Energy transfer to a system of coupled oscillators by a strong laser pulse

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Abstract

   This report is a summary of my work at Desy as a Summer Student. In my project, I focus on the analyse of a molecular Hamiltonian with harmonic and morse potentials. This is to change the harmonicity of our model an to see how it responds under an oscillating electric field. This work is mainly a computer simulation of such a system and I use the MCTDH program to do necessary calculations and plots.

Contents

1 Introduction

In this work, we consider the quantum mechanical approach to write a Hamiltonian for a molecule. In the first case we use two harmonic potentials and also a coupling term. In order to write this term, we follow the article "Theory of nonlinear phononics for coherent light-control of solids" Reference [1], where they use a similar way to write the interaction between IR and Raman modes for magnetoresistive manganites (PMO). Throughout in this profect, IR mode stands for the first oscillator q_1 and Raman mode stands for the second one q_2. We will only consider a cubic coupling in the molecular hamiltonian which looks like $\lambda q_1^2 q_2$. Then we create an electric field, which has the shape of a Gaussian envelope, around the molecule to excite the energy levels of the potential and to reach higher ones. Additionaly, as we are dealing with a system in molecular scale, we have to use atomic units for length and mass in this way we are near to bond length in a molecule and we can express the weight around proton mass scale. For this purpose we will use the mass-weighted coordinate system.

In the second case, we change the first harmonic potential to a morse potential and we keep the rest of the system same as before. In this way, the system gets more anharmonic depending on the value of the dissociation energy. Our main goal here is to study how the excitation levels change depending on the harmonicity of the system. In this procedure, we use MCTDH program to analyse the different eigenstates that the Schrödinger equation reaches as well as to plot the variation of position with respect to time and also to observe the exitation levels of the system, additionaly, all the plots and graphs are created by Gnuplot scripts.

2 Time Dependent Quantum Mechanics

A very general way to analyse a quantum mechanical system is to propagate wave packets. In order to solve such a system, one needs to specify (time dependent) Hamiltonian operator, and than one solves the time-dependent Schrödinger equation ($i\hbar\dot{\psi} = H\psi$). The Hamiltonian operator acts on a wavefunction ψ which has to be splitted into some basis functions. This procedure is called the basis expansion method and in our project it is done by MCTDH program. Consider a wavefunction:

$$\psi(q_1, q_2, ..., q_n; t) = \sum_{j_1 j_n} A_{j_1..j_n}(t)\phi_{j_1}^{(1)}(q_1, t)\phi_{j_2}^{(2)}(q_2, t)....\phi_{j_n}^{(n)}(q_n, t)$$

where n is the degrees of freedom of the system, ϕ_j's are the time dependent basis functions and $A'_j s$ are the expansion coefficients. The ϕ_j can also be expended like :

$$\phi_{j_1}^{(1)}(q_1, t) = \sum_{i_1}^{N_1} c_{i_1,j_1}(t).\chi_{i_1}^{(1)}(q_1)$$

Finally the wavefunction can also be defined as :

$$\psi(q_1, q_2, ..., q_n; t) = \sum_{i_1 i_n}^{N_1, N_n} C_{i_1..i_n}(t)\chi_{i_1}^{(1)}(q_1)\chi_{i_2}^{(2)}(q_2)....\chi_{i_n}^{(n)}(q_n)$$

We expanded the wave packet into finite terms, linear combination of vectors and now the time-dependent Schrödinger equation looks like a set of coupled ordinary differential equations $i\dot{\psi} = H\psi$ where ψ is a vector and H is a matrix. The MCTDH (multi-configuration time dependent Hartree) program uses a numerical algorithm to propagate the wave packet. In this project we will be using MCTDH to analyse the molecular Hamiltonian. You can find the User's Guide for the program in the Reference [2].

3 Hamiltonian

In order to write a moldecular hamiltonian we need to introduce mass-weighted coordinate system. For this purpose put q = $\sqrt{m}.x$ and the energy is :

$-\frac{1}{2m}\frac{\partial^2}{\partial x^2} + \frac{1}{2}m\omega^2 x^2$, where, $k = m\omega^2$ or $\omega = \sqrt{\frac{k}{m}}$.

