

Homework 2, Due: Tuesday, March 4

1. Rabi Oscillation (the strong field limit of spectroscopy):

In this problem you will solve the coupled equations of ground and excited state wavefunction coefficients and retrieve the Rabi oscillation of populations under the influence of a strong field. It will, hopefully, reinforce in your mind that most spectroscopy occurs in the perturbative limit.

a)- Start with the coupled set of equations shown in class:

$$\dot{C}_e(t) = -\frac{i}{\hbar} H'_{eg} C_g(t) e^{i\omega_0 t}$$

$$\dot{C}_g(t) = -\frac{i}{\hbar} H'_{ge} C_e(t) e^{-i\omega_0 t}$$

Assume that the perturbation matrix elements linking the two states is:

$$H'_{eg} = \frac{\mu E_0}{2} e^{-i\omega t}$$

$$H'_{ge} = \frac{\mu E_0}{2} e^{i\omega t}$$

To keep your notation concise, you may use the following abbreviations:

$$\Delta = \omega_0 - \omega$$

$$\alpha(t) = -\frac{i}{\hbar} \frac{\mu E_0}{2} e^{i\Delta t}$$

Rewrite the coupled equations, using the above replacements.

b)- As is customary in handling two first order coupled equations, take the derivative of one and replace it in the other. You should arrive at one second order equation for C_e .

c)- Assume a solution of the form:

$$C_e(t) = e^{i\lambda t}$$

and replace in the derived equation and solve for λ .

d)- The general solution should be of the form:

$$C_e(t) = C_+ e^{i\lambda_+ t} + C_- e^{i\lambda_- t}$$

Use the initial condition $C_e(0) = 0$ and $C_g(0) = 1$ to find an expression for $C_e(t)$.

e)- Write an expression for the population of the excited state $P = |C_e|^2$. At what frequency does this population oscillate? This frequency is called the Rabi frequency, and your result should show that it is a function of the strength of the field (i.e. the stronger the field, the faster the oscillations).

f)- How strong should the intensity of a 500 nm laser field be to be able to fully drive the population of the ground state of a system with an energy gap of 505 nm and a transition dipole moment of 30 D fully to the excited state within 100 fs?

2. Rabi oscillations manifested in the fluorescence spectrum of a quantum dot:

To give you an idea that the above can happen in reality (in the case of strong fields and large dipole moments), read the following paper:

Direct detection of time-resolved Rabi oscillations in a single quantum dot via resonance fluorescence

Phys. Rev. B (87), 115311 (2013).

The fluorescence signal can be interpreted as a proxy for the population of the excited state. Based on the results of problem 1, explain the observations in Figure 5 of this paper.

3. Vibrational Normal Modes (A Simple Molecule to Get a Feel for the k Matrix):

To make sure that you understand the meaning of the force constant matrix (Hessian of the potential), we will work with a simple linear molecule CO₂. Let a CO₂ molecule lie along the x axis with C at the origin. The atoms may be labeled as 1: O, 2: C and 3: O. An approximate k matrix for this molecule may be written as:

$$H = \begin{pmatrix} 1600 & 0 & 0 & -1600 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ -1600 & 0 & 0 & 3200 & 0 & 0 & -1600 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1600 & 0 & 0 & 1600 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \end{pmatrix}$$

The unit of force constant in this matrix is N/m.

a)- Justify the large number of zeros in this approximate matrix. (Including these zeros is part of the approximation. Explain in your language the approximation.)

b)- Why is the number 1600 N/m repeated twice on the diagonal and with a negative sign on the off-diagonal?

c)- Why is the middle diagonal number twice the number 1600 N/m?

- d)- Construct the mass-weighted version of this matrix and find its eigenvalues and eigenfunctions.
- e)- How many nonzero eigenvalues do you end up with? Does it equal the number of vibrational modes that you expect for this molecule?
- f)- Which vibrational modes are missing due to our simplistic construction of the force constant matrix? What elements of the matrix need to be changed to let those eigenmodes emerge with nonzero frequency?
- g)- Calculate the frequencies of the resulting vibrational modes (in units of cm^{-1}) and compare with experimental vibrational frequencies of CO_2 . Do not be surprised if your numbers are a bit off, but overall they should make sense.

4. Vibrational Normal Modes of cis-1,2 dichloroethylene:

Now that you know the details of the k matrix, we will do a more complicated problem. The force constant matrix and the geometry (coordinates of atoms) for cis-1,2 dichloroethylene is available for download from the website. The order of atoms is the following: 1:C, 2:C, 3:Cl, 4:H, 5:Cl, 6:H. Some useful unit conversions for this problem are listed below:

```
au = 1.66e-27; % atomic unit of mass in kg
bohr = 5.29e-11; % in m
eV = 1.602176e-19; % in J
hartree = 27.21138505*eV; % in J
c = 3e8; % in m/s
cm = 1e-2; % in m
```

- a)- The force constant matrix is in units of hartree/(bohr²). Convert this to SI units.
- b)- Prepare a mass matrix as discussed in class used for converting the Newton's equation for the small harmonic vibrations into an eigenvalue equation.

Matlab hint: If unfamiliar with Matlab, try the following (related) exercise first.

```
ones(1,3) % makes an array of ones
ones(1,3)*5
A = [ones(1,3)*5, ones(1,3)*8, ones(1,3)*17] % concatenates many arrays
diag(A) % creates a diagonal matrix from array A
```

- c)- Find eigenvalues and eigenvectors of the mass-weighted force matrix.

Matlab hint:

```
[eigvectors, eigvalues] = eig(B) % finds eigenvectors and eigenfunctions of
matrix B
```

d)- Find all vibrational frequencies in units of cm^{-1} . How many modes have frequencies that are practically equal to zero? What do the zero frequency modes correspond to?

e)- Now we will plot the vibrations. You may use any sophisticated method that you would like. I suggest the following simple code.

```
geomEq = load('CisDichloroethyleneGeometry.txt');
close all
for j = 1:18
    modeindex = j;
    geomt = zeros(size(geomEq));
    displacement = 3e-14* massweightmatrix*v(:,modeindex);
    figure(j)
    plotlim = [-3,3];
    xlim(plotlim);    ylim(plotlim);    zlim(plotlim);

    plotgeom(geomEq, j, 'g')
    plotgeom(geomEq + displacement,j,'r');
    plotgeom(geomEq - displacement,j,'r');

end
```

Where the function plotgeom is defined in a separate file as:

```
% function to plot geometry
function plotgeom(geom, fignum, colorofpoint)
figure(fignum)
hold on
for j=1:3:18
    plot3(geom(j), geom(j+1), geom(j+2), ...
        'o','MarkerSize',10,'MarkerEdgeColor','k', ...
        'MarkerFaceColor',colorofpoint)
end
```

In the above, note that a scaling factor for the each eigenmode is used (Remember that any eigenfunction multiplied by a constant is still an eigenfunction. For that reason the eigenfunctions produced by Matlab can have an arbitrary scale). In the plots, the green dots are the equilibrium geometry positions and the red dots are the extremes of oscillation.

Remember that you can use the rotate button of Matlab figure to rotate the plot in 3D space. Print the picture of 4 or 5 vibrational modes of your choice.

For each plot, explain in words what is happening in the molecule.

f)- (NOT REQUIRED): If you are not entertained enough yet, you may choose to “animate” each eigenmode in a loop by multiplying the displacement by a time varying sine function at the frequency of the eigenmode and have Matlab produce a movie of the vibration.