3 Exercise 3. Non-adiabatic Dynamics

We shall now try a multi-dimensional, multi-state calculation that uses the MCTDH algorithm. We shall thus also have to check the quality of the calculation in addition to plotting the spectrum and analysing the dynamics.

3.1 Jahn-Teller coupled surfaces

An $E \odot e$ Jahn-Teller system has 2-electronic states that are degenerate at a high symmetry, but the symmetry is lowered by coupling to 2 degenerate vibrational modes. The Hamiltonian to first-order can be written

$$\mathbf{H} = \sum_{i=x,y} \frac{\omega_i}{2} \left(\frac{\partial^2}{\partial Q_i^2} + Q_i^2 \right) + \begin{pmatrix} \kappa_i^{(1)} Q_1 & \lambda Q_2 \\ \lambda Q_2 & \kappa^{(2)} Q_1 \end{pmatrix} \tag{1}$$

This Hamiltonian has been coded up in the file `jt_2d.op` with the input file `jt_2d.inp`

View the PES:

- `mkdir jt_2d`
- `quantics -t jt_2d`
- `cd jt_2d`
- `showsys -pes`

Use menu item 60 to plot both electronic surfaces. Look at the differences between the diabatic and adiabatic pictures (choose using option 10). The "mexican hat" structure is clear in the adiabatic picture with the conical intersection at $(Q_1, Q_2) = (0, 0)$ where the surfaces meet. The best plot is to set the surfaces (option 160) and the z-axis to be between 0 and 2.0 (option 70).

3.2 First Simulation

Now move back up to the starting directory and run the dynamics.

- `quantics -w jt_2d`

which starts with the system moved 2 units along v2. This simulates either a Jahn-Teller system that has been disturbed by exciting one vibration, or it simulates a vertical excitation from the ground-state that is displaced with respect to the excited JT pair.

Move back into the *name* directory `jt_2d` to analyse the calculation.

First, we need to check that the calculation is of a good enough quality, i.e. check for convergence of the basis sets. Start up the analysis program

- `analysis`

Check the SPF basis by choosing option 3 `‘‘plot populations of natural orbitals’’`. The natural orbitals are an ordered representation o f the SPFs and for a good calculation the population of the highest natural orbital must be small, i.e. the basis function plays a small role in the wavefunction. This calculation has 2 states and 2 modes. Choose state 2 and mode 1. As the calculation starts with the system in state 2 the lowest natural orbital starts with a population of 1.0 (it is the initial wavefunction) which then drops as the initially unpopulated functions start to be used. The highest orbital has a population of approximately 0.01, so it accounts for 1 % of the wavefunction. Repeat the plot for state 2 and mode 2, then the 2 modes and state 1. For state 1 you will see that all functions are initially unpopulated. These final populations are quite large and more SPFs may be required for a converged spectrum.

Next check the “primitive grid” - we are actually using a DVR basis here so we will be checking whether we have enough primitive basis functions to describe the SPFs but loosely refer to this basis as the grid. Choose option 4 `‘‘plot populations of grid edges’’`. In answer to the question “`‘‘no.  ==?’’` enter 1. This will return the population of the last grid point at either end. Entering a larger number will provide a population summed over the selected no. of points from the end. Select `dof` 1. The resulting plot shows that along DOF 1 the population at the ends of the grid rises to 0.001. The population of the highest basis function rises to 0.0001. These are quite large indicating that the basis set might be too small. Repeat the plot for DOF 2. The grid populations now are seen to reach nearly 0.1 at times.

It looks as though the basis set is not converged. Nevertheless, we shall now plot the spectrum. First return to main menu, option 0, Select option 4 `‘‘analyse results’’` then 3 `‘‘Plot spectrum from autocorrelation function’’`. Enter `0 2 eV` for the required energy range `200` for the damping time (a smaller number leads to broader peaks in the spectrum) and `1` for `iexp` (this is the exponent of the cutoff function that ensures the correlation function goes to zero at time T). Select 1 to plot spectrum. There are 2 progressions and it looks reasonable, but there is what could be noise between the bands.