From the chain rule, we can write partial x as; $\frac{\partial}{\partial x} = \frac{\partial q}{\partial x}\frac{\partial}{\partial q}$. We use the relation $x = \frac{q}{\sqrt{m}}$ to determine $\frac{\partial q}{\partial x} = \sqrt{m}$, then we get $\frac{\partial}{\partial x} = \sqrt{m}\frac{\partial}{\partial q}$ and after taking the second derivative we finally have; $\frac{\partial^2}{\partial x^2} = m\frac{\partial^2}{\partial q^2}$.

So, by using the mass-weighted coordinates, the energy looks like: $-\frac{1}{2}\frac{\partial^2}{\partial q^2} + \frac{1}{2}\omega^2 q^2$

Now, remember our system with two oscillators in an electric field with a coupling term. The hamiltonian for this system has the form:

$H(q_1, q_2, t) = -\frac{1}{2}\frac{\partial^2}{\partial q_1^2} - \frac{1}{2}\frac{\partial^2}{\partial q_2^2} + V_1(q_1) + V_2(q_2) + V_{12}(q_1, q_2) + \mu(q_1).\epsilon(t)$, where, $\epsilon(t)$ is the electric field and $\mu(q_1)$ is the dipole operator. Our main purpuse to use these two terms together is to have energy units in the hamiltonian. We will use a simple dipole term and an oscillating pulse in our system. Let me define these terms in the following way: $\mu(q_1) = c.q_1$ and $\epsilon(t) = A(t).\cos(\omega t + \phi)$ and for the cubic coupling we put $\lambda.q_1^2.q_2$. The time dependent electric field A(t) has the form of a gaussian envelope and it is explicitly written as $A(t) = A.exp(\frac{-t^2}{2\sigma^2})$,where A and σ are the amplitude and the width of the pulse respectively, (we could use a $\sin^2$ envelope which has mainly the same shape of the exponential one, but follow the same model as in the article,Ref[1]). All the constants used in the Hamiltonian will be specified later. For our first model, where we use two harmonic oscillators, the Hamiltonian becomes:

$H(q_1, q_2, t) = -\frac{1}{2}\frac{\partial^2}{\partial q_1^2} - \frac{1}{2}\frac{\partial^2}{\partial q_2^2} + \frac{1}{2}m\omega_1^2 q_1^2 + \frac{1}{2}m\omega_2^2 q_2^2 + \lambda.q_1^2.q_2 + A(t).q_1.\cos(\omega t + \phi)$

For our second model, we introduce the morse potential. Our aim in using this potential is to change the harmonicity of the system. Basically, a morse potential is a way to describe the potential energy of a diatomic molecule. Unlike the energy levels of the harmonic oscillator potential, which are equally spaced by a distance $\hbar.\omega$, morse potential spacing between energy levels decreases as the energy appoaches the dissociation energy, since after this limit, the bond in the molecule is broken. A morse potential can be written as; $M(x) = D.(\exp(-\alpha(x - x_0)) - 1)^2$, where D is the dissociation energy, x_0 is the equilibrium position and α is defined as; $\alpha^2 = \frac{m.\omega^2}{2.D}$. So, for this second model the Hamiltonian becomes;

$H(q_1, q_2, t) = -\frac{1}{2}\frac{\partial^2}{\partial q_1^2} - \frac{1}{2}\frac{\partial^2}{\partial q_2^2} + D.(\exp(-\alpha(q_1)) - 1)^2 + \frac{1}{2}m\omega_2^2 q_2^2 + \lambda.q_1^2.q_2 + A(t).q_1.\cos(\omega t + \phi)$

Finally, we define all the constants of the hamiltonian as follows: for ω_1 and ω_2 we

take the same frequency values of the Raman and IR modes in the article, Ref[1]. So, $\omega_1 = 622cm^{-1}$ and $\omega_2 = 155cm^{-1}$. For the value of the λ we take the g value for PMO in the article, Ref[1], $\lambda = 51.74\frac{meV}{amu^{3/2}\mathring{A}^2}$, but we have to be careful about its units. As we deal with a system in a molecular scale, we use atomic units throughout in this project. After having done the appropriate conversion we get, $\lambda = 1,889.10^{-6}a.u..$ For the width of the pulse, σ, we will use different values to make the electric field more wide since in this way much more photons are transmitted from the pulse to the system, which, obviously changes the excitation levels of the system.

