Rerun the dynamics with different values of the parameter `kappa` in the `ho_ex.op` operator file. First try `kappa = -0.5 , ev` and then `kappa = -1.0 , ev`. As the linear parameter is increased in value, the equilibrium geometry of the excited state shifts further from that of the ground state and the minimum drops in energy. From the Harmonic oscillator potential function it can be shown that the geometry shift is κ/ω and the energy shift $-\kappa^2/2\omega$. Plot the potential energy surface each time (use `showsys`) and see that this is the case.

Now plot the spectra. As κ increases, the progression of lines becomes wider. With the initial value of `-0.2 eV` there was only 2 peaks. With `0.5 eV` there are 4 peaks and with a value of `1.0 eV` there is a number of peaks initially rising in intensity. These progressions are due to the changing Franck-Condon factors of the oscillator as the equilibrium geometry is shifted further. On plotting the autocorrelation function for the different runs you will see that the absolute value drops lower with the larger shift values as the wavepacket moves further from its initial position.

The damping time parameter controls the width of the peaks. Try changing this value either on starting `autospec` or from the menu using option `800`. If this value is made small (e.g. `35 fs`) the peaks are much wider. If it is made bigger (e.g. `200 fs`) the peaks are narrower, but due to the finite length of the propagation a larger value will start to cause errors and spurious peaks appear.

2.3 A pair of harmonic oscillators

Repeat the excited state calculation for a pair of oscillators using `ho_ex2.inp` and `ho_ex2.op`. One of these has the same parameters as the original oscillator with $\omega = 3335.6 \text{ cm}^{-1}$ and $\kappa = -0.5 \text{ eV}$. The second has a different frequency and shift. As a result the spectrum has 2 progressions, the original combined with a new one, a few smaller peaks to the lower frequency side.

Plot the potential surface (in the output directory use `showsys` selecting plotting the pes from option 10). You will be asked the desired contour levels. Accept the defaults and now the surface is displayed as a contour plot of a well centred at 0. Select 160. On plotting now produces a 3D surface. Initially the units are au. Use option 90 to change to eV (enter `ev`). Plot again using 1. Now use option 70 to control the depth of the well plotted. Plot it between 4 and 8 eV. You will find the return key needs to be pressed between plots often enough that the menu appears before selecting the next option.

Using option 10, now plot a movie of the reduced density.

2.3.1 Coupling the oscillators

To see the effect of coupling between the vibrational modes, copy `ho_ex2.op` to a new file, e.g. `ho_ex2c.op`. Add the following line

- `gamma = 700, cm-1`

to the PARAMETER-SECTION, and the coupling term

- `gamma | q | q`

to the HAMILTONIAN-SECTION. Copy the input file in the same way and after altering the relevant file names for operator and output directory, run the new calculation.

- Plot the potential surface. In the uncoupled case the well is an oval with the 2 axes of symmetry along the modes. Now the axes of symmetry lie between the modes.
- Plot the spectrum, again between 3 and 7 eV. Notice that there is a dip around 4 eV. This is indicative of an error as a spectrum should always be positive.

The reason for this is that the coupling between the modes requires more basis functions to describe it properly. In `ho_ex2c.inp` change the SBASIS-SECTION to read

```
SBASIS-SECTION
x = 5
y = 5
end-sbasis-section
```

This increases the number of dynamical basis functions from 1 to 5 on each mode, enough for this simple model. Plot the spectrum again and the negative dip will have disappeared. The spectrum is quite different from that of the uncoupled oscillators.

2.4 HO + laser

Finally we shall look at exciting a 1D harmonic oscillator with a laser pulse. Take the files `ho_laser.op` and `ho_laser.inp`. Look at the operator file. You should recognize that there are 2 harmonic potential surfaces with the upper, S_1 , state shifted along the x -axis. The last line in the HAMILTONIAN-SECTION specifies a laser pulse with the formula

$$I(t) = \frac{Cs}{\sigma} \Theta(x) G(x) \cos \omega(t - t_0)$$

where the pulse envelope is a Gaussian functions $G(x) = \exp -\frac{A}{2\sigma^2}(t - t_0)^2$ centred at t_0 with width σ , defined as the width at the pulse half maximum height. ω is the driving, or central, frequency. A, C are some physical constants and s the laser strength.

Run the calculation and move into the output directory.

- Plot the pulse. To do this use the program `showfield`
- Plot the wavepacket motion and potential surfaces using `showsys`

Rerun the calculation using different pulse widths. This can be done from the input file. Copy `ho_laser.inp` to a new name. Edit this file to write to a new directory, which will have to be created before running the calculation. Change the `width1` parameter in the OPERATOR-SECTION to a value of 1 fs. Run the calculation and look at the results. Repeat with a width of 100 fs.

The 3 calculations result in very different dynamics. A width of 1 fs corresponds to a broad band excitation, at 100 fs only a single energy level is excited etc.