3.3 Second Simulation

Copy the input file to `jt_2da.inp`. Change the argument of the `name` keyword in the `RUN-SECTION` to `jt_2da`. Change the number of grid points in the `PRIMITIVE-BASIS-SECTION` for both DOFs to 41. Change the number of SPFs in the `SPF-BASIS-SECTION` to 2 for all states and modes. The file should now have the lines:

```
SPF-BASIS-SECTION
multi-set
      v1   =    10, 10
      v2   =    10, 10
end-spf-basis-section

PRIMITIVE-BASIS-SECTION
    v1     HO     41   0.0     1.0     1.0
    v2     HO     41   0.0     1.0     1.0
    el     el      2
end-primitive-basis-section
```

Make the new name directory `jt_2da`, run the calculation and repeat the analysis of before. The calculated spectrum is subtly different - less noise between the bands and, e.g. the fourth peak in the second band has split into 2. Further SPFs would be needed to test whether this spectrum is now converged. But the agreement between the 2 calculations certainly supports the fact that the result is at least qualitatively correct.

As a final evaluation, first plot the diabatic state populations. In `analysis` choose option 5 (analyse system evolution) followed by 3 (Plot diabatic state population). The resulting plot shows how the system begins in one of the components of the degenerate state and oscillates rapidly between the two. Now plot the adiabatic populations. To do this we need to generate the populations and use `gnuplot` to plot them. Type

- adpop
- gnuplot

In gnuplot, type

- plot "adp" u 1:2 w l
- replot "adp" u 1:3 w l

The resulting plot shows that the system starts initially populating the two adiabatic states equally. As time goes on, the population moves to the lower adiabatic state.

3.4 Stick Spectrum

For small systems it is possible to solve the time-independent Schrödinger equation and diagonalise the Hamiltonian to produce a stick spectrum of the eigenvalues.

Take the input file `jt_2dst.inp`, set-up the directory `jt_2dst` and run the calculation. Move into the results directory. There will be a file `eigval`. Plot the stick spectrum using the `analysis` program options 4 ("analyse results") followed by 4 ("Plot eigenvalues from matrix diagonalisation"). Compare the resulting spectrum to that from the time-dependent calculation (plot both between 0 and 2 eV), the same peaks should be present in both. The time-dependent spectrum could be improved by a longer propagation time and longer damping factor in the spectrum calculation to make the lines sharper.

3.5 Non-adiabatic crossing

The files `pyr4.op` and `pyr4.inp` are for a 2-dimensional model of the pyrazine absorption. The Hamiltonian is similar to the Jahn-Teller model above, but the diabatic states are not degenerate at $\mathbf{Q} = 0$.

$$\mathbf{H} = \sum_{i=10a,6a} \frac{\omega_i}{2} \left(\frac{\partial^2}{\partial Q_i^2} + Q_i^2 \right) + \begin{pmatrix} -\Delta + \kappa^{(1)} Q_{6a} & \lambda Q_{10a} \\ \lambda Q_{10a} & \Delta \kappa^{(2)} Q_{6a} \end{pmatrix} \qquad (2)$$

The gap between the states is 2Δ, the mode ν_{10a} couples the 2-states and ν_{6a} the strongest tuning mode that modulates the gap between the states.

Run the propagation:

- quantics pyr_2d

Move into the directory `pyr_2d` and check the convergence of the SPF basis and the grid. Population of the highest natural orbital and Maximum population at the edge of the grids should be small. Then plot the potential surfaces. Unlike the Jahn-Teller system the 2 adiabatic surfaces meet at a point away from the the Franck-Condon point. The lower adiabatic surface is broad and distorted due to the conical intersection, while the upper surface is a narrow cone. The diabatic surfaces are 2 intersecting wells.

- plot the spectrum between -1 and +1 eV (use option 2 "Plot Fourier Transform of autocorrelation function" as the model has negative energy states)
- plot the diabatic state populations
- plot the adiabatic state populations

The spectrum shows a weak set of peaks at low (negative) energies due to intensity borrowing from vibronic states in the dark lower electronic state. The intense high energy peaks are in the bright, S_2 state. The diabatic states populations show a transfer of population with a maximum at 60 fs. The adiabatic populations have a similar form but with less structure. This similarity is due to the fact the diabatic and adiabatic states are very similar away from the conical intersection - this is not a general fact.

Finally, plot the evolving wavepacket (either use `showsys` or options 5 followed by 2 in `analysis`). To select the adiabatic or diabatic wavefunction use option 10. To select the wavepacket on either state use option 60. Both pictures give a similar result. The packet in the upper state remains compact and oscillates in the upper cone along v6a. The wavepacket appears in the lower state at around 30 fs when the wavepacket has reached the intersection. It then oscillates round the ground-state surface, spreading in both directions showing that the torsion, v10a, has been excited by the internal conversion through the intersection.spreading in both directions showing that the torsion, v10a, has been excited by the internal conversion through the intersection.