4 Molecular Hamiltonian with two harmonic oscillators

For the first case we use the hamiltonian :

$$H(q_1, q_2, t) = -\frac{1}{2}\frac{\partial^2}{\partial q_1^2} - \frac{1}{2}\frac{\partial^2}{\partial q_2^2} + \frac{1}{2}m\omega_1^2 q_1^2 + \frac{1}{2}m\omega_2^2 q_2^2 + \lambda.q_1^2.q_2 + A(t).q_1.\cos(\omega t + \phi)$$

And we write it in a operator directory which has the form:

```
HAMILTONIAN-SECTION
------------------------------------
modes        | q1   | q2    | Time
------------------------------------
-0.5/m       | dq^2 | 1     | 1
 w1*w1*0.5*m | q^2  | 1     | 1
-0.5/m       | 1    | dq^2  | 1
 w2*w2*0.5*m | 1    | q^2   | 1
lambda       | q^2  | q     | 1
A            | q    | 1     | E*C
------------------------------------
end-hamiltonian-section
LABELS-SECTION
C = cos[w,ph]
E = gauss[k,tc]
end-labels-section
```

Figure 1: The hamiltonian operator with corresponding functions

Here; we include the term 'm' which obviously stands for the mass and it is not appear in the above hamiltionian since we are using a mass-weighted coordinate system. But we have to add this term to get atomic units in the system, so, actually the value of m = 1 a.m.u. On the other hand, the E stands for the electric field which is a gaussian function and it is defined in the MCTDH user's guide, Ref [2]. Then we multiply it with a periodic function where we used a cosine function $(A(t) = 100.exp(\frac{-(t-500)^2}{100^2})cos(622t))$. For the amplitude of the pulse times dipole, we used $100cm^{-1}$ which is a reasonable number and with this number we can reach sufficiently high levels. Additionally, we used the same frequency of q_1 which is $622cm^{-1}$ for the cosine function and this is basically to have a resonance between the field and the first degree of freedom. So; the electric field for our system has the following shape:
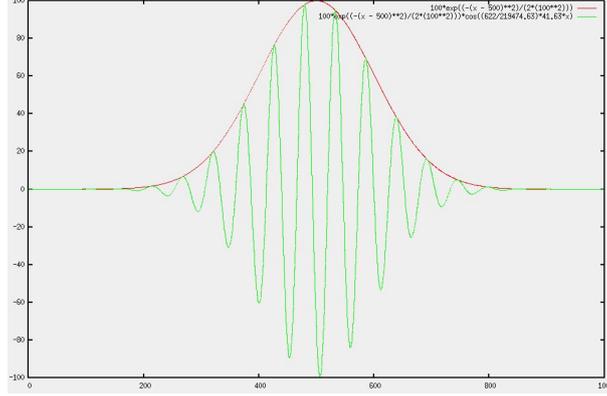
Figure 2: The electric field

This pulse excites the first degree of freedom q_1 by transmitting energy to it, this is because we multiply the Gaussian envelope with q_1 as a dipole operator, and in the potential energy it climbs up to higher levels as long as the pulse is resonant with the energy separations. Since the energy levels are discrete, when the photon energy $\hbar\omega$ and the energy of the first degree of freedom $\hbar\omega_1$ is $\hbar\omega \approx \hbar\omega_1$ then we get an excitation. This regime continues until the pulse calms down and ultimately dies. While the exitation happens, obviously there is a displacement or a oscillation on q_1 that we will show the plot. However, as there exists an interaction between two degrees of freedom by the coupling term, we expect a displacement in q_2 created by the displacement in q_1. After the calculations, we get the following graphs which shows the variation of position with respect to time for two degrees of freedom:
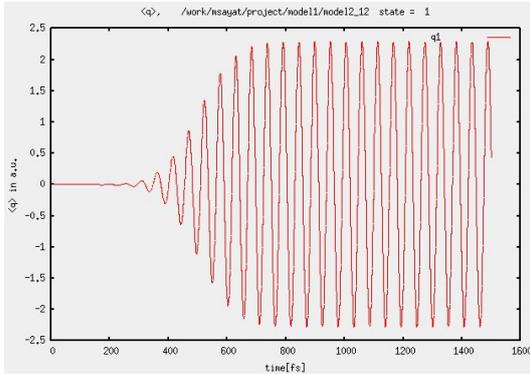
Figure 3: Variation of q_1
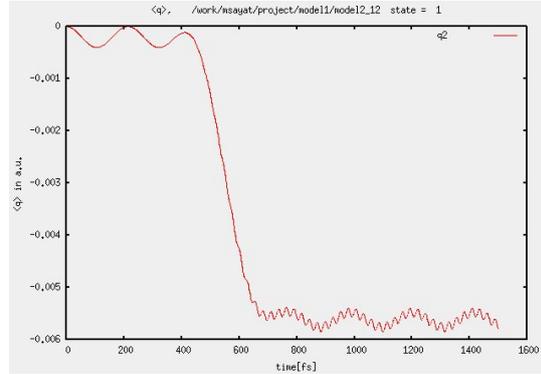
Figure 4: Variation of q_2

