Bachelor thesis

Quantum interference and interaction free measurement in a diatomic molecule

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Abstract

This thesis utilizes the *split operator method*, and a quantum mechanical numerical model, to study a phenomenon where a supposedly unstable molecule becomes more stable – or *meta-stable* – through matter wave interference. The model of the molecule and the split operator method are both discussed in detail, and then used in numerical calculations to arrive at results in two separate investigations. The first is a successful replication of an earlier paper where the meta-stable behaviour is optimized for and found. The second investigation models an interaction-free measurement of the electronic state of the molecule by incorporating a quantized electromagnetic field. Entanglement between field and molecule is calculated to confirm the assumption that increasing entanglement means a larger risk for dissociating the meta-stable molecule. The assumption is shown to be consistent with the results from the numerical model.

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1 Introduction

This bachelor thesis replicates and expands similar investigations that have been an active field of research since at least 1996 [1], and has continued to present day [2].

The project is based on numerical studies of a quantum mechanical model of a diatomic molecule (section 2) – i.e. a molecule comprised of two atoms. The objective is not to consider a specific molecule, but instead a particular phenomenon that can occur in diatomic molecules.

In general, it is the vibration of the molecule along the axis connecting the two atoms that is studied, and in detail, a stabilizing interference effect holding the molecule together (section 2.4). Notice that there only exists one vibrational degree of freedom in a diatomic molecule – along the axis connecting the two atoms.

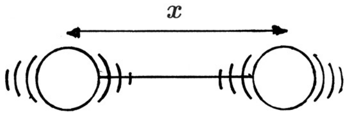

Figure 1: Illustration of molecular vibrations.

Depending on the electronic state – i.e. the configuration of electron wave functions – the molecule can either exist in an attractive potential holding it together, or a repulsive potential that will cause it to dissociate. Even if transitions between these states are allowed, there can exist favourable conditions where the molecule is prevented to assume a state where it dissociates, and thus is stable over longer time scales than you would believe from a naïve investigation. These so called *meta-stable states* exist solely due to quantum interference effects and cannot be explained in terms of classical models. Presenting the methods for modelling the molecule, and finding such favourable conditions, is the main discussion in this thesis (section 2.1 - 2.4, 3, 4, and results in 5.1).

After such favourable conditions are found, a model of *interaction free measurement* is incorporated (section 2.5) to investigate a correlation between entanglement and the meta-stable state (section 2.6, and results in 5.2). This measurement is modelled with a quantized electromagnetic field, which causes interactions with a third electronic state of the molecule. The new electronic state will correspond a third potential for the molecular vibrations. However, we will restrict the electromagnetic field to be of a single frequency that is not resonant with the energy required to excite the molecule to the third electronic state. Thus the state is prevented from being populated and the only remaining effect is the impact of the electromagnetic coupling on the initial potentials.

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I have found that some foundational concepts in the mathematical model of the molecule often are a bit unclear. So I will begin section 2 with an outline the underlying ideas in the construction of the model.

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2 A quantum mechanical model of the system

2.1 Representing the system with wave functions

To model the vibrations of a diatomic molecule we want to find the position of the two nuclei as a function of time. Note that the nuclei are carrying close to all the weight of the molecule. First we make life easy by ignoring rotations and overall translations of the molecule. Then we can model the system in only one dimension by choosing an appropriate coordinate system, and assign wave functions to describe the positions of the nuclei (x_1 and x_2), see figure 2.

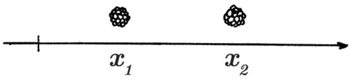

Figure 2: Modelling the position of two nuclei by their respective coordinates x_1 and x_2.

However, such a starting point would be superfluous. When looking at vibrations the only interesting part is the distance between the nuclei, and therefore we would prefer to describe the molecule with the distance between the nuclei and position of the centre of mass. Then we will have removed one degree of freedom that we do not care about (the position of the entire molecule) and there is only one left, as depicted in figure 3.

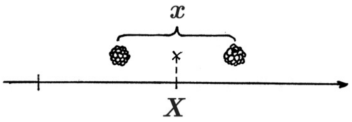

Figure 3: A center of mass model. X denoting the position of the molecule and x the distance between the nuclei.

Doing a transformation from $\{x_1, x_2\}$ to $\{x, X\}$ will – for our purposes – most importantly result in the wave function $\psi(x)$, which will contain information of the probability density to find a certain distance between the nuclei. This is the one we will work with in this thesis! The other wave function $\phi(X)$ (describing the probability density of the position of the entire molecule) will be disregarded since it has no relevance here.