Recall the coupling term: $\lambda.q_1^2.q_2$. The first degree of freedom q_1 appears quadraticaly in the coupling. So it is not surprising that the oscillation of q_1 is symmetric with respect to the y = 0 axis. And also notice that the oscillations start when the pulse becomes active i.e. between 200-400 fs. Now, we can make a correlation between the variation of

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q_1 and q_2. Until the pulse starts to be active q_2 oscillates around $y = 0$. However, when the electric field excites the first degree of freedom, q_2 has a very sharp fall until the pulse calms down and keep oscillating again. Because of the coupling term the displacement in q_1 causes an obvious change in the displacement of q_2. We can also have a look at the excitation level that q_1 reaches by the following graph:
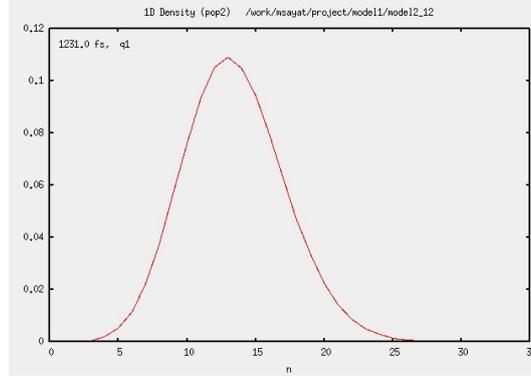
Figure 5: exitation level of q_1

This plot shows the population density of the first degree of freedom. Notice that the peak of the curve stands approximately at 14 or 15th level. The excitation up to this level causes an energy change of the system. From the output file that the MCTDH program creates after the calculation, we can read the initial energy of the system as $E_{intitial} = 0.048168eV$ and the final energy is $E_{final} = 1.086881eV$, which gives us an energy difference of $\Delta E = 1.038713eV$. We can do the same calculations by changing the value of sigma i.e. by widening the pulse. In this way, the pulse acts longer time on the system and we expect to reach higher levels. So, if we put $\sigma = 1000fs$ instead of 100 fs, the electric field is like :
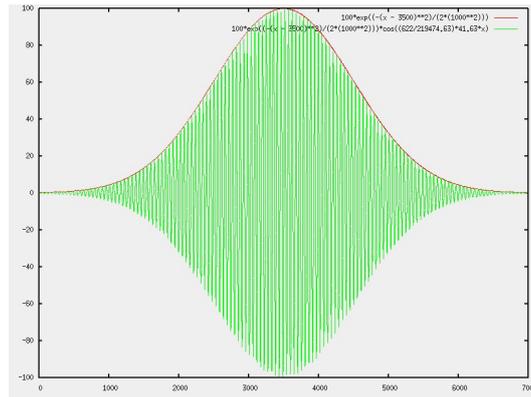
Figure 6: The electric field with longer puls witdh

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As you can see, the pulse is wider and there are more oscillations inside the Gaussian envelope. With this new pulse, the population density of the system is like:
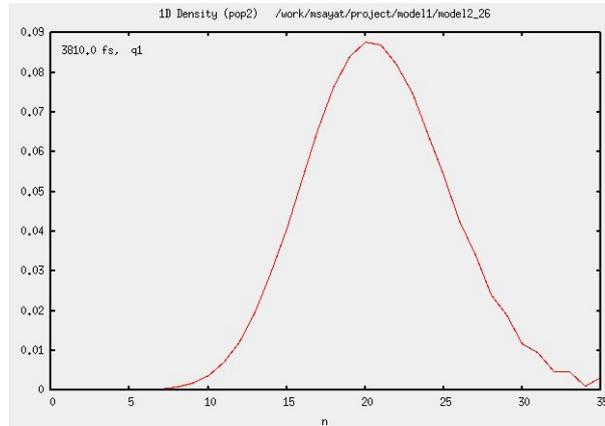
Figure 7: Excitation level of q_1 with a wider pulse

The top of the curve reaches around the 20th level, obviously higher than the previous one. The initial energy of the system is again $E_{intitial} = 0.048168eV$ but the final energy is $E_{intitial} = 1.762525eV$ and the energy difference ($\Delta E = 1.714357eV$) is remarkably changed and increased. After these calculations we can see the relation between pulse witdh, excitation levels and the energy change. Now, we continue by changing the harmonicity of the system by using the morse potential in the following section.

5 Morse Potential: Anharmonic Case

For the second case, we change the potential of the first degree of freedom. Instead of the harmonic oscillator potential, now we consider a morse potential with different dissociation energy values. In the plots below, one can see the shape of the morse potential in comparison with the harmonic potential:
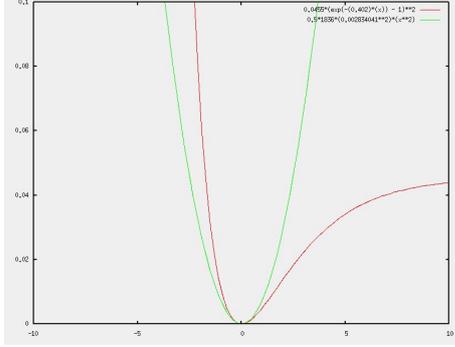
Figure 8: Morse potential with D = 10000 cm^{-1}
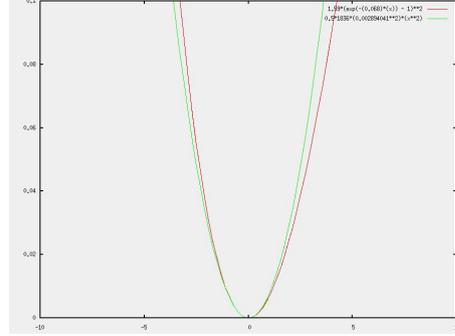
Figure 9: Morse potential with D = 350000 cm^{-1}

In these graphs, we plotted two extreme cases with a small and a very large dissociation energy, D. The morse potential with small D tends to diverge from harmonic potential in a very short range, however, if we put D a very huge number the morse and harmonic potentials gets closer. Now, we do the same calculations with different D values to see how the harmonicity of the system effects the excitation levels. The hamiltonian for this model is explicitly written as:

$$H(q_1, q_2, t) = -\frac{1}{2}\frac{\partial^2}{\partial q_1^2} - \frac{1}{2}\frac{\partial^2}{\partial q_2^2} + D.(\exp(-\alpha q_1) - 1)^2 + \frac{1}{2}m\omega_2^2 q_2^2 + \lambda.q_1^2.q_2 + A(t).q_1.\cos(\omega t)$$

For the beginning we use the first electric field that we used in the previous section where $\sigma = 100 fs$. With $D = 10000 cm^{-1}$ the variation of position with respect to time for two degrees of freedom is as follows:
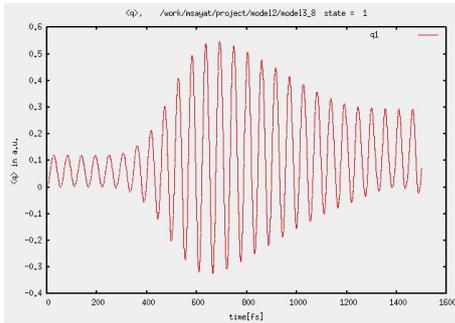
Figure 10: Variation of q_1
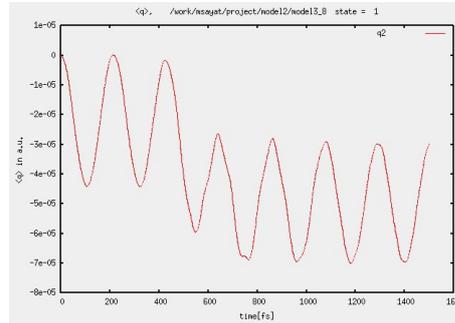
Figure 11: Variation of q_2

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The displacement of q_1 is again symmetric as in previous section, but here the interesting one is the second degree of freedom. There is only a slight change in the displacement of q_2 which is obviously different from the two harmonic oscillator case where we had a very sharp fall in the the displacement of q_2. We can also have a look at the energy difference for this system from the output file. The initial energy for this system is $E_{initial} = 0.048699eV$ and the final energy is $E_{final} = 0.090379eV$, so, the energy difference is only $\Delta E = 0.04168eV$ which is a small number if we compare with the case of two harmonic potentials. Additionaly, the population density for the first degree of freedom is:
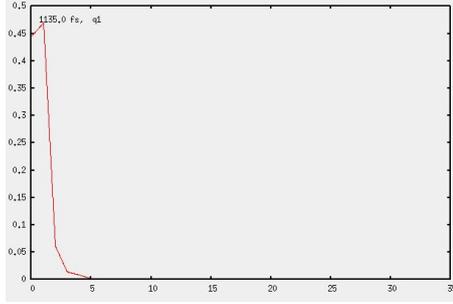
Figure 12: Excitation level of q_1 for $D = 10000cm^{-1}$

The excitation of the first degree of freedom reaches only 2 or 3th level which is quite low when it is compared again to the previous model. The obvious reason for this low excitation level is the resonance of the pulse with the first degree of freedom. As the dissociation energy is a small number, the energy separations of the morse potential gets narrower in a very short time so that the pulse cannot excite any more. We can have the same deduction with the following example. We change the dissociation energy from $D = 10000cm^{-1}$ to $D = 35000cm^{-1}$. In this case the variation of position with respect to time for two degrees of freedom is shown below:
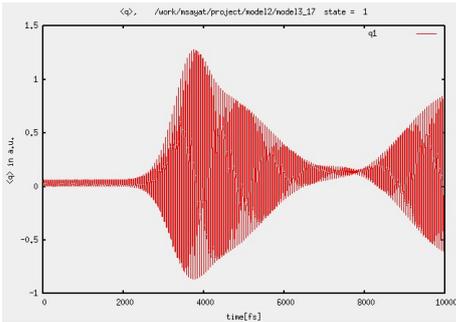
Figure 13: Variation of q_1 Figure 14: Variation of q_2
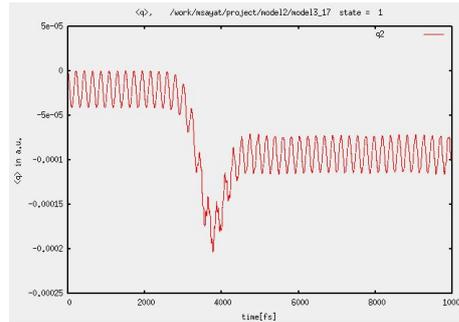
As you can see, the displacement of q_2 is more than the above example but the fall is not as sharp as the two harmonic oscillator case. The initial energy of the system is $E_{initial} = 0.048318eV$, the final energy is $E_{final} = 0.175568eV$ and the energy difference

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is $\Delta E = 0.12725 eV$ which means that more energy is transmitted from the pulse to the system when we compare to the above example. Also, the population density for the first degree of freedom is:
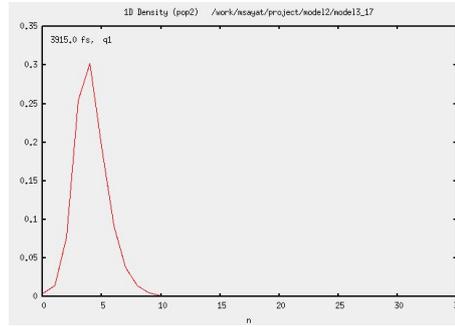
Figure 15: Excitation level of q_1 for $D = 35000 cm^{-1}$

The peak of the curve reaches approximately 5th energy level which is also higher than the above example. So, these to examples shows us the correlation of the value of dissociation energy and the excitation levels. If D increases, we approach to the harmonic case where we have more excitations.

Finally, we have this last example with a huge D. We put D ten times larger than the previous one $D = 350000 cm^{-1}$ and we have the following results:
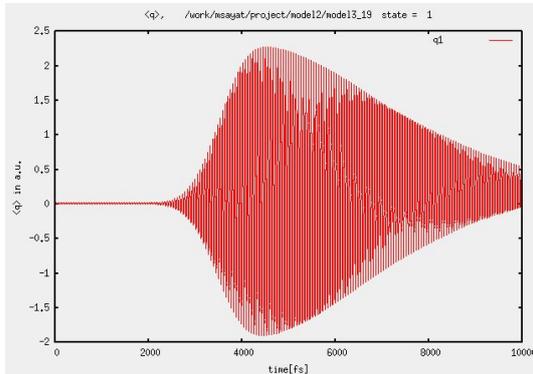
Figure 16: Variation of q_1
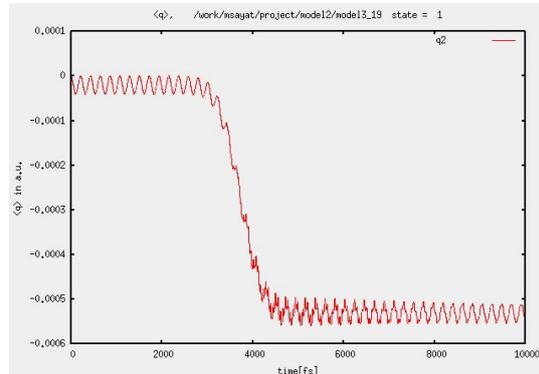
Figure 17: Variation of q_2

This results are not surprising since we are geting closer to the harmonic case. In the displacement of the second degree of freedom we have the similar sharp fall as in the example of two harmonic oscillators. the energy difference of this system is $\Delta E = 0.939893 eV$ because much more energy is transmitted to the system by the pulse. The population density for this last example is shown by the following plot:
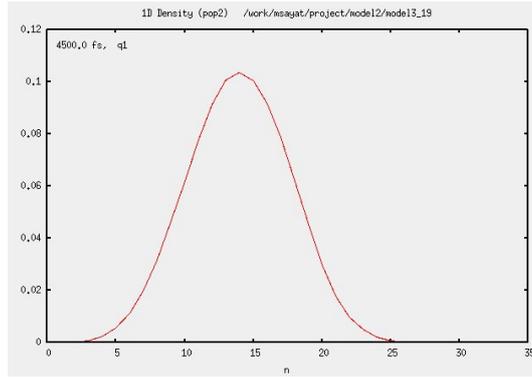
Figure 18: Excitation level of q_1 for $D = 350000 cm^{-1}$

The peak of the curve is around approximately the 15th excitation level which is very close to the level that we observed with two harmonic oscillators.

To sum up, have a look at the following plot which shows the displacement of q_2 for different D values and also with the example of two harmonic oscillator:
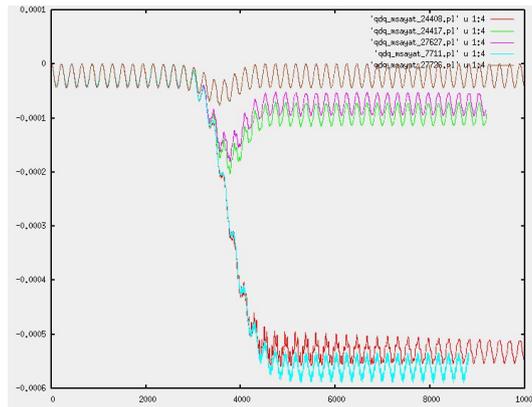
Figure 19: displacement of q_2 for different D values

The brown curve is the case where we used a small D value and the blue curve is the two harmonic oscillator example. So, this plot shows clearly that the system converges to the harmonic case when D gets larger.

6 Conclusion

In this project, we demonstrated mainly the relation between the harmonicity of the system and the excitation levels. In our first exemple with two harmonic potentials, we can excite the system as long as the pulse is active, and also the excitation amount is dependent on the amplitude and the width of the pulse as well as the coupling coefficient λ. Obviously if we use a wide pulse with a high amplitude, more energy is transmitted to the system. However, when we consider the morse potential, the harmonicity of the system is broken. Even if we use a very wide pulse, it is impossible to excite the system near the dissociation energy where the pulse is no longer resonant with the energy separations of the potential and the system reaches saturation. Another important result that we observe during our calculations is the effect of D value on the system. As we increase the dissociation energy the system converges to the harmonic case and with a very large D value we can reach very high excitation levels.

7 Acknowledgment

References

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[2] The Heidelberg MCTDH Package:A set of programs for multi-dimensional quantum dynamics, User's Guide, Version 8. *G. A. Worth, M. H. Beck, A. Jäckle, H.-D. Meyer, F. Otto, M. Brill and O. Vendrell*