In this model we will also include two separate *electronic states* (i.e. two different states of the electron wave functions) that the molecule can assume. Each such state is represented by a unique potential (section 2.2) that the nuclei will feel as they move. To keep track of which electronic state the molecule is in, we consider two corresponding wave functions – $\psi_1(x,t)$ and $\psi_2(x,t)$ – and the entire state of the molecule is descried by a vector composed of the wave functions

$$|\Psi\rangle = \begin{bmatrix} \psi_1 \\ \psi_2 \end{bmatrix} \tag{1}$$

The norm over the entire state is of course 1, since the probability that the molecule is in either state must be 1.

$$\langle\Psi|\Psi\rangle = \int |\psi_1|^2 + |\psi_2|^2 dx = 1 \tag{2}$$

There are however some subtleties with normalization in numerical models. This is discussed further in section 4.1.

2.2 Constructing the Hamiltonian

As mentioned in section 2.1, there are two electronic states for the molecule corresponding to two potentials. The first is attractive and modelled by a *Morse potential* [3] – illustrated by $V_{11}(\hat{x})$ in figure 4. When the molecule is in this electronic state the atoms are bound together. (It could of course dissociate but such high vibrational energies will not be simulated.) The second potential is repulsive – illustrated by $V_{22}(\hat{x})$ in figure 5. When the molecule is in this electronic state the distance between the nuclei would increase with time, and the molecule dissociates.

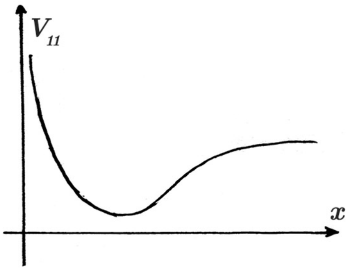

Figure 4: Illustration of an attractive Morse potential.

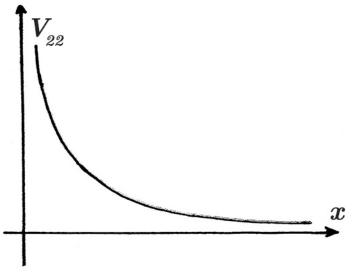

Figure 5: Illustration of a repulsive exponential potential.

It is possible for the molecule to be in any of the two states, as well as in superpositions of the two. Each state has (as mentioned in section 2.1) a wave function associated with it. The point is then that, if the electron wave functions corresponding to the two states have the same spatial symmetries – which we will assume that they have – the molecule can transition between the states[1]. Note that the system can only do so as the wave function approaches a region where the two potentials have energies very close to each other. In practice – to create a higher probability for transitions to occur – the curves of the potentials should intersect and cross over at some point in this region.

The strength and position of this coupling between the states are modelled by Gaussian functions, $V_{12}(\hat{x})$ and $V_{21}(\hat{x})$[2], centred at the intersection of the potentials, i.e. at x_c in figure 6. We naturally assume that the probability of

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[1] Actually it depends on which process is creating the coupling between the electronic states. If a matrix element for an operator is non zero – meaning that the states are symmetric with respect to the operator – we have a coupling between the states. So if $\langle\Psi_\alpha|\hat{A}|\Psi_\beta\rangle \neq 0$ then $\hat{A}$ is creating coupling between Ψ_α and Ψ_β.

[2] $V_{12}(\hat{x})$ determines the probability of transition from state 2 into 1, and $V_{21}(\hat{x})$ determines the probability in the opposite direction.

transition is equal in both directions so $V_{21}(\hat{x}) = V_{12}(\hat{x})$, otherwise the Hamiltonian would not be Hermitian. To emphasize that they are equal we shall call the coupling potential $V_c(\hat{x})$. Note that the coupling is real (i.e. has no imaginary component).

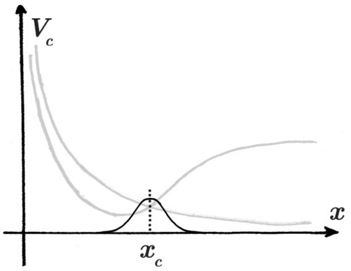

Figure 6: In the neighbourhood of x_c, where $V_{11} = V_{22}$, there is a coupling V_c between the two states, modelled with a Gaussian.

With these representations of the potentials and the coupling between the two states we can form our Hamiltonian for the two state system – using the regular kinetic energy operator, and the reduced mass m of the molecule.

$$\hat{H} = \hat{T} + \hat{V} = \begin{bmatrix} \hat{p}^2/2m & 0 \\ 0 & \hat{p}^2/2m \end{bmatrix} + \begin{bmatrix} V_{11}(\hat{x}) & V_c(\hat{x}) \\ V_c(\hat{x}) & V_{22}(\hat{x}) \end{bmatrix} \tag{3}$$

2.3 Joining the parts in the Schrödinger equation

Like any non-relativistic quantum system, the evolution of our diatomic vibration is described by the Schrödinger equation.

$$i\hbar \frac{\partial}{\partial t} |\Psi\rangle = \hat{H} |\Psi\rangle \tag{4}$$

Inserting the state vector from equation (1), and the Hamiltonian from (3), makes our model of the system complete.

$$i\hbar \frac{\partial}{\partial t} \begin{bmatrix} \psi_1 \\ \psi_2 \end{bmatrix} = \begin{bmatrix} \hat{p}^2/2m + V_{11}(\hat{x}) & V_c(\hat{x}) \\ V_c(\hat{x}) & \hat{p}^2/2m + V_{22}(\hat{x}) \end{bmatrix} \begin{bmatrix} \psi_1 \\ \psi_2 \end{bmatrix} \tag{5}$$

Unfortunately we will not be able to find a gorgeous analytical solution. The potentials are quite complicated and the coupling between them makes it worse. Instead, in section 3 we will be investigating a method of solving this problem numerically, called the *split operator method.*

2.4 The path of the wave packet

Throughout this thesis the initial state of the system is quite similar. A Gaussian wave packet has been places in the attractive Morse potential V_{11}, illustrated in figure 7. The wave packet is then propagated in time using the split operator method (described in section 3). As the wave packet responds to the potential, it will start moving towards the left and pass through the region where the two states couple to each other, this will split up the wave packet and put the molecule in a superposition of the two electronic states.

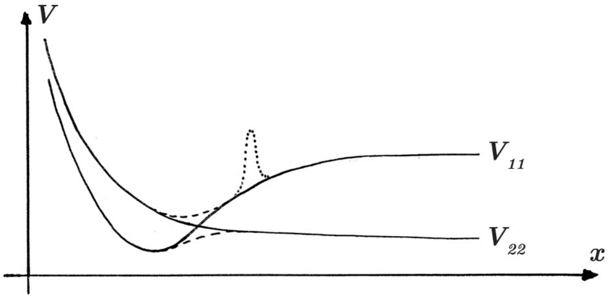

Figure 7: Illustration of the initial state of the system. V_{11} and V_{22} are the two electronic potentials. The dotted line gives an idea of the width and position of the initial wave packet. The dashed lines are the *adiabatic potentials*, obtained by diagonalization of the potential matrix. Where the dashed lines are visible signifies the region where the two states are coupled.

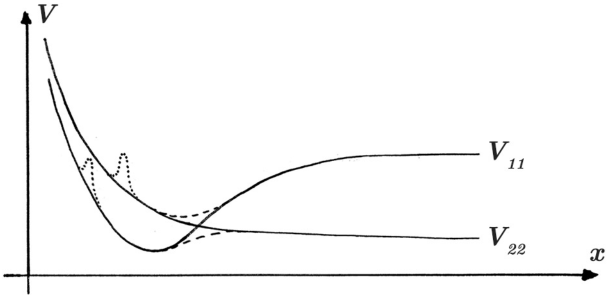

Figure 8: Illustration of the system at the later time (one half a classical period). The wave packet has passed through the area where the two electronic states couple and, as a result, split up in a superposition of the two electronic states.

At half the *classical period* (a time corresponding to half the period of a classical particle) the split wave packets have reached their turning points – illustrated in figure 8 – and start moving back towards the right. Later, as they return to the region where there is a coupling between the states, they will interfere[3], and the interference will determine whether the majority of the wave packet will follow V_{11} and make the molecule more stable, or follow V_{22} and make the molecule more likely to dissociate.

With finely tuned parameters for the potentials, we can find a *meta-stable behaviour* where only a very small portion of the wave function "leaks out" to the right of the coupling area on the potential V_{22}, essentially then returning the state to its initial condition – illustrated in figure 7 – and the oscillation can start over.

In practice there is a clear degrading in the shape of the wave packet after a couple of periods, but the proportion of the wave function that "leaks out"

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[3] This requires of course that the potentials are tuned such that the wave packets return into the region of the coupling at the same time.

of the system remains low, and after sufficient time it is possible to observe revivals in the shape of the wave function.

It is crucial for the meta-stable behaviour that we can create interference between two recombining wave packets at the region of the coupling. Thus if we were to perform any measurement that would collapse the superposition of states (illustrated in figure 8) we would immediately lose the possibility of interference, and the meta-stable behaviour would disappear. Just like in the classic double slit experiment, the behaviour of the system is resting on our ignorance of which path the particle is taking.

2.5 Interaction with a quantized electromagnetic field

Even though we cannot directly measure the electronic state of the system without destroying the meta-stable state, quantum mechanics allows for gaining some information about a system without fully collapsing it. This can be accomplished by *interaction free measurement.* The details of such measurement will not be investigated here, but they are outlined by Avshalom C. Elitzur and Lev Vaidman [4].

The idea for our measurement is to create an entanglement between the state of the molecule and the state of an electromagnetic field. Then we can perform a measurement on the state of the field, and leave the molecule "untouched". However – as we will see in section 5.2 – the more entanglement we have between the field and the molecule, the more we will destroy the meta-stable state of the molecule. There is always a trade-off – the more you want to know, the more you will have to disturb.

The set-up is this: An electromagnetic field of a single polarisation and mode ω_c is applied to the molecule. We assume that the molecule has a third electronic state – and a corresponding potential V_{33} – that is *dipole coupled* to only the second electronic state – corresponding to V_{22}. For simplicity we further assume that the potentials V_{22} and V_{33} both have the same shape so that their energy difference is not dependent on x. The energy difference of the two states corresponds to a transitional frequency of ω_a. This set-up is illustrated in figure 9.

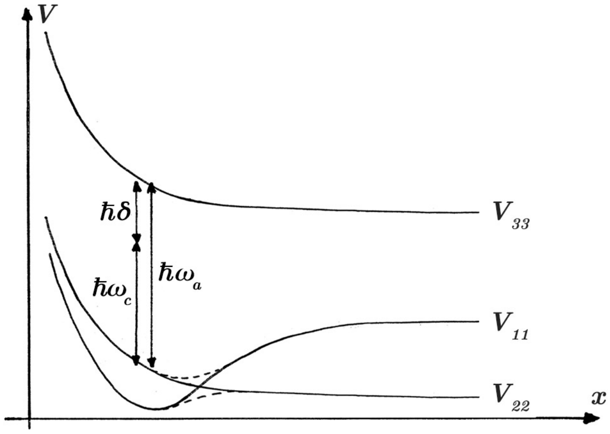

Figure 9: Schematic picture of potentials corresponding to three electronic states, and a dipole coupling between the second and third state.

Then the interaction between energy levels can be described with the *Jaynes-Cummings model*, as discussed in appendix A.4. Specifically we assume that the *detuning* $\delta := \omega_a - \omega_c$ is large – i.e. the frequency of the electromagnetic radiation ω_c is far from resonant with the transitional frequency of the molecule, ω_a. This is the so called *dispersive regime*, and in appendix A.4.1 we find that such a system will receive specific energy corrections on the two energy levels.

$$\hat{H}_{jc}^{(n)} = \hbar \begin{bmatrix} \delta + \frac{g^2 n}{\delta} & \\ & -\frac{g^2 n}{\delta} \end{bmatrix} \tag{6}$$

Here, δ is detuning, g is a parameter for the coupling strength of the interaction between the electric field and the molecule, and n is the number of photons in the field.

The Hamiltonian in (6) describes the energies of a two level system, where the first diagonal term is the energy when the molecule is in the excited state, and the second diagonal term correspond to the ground state. In our model the ground state is represented by V_{22}, and the excited state is V_{33} (see figure 9). So, on the face of it, we need to add a third electronic state (corresponding to V_{33}) to our Hamiltonian in equation (5) (thus making it a 3×3 matrix), and then incorporate the corrections from (6). But remember, we are operating in the dispersive regime, and the third state will not be populated. Therefore there is no need to keep it (and its correction) in our model, and we have returned to the familiar 2×2 matrix – only now, we have introduced an energy correction to the ground state (corresponding to V_{22}).

$$i\hbar \frac{\partial}{\partial t} \begin{bmatrix} \psi_1 \\ \psi_2 \end{bmatrix} = \begin{bmatrix} \hat{p}^2/2m + V_{11}(\hat{x}) & V_c(\hat{x}) \\ V_c(\hat{x}) & \hat{p}^2/2m + V_{22}(\hat{x}) - \hbar \frac{g^2 n}{\delta} \end{bmatrix} \begin{bmatrix} \psi_1 \\ \psi_2 \end{bmatrix} \tag{7}$$

In the end, the energy of the second electronic state depends on n, i.e. the number of photons in the electromagnetic field.

However, n should not be taken to be a simple integer. It is experimentally hard to create a field with one definite number of photons – especially when that number grows large – so instead we will use a distribution of the states $|n\rangle$. The easiest state to create in an experimental set-up is a *coherent state*, and from the principles of quantum optics, and assuming that the electromagnetic field is coherent, we can find the amplitudes for the different numbered states $|n\rangle$, of a coherent state $|\alpha\rangle$ (details are outlined by Göran Johansson and Thilo Bauch [5]).

$$|\alpha\rangle = \sum_{n=0}^{\infty} e^{-|a|^2/2} \frac{\alpha^n}{\sqrt{n!}} |n\rangle \tag{8}$$

The parameter α is the eigenvalue of the annihilation operator $\hat{a}$ and it is a complex number (not an observable). If we calculate the probability of finding a particular number of photons $|n\rangle$ we will get a Poisson distribution.

$$P_n = |\langle n|\alpha\rangle|^2 = \left| e^{-|a|^2/2} \frac{\alpha^n}{\sqrt{n!}} \right|^2 = e^{-\langle n\rangle} \frac{\langle n\rangle^n}{n!} \tag{9}$$

So the complex amplitude α has a very simple reation to $\langle n \rangle$ (the average value of n).

$$|\alpha|^2 = \langle n \rangle \tag{10}$$

The total initial state of the system is now the tensor product between the wave function and the number of photons.

$$|\Psi\rangle = \begin{bmatrix} \psi_1 \\ \psi_2 \end{bmatrix} \otimes \sum_{n=0}^{\infty} e^{-|\alpha|^2/2} \frac{\alpha^n}{\sqrt{n!}} |n\rangle \tag{11}$$

Remembering that the coefficients squared correspond to a Poisson distribution around some average $\langle n \rangle$, let us name them c_n, and rewrite the total initial state in a somewhat friendlier way.

$$|\Psi\rangle = \sum_{n=0}^{\infty} c_n \begin{bmatrix} \psi_1 \\ \psi_2 \end{bmatrix} \otimes |n\rangle \tag{12}$$

In theory, the state $|n\rangle$ is an infinite dimensional vector, but when working with numerical models we can observe that the coefficients c_n will quickly go to zero as we go above the value $n = \langle n \rangle$, and at some point we can just truncate the sum in (12) because the rest has a negligible effect. It is from this state that we will be able to calculate the entanglement of the molecule with the field using the formalism of *density operators* and *von Neuman entropy* that are briefly discussed in the next section.

2.6 Evaluating entanglement with density operators and von Neumann entropy

The details for the theory of density operators will not be presented here. Instead the reader is referred the to Reinhold Bertlmann [6] and Jens Eisert [7]. However, some theory is vital in order to motivate how entanglement is calculated in this thesis. So let us outline the key points with some examples.

A *density operator* ρ is constructed by taking the outer product of a state vector.

$$\rho = |\psi\rangle\langle\psi| \tag{13}$$

This corresponds to a so called *pure state.* Adding further outer products of linearly independent state vectors, we can also construct a density operator in a so called *mixed state.*

$$\rho = \alpha\, |\psi\rangle\langle\psi| \; + \; \beta\, |\phi\rangle\langle\phi| \qquad , \qquad \alpha + \beta = 1 \tag{14}$$

This mixed state would be useful if we for instance tried to prepare an atom in $|\psi\rangle$, but our atom preparation device was not perfect, and in 1% of the cases we got $|\phi\rangle$ instead. In that case we can represent the system by forming a mixed state.

$$\rho = 0.99\, |\psi\rangle\langle\psi| \; + \; 0.01\, |\phi\rangle\langle\phi| \tag{15}$$

This kind of description of a system requires the formalism of density operators, since the usual state vectors cannot describe the situation above. If you tried doing something similar with state vectors you will not get a *mixed state*, instead what you end up with is a *superposition of states*:

$$|\Psi\rangle = \sqrt{0.99}\,|\psi\rangle \; + \; \sqrt{0.01}\,|\phi\rangle \tag{16}$$

This cannot describe the situation in (15) because we could construct another, different, state with the same probabilities by changing the phase between $|\psi\rangle$ and $|\phi\rangle$. So when we lack information about the phase factor one is forced to introduce density operators, like in equation (15).

Now, consider a *composite system* made from two subsystems. That could be for instance two distinct particles emitted in some reaction, an experimental set-up and the rest of the universe, or a diatomic molecule and an electromagnetic field (as in the case of this thesis). From the density operator describing the total composite system it is possible to find how much information the first subsystem has about the second, and vise versa. That is, the entanglement between the subsystems[4]. For simplicity in this example, let both the subsystems be described by basis $\{|0\rangle, |1\rangle\}$.

$$|\psi\rangle_1 = a_1\,|0\rangle + b_1\,|1\rangle \tag{17}$$

$$|\psi\rangle_2 = a_2\,|0\rangle + b_2\,|1\rangle \tag{18}$$

The total state is then formed from the tensor product[5].

$$|\Psi\rangle = |\psi\rangle_1 \otimes |\psi\rangle_2 := |\psi_1, \psi_2\rangle \tag{19}$$

Then, depending on what state vector we begin with we have states with various degrees of entanglement. Take for instance the situation where $|\psi_1, \psi_2\rangle$ is a superposition of $|0,0\rangle$ and $|1,1\rangle$.

$$|\Psi_{max}\rangle = \frac{1}{\sqrt{2}}\big(\,|0,0\rangle + |1,1\rangle\,\big) \tag{20}$$

$$\rho_{max} = \frac{1}{2}\big(\,|0,0\rangle + |1,1\rangle\big)\,\big(\langle 0,0| + \langle 1,1|\,\big) \tag{21}$$

From $|\Psi_{max}\rangle$ we can see that if you would measure the first subsystem to be in state $|0\rangle$ you know that the second will be in $|0\rangle$ too. So this comprise a simple example of a composite system with entanglement. Now, a different example!

$$|\Psi_{min}\rangle = \frac{1}{\sqrt{2}}\big(\,|0,1\rangle + |1,1\rangle\,\big) \tag{22}$$

$$\rho_{min} = \frac{1}{2}\big(\,|0,1\rangle + |1,1\rangle\big)\,\big(\langle 1,0| + \langle 1,1|\,\big) \tag{23}$$

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[4] An *entangled state* is defined as a composite state where it is impossible to express the total state as a product of the states of the subsystems.

[5] For the bra-state, the states for the sub-systems will be printed in reverse order: $\langle\psi_2, \psi_1|$.

In this situation, if you measure the first subsystem you can get either $|0\rangle$ or $|1\rangle$, but that has no bearing on the second subsystem which is always going to be $|1\rangle$. Thus we can not have any entanglement in this system.

For the situations in (20) and (22) it is sufficient to just look at the states to determine if there is entanglement in the system. But as we construct more elaborate states for a composite system we need a way to quantify the amount of entanglement – at least qualitatively – so we can say that some state has more or less entanglement than some other state. This is done by taking the *partial trace* – described in appendix A.3 – over one of the subsystems in question. If the density operator that remains – the *reduced density operator* – has a *mixed state* then there is entanglement in the system, and if the operator has a *pure state* there is no entanglement. The more mixed a reduced density operator is, the more entanglement we have between our two subsystems.

Let us do a simple demonstration of how this works by taking the partial trace over the first state $|\psi\rangle_1$, of ρ_{max} and ρ_{min} in equations (21) and (23), to show that we get a mixed state from (21) and a pure state from (23).

$$\rho_{max}^{(2)} = Tr_1[\rho_{max}] = \sum_{k=0}^{1} {}_1\langle k| \left(\frac{1}{2}\big(|0,0\rangle + |1,1\rangle\big) \big(\langle 0,0| + \langle 1,1|\big) \right) |k\rangle_1 = \tag{24}$$

$$= \frac{1}{2}\, |0\rangle_2\, {}_2\langle 0| \; + \; \frac{1}{2}\, |1\rangle_2\, {}_2\langle 1| \tag{25}$$

This reduced density operator has two orthogonal terms, which means it is impossible to rewrite as one term only, regardless of the basis. Thus it is a mixed state, like in equation (14). This is consistent with our starting point of having entanglement in the system. In fact it is maximally mixed (all possible coefficients have the same value, 1/2).

Now let us try taking the partial trace of ρ_{min} where we expect to see no entanglement.

$$\rho_{min}^{(2)} = Tr_{(1)}[\rho_{min}] = \sum_{k=0}^{1} {}_1\langle k| \left(\frac{1}{2}\big(|0,1\rangle + |1,1\rangle\big) \big(\langle 1,0| + \langle 1,1|\big) \right) |k\rangle_1 = \tag{26}$$

$$= |1\rangle_2\, {}_2\langle 1| \tag{27}$$

This reduced density operator has only one term, which means it must be a pure state – like in equation (13) – and there is no entanglement between the subsystems.

To evaluate exactly *how much* mixed a reduced density operator is, we can use the method of *von Neumann entropy.*

$$S_{vN} := -\mathrm{Tr}[\rho \ln(\rho)] \tag{28}$$

Here $\mathrm{Tr}[\cdot]$ simply means calculating the total trace. If ρ is written in terms of its eigenvectors, then (28) is easy to calculate from the eigenvalues $\{\lambda_1, \lambda_2, \ldots\}$ of the density matrix ρ.

$$S_{vN} := -\sum_k \lambda_k \ln(\lambda_k) \tag{29}$$

If the von Neumann entropy is zero we have a pure state, and no entanglement. If instead the entropy increases, the entanglement in the compound system must also be increasing, and the maximum value is reached when the eigenvalues are equal.

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The great mathematician Carl Friedrich Gauss is known to have said "No self-respecting architect leaves the scaffolding in place after completing the building" when answering to criticism about his work being hard to follow and devoid of any motivations.

With this I thoroughly disagree. I make an effort to erect as much scaffolding as possible around my work and then make them accessible for climbing. Unlike real buildings, in the metaphorical case you might want to get up on the roof and inspect how the ceramic roofing tiles were attached to the trusses.

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3 The split operator method

3.1 The time evolution operator

Reference for this section: Prof. Paola Cappellaro [8].

The goal here is to express a solution of the time dependent Schrödinger equation in a form that is useful for numerical computation, given some initial wave function.

Suppose that we could write the general time dependent solution $\psi(t)$ in terms of some initial state $\psi_0 = \psi(0)$ that a time dependent operator $\hat{U}$ is acting on to give us the state at a later time.

$$|\psi(t)\rangle = \hat{U}(t)\,|\psi_0\rangle \tag{30}$$

This would indeed be very useful. If the wave function is known at some initial state ψ_0, we can apply the operator $\hat{U}(t)$ to find it at any later time.

However we need to make sure that equation (30) makes sense. In other words it has to be a solution to the Schrödinger equation. Also, if it is a solution then what does $\hat{U}$ look like, and what are its properties? Let us begin the investigation by simply inserting (30) into (4) to see what $\hat{U}$ must look like if (30) really was a solution.

$$i\hbar\frac{\partial \hat{U}}{\partial t}\,|\psi_0\rangle = \hat{H}\hat{U}\,|\psi_0\rangle \tag{31}$$

Remember that ψ_0 is not a function of t so it just pops out of the partial time derivative. If equation (31) should hold for any wave function ψ_0 then we must also have strict equality between the operators themselves on both sides. Thus we can conclude that under the initial assumption that (30) solves (4) we must have:

$$i\hbar\frac{\partial \hat{U}}{\partial t} = \hat{H}\hat{U} \tag{32}$$

This differential equation for $\hat{U}$ has a simple solution, if we treat $\hat{U}$ as an ordinary function of t, and the Hamiltonian as an ordinary function independent of t. Such a constraint on $\hat{H}$ would be quite reasonable since most systems we want to investigate are autonomous. So observing this constraint on $\hat{H}$ we can write down a solution.

$$\hat{U} = e^{-i\frac{\hat{H}}{\hbar}t} \tag{33}$$

But this does not immediately make sense. What does it mean with an exponential function of an operator? Is this really a solution at all? Not to spoil the exciting suspense, but it is! Closer investigations will follow shortly (section 3.2). First we should observe that since the Hamiltonian is Hermitian (i.e. $\hat{H}^\dagger = \hat{H}$) the following manipulation is possible.

$$\hat{U}\hat{U}^\dagger = e^{-i\frac{\hat{H}}{\hbar}t}e^{i\frac{\hat{H}}{\hbar}t} = \mathbb{1} \Rightarrow \tag{34}$$

$$\hat{U}^\dagger = \hat{U}^{-1} \tag{35}$$

So $\hat{U}$ is a unitary operator[6]. This means that the operator preserves inner products [9], and in particular the norm of a wave function. This is good news!

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[6] A unitary operator is defined by having its complex conjugate being equal to its inverse.

Actually it is required for this formalism to work since the wave function has to stay normalized when the evolution operator is applied, and unitary operators conserve that property of functions.

3.2 Making sense of the evolution operator

So, how should the time evolution operator that we found in equation (33) be interpreted? What does it mean to put an operator in the exponent? Retreating back to the series definition of the exponential will shed some clarity.

$$e^{-i\frac{\hat{H}}{\hbar}t} := \mathbb{1} - i\frac{\hat{H}}{\hbar}t - \frac{\hat{H}^2}{2!\hbar^2}t^2 + i\frac{\hat{H}^3}{3!\hbar^3}t^3 + \frac{\hat{H}^4}{4!\hbar^4}t^4 - \dots \tag{36}$$

Great! This is something explicit. For each term we will just apply the Hamiltonian the appropriate number of times and multiply by the complex coefficient of that term. Granted, we have to do that up to infinity, but at least the expression now makes sense.

In fact, it is worth noting that this series expansion solves the differential equation that we started with in equation (32). So we must argue that – *this is the actual solution, and the exponential is just a notation for the series.*

What about the infinity? Computers do not handle those particularly well. In the coming sections we will make an effort to solve this by splitting up the Hamiltonian in different parts, each of which we will try to diagonalize, and then use the fact that taking the exponential of a diagonal matrix is just a diagonal matrix of the exponentials.

$$A := \begin{bmatrix} a_1 & & & \\ & a_2 & & \\ & & \ddots & \\ & & & a_n \end{bmatrix} \quad \Rightarrow \quad e^A = \begin{bmatrix} e^{a_1} & & & \\ & e^{a_2} & & \\ & & \ddots & \\ & & & e^{a_n} \end{bmatrix} \tag{37}$$

This relation is shown in appendix A.1.

3.3 Splitting the evolution operator

The next step is to construct the so called *split operator* that will be used to advance a wave function in time. The expression in equation (36) is satisfying from a theoretical point of view, but it is not really practical. The Hamiltonian has many terms and summing to infinity will give us problems if we want to apply that operator to a state.

Let us begin with a common expression for the Hamiltonian – split into the kinetic energy $\hat{T}$ and potential energy $\hat{V}$. As it so happens, this is the kind of Hamiltonian employed throughout the thesis.

$$\hat{H} = \hat{T} + \hat{V} \tag{38}$$

It is now tempting to do something like this.

$$e^{-i\frac{\hat{T}+\hat{V}}{\hbar}t} = e^{-i\frac{\hat{T}}{\hbar}t}e^{-i\frac{\hat{V}}{\hbar}t} \tag{39}$$

Then we can treat the kinetic and potential energy separately, applying them one at a time. However, this equation (39) does not hold! To show this, let us go back to the series definition in (36), and expand both the left-hand-side and the-hand-side of (39).

$$e^{-i\frac{\hat{T}+\hat{V}}{\hbar}t} = \mathbb{1} - i\frac{\hat{T}+\hat{V}}{\hbar}t - \frac{(\hat{T}+\hat{V})^2}{2!\hbar^2}t^2 + i\frac{(\hat{T}+\hat{V})^3}{3!\hbar^3}t^3 + \dots \tag{40}$$

$$e^{-i\frac{\hat{T}}{\hbar}t}e^{-i\frac{\hat{V}}{\hbar}t} = \left(\mathbb{1} - i\frac{\hat{T}}{\hbar}t - \frac{\hat{T}^2}{2!\hbar^2}t^2 + i\frac{\hat{T}^3}{3!\hbar^3}t^3 + ..\right)\left(\mathbb{1} - i\frac{\hat{V}}{\hbar}t - \frac{\hat{V}^2}{2!\hbar^2}t^2 + i\frac{\hat{V}^3}{3!\hbar^3}t^3 + ..\right) \tag{41}$$

In order for equation (39) to hold, the expansions in (40) and (41) must be equal. But they are not! If $\hat{T}$ and $\hat{V}$ were simple numbers they would be, we could expand both (40) and (41) further and with some effort show that any general term with k $\hat{T}$'s and $(n-k)$ $\hat{V}$'s would be the same in both expressions. But $\hat{T}$ and $\hat{V}$ are operators, and they do not commute. So expression (40) would have all manners of arrangements of the operators (like for instance $\hat{V}^2\hat{T}^2\hat{V}\hat{T}^3$), whereas every term from (41) would have all the $\hat{T}$'s to the left of the $\hat{V}$'s.

So did we reach an impasse? We need to somehow untangle the kinetic energy and potential energy operators if we hope to be able to apply them sequentially in a computer.

We can get out of this fox trap situation if we turn to approximations, the next best thing. So far we have tried to use the evolution operator to give us the wave function at all later times. What if we limit to the case when t is small. So let $t \to \Delta t$. In this case the higher order terms in (40) will be small. (Remember, equation (40) was the true series expansion of the operator.) If expanded up to the second order

$$\begin{aligned} e^{-i\frac{\hat{T}+\hat{V}}{\hbar}\Delta t} &= \qquad\qquad (42) \\ \mathbb{1} - i\frac{\hat{T}}{\hbar}\Delta t - i\frac{\hat{V}}{\hbar}\Delta t - \frac{\hat{T}^2}{2!\hbar^2}\Delta t^2 + \frac{\hat{V}^2}{2!\hbar^2}\Delta t^2 &+ \frac{\hat{T}\hat{V}}{2!\hbar^2}\Delta t^2 + \frac{\hat{V}\hat{T}}{2!\hbar^2}\Delta t^2 + O(\Delta t^3) \end{aligned}$$

Now we need to make a slight intellectual jump. Let us investigate this product:

$$e^{-i\frac{\hat{T}}{2\hbar}\Delta t}e^{-i\frac{\hat{V}}{\hbar}\Delta t}e^{-i\frac{\hat{T}}{2\hbar}\Delta t} \tag{43}$$

It looks a bit like what we naïvely were trying to do in (39) when you observe that the first and last factor have both had their exponents divided by 2. We will start with the expression in (43), then make a series expansion up to the second order for each factor, and multiply everything together – keeping every resulting term up to the power of 2. It turns out that what we get back is exactly the expansion in (42), except of course a different error term. (This is left to the curious reader to check.) Thus we can equate the expansion of (43) with the exact expression for the propagation operator if we accept an error of order Δt^3.

$$e^{-i\frac{\hat{H}}{\hbar}\Delta t} = e^{-i\frac{\hat{T}}{2\hbar}\Delta t}e^{-i\frac{\hat{V}}{\hbar}\Delta t}e^{-i\frac{\hat{T}}{2\hbar}\Delta t} + O'(\Delta t^3) \tag{44}$$

As long as Δt is kept small we have been able to split up the time evolution operator into kinetic and potential energy, and we only got an error term that goes as Δt^3 – which is pretty good!

Note that we would want to apply this operator repeatedly, which means that in the middle of the sequence we will compute

$$\dots \cdot e^{-i\frac{\hat{T}}{2\hbar}\Delta t} \cdot e^{-i\frac{\hat{T}}{2\hbar}\Delta t} \cdot \dots \tag{45}$$

This is of course equivalent of removing the 1/2 from the exponent and instead taking

$$\ldots \cdot e^{-i\frac{\hat{T}}{\hbar}\Delta t} \cdot \ldots \tag{46}$$

The only concern is then in the beginning and end of the sequence, but as it turns out that introduces an error that is completely negligible. Thus in the interest of computational speed, we let our *time propagation split operator* be:

$$\hat{U} = e^{-i\frac{\hat{T}}{\hbar}\Delta t} e^{-i\frac{\hat{V}}{\hbar}\Delta t} \tag{47}$$

In section 3.4 we will straighten out what kind of object this is (we are still dealing with exponentials of operators!).

Note that this operator is unitary, so even though it is found with approximative methods it will always conserve the norm of the wave function.

$$e^{-i\frac{\hat{T}}{\hbar}\Delta t} e^{-i\frac{\hat{V}}{\hbar}\Delta t} \left(e^{-i\frac{\hat{T}}{\hbar}\Delta t} e^{-i\frac{\hat{V}}{\hbar}\Delta t}\right)^{\dagger} = e^{-i\frac{\hat{T}}{\hbar}\Delta t} e^{-i\frac{\hat{V}}{\hbar}\Delta t} e^{i\frac{\hat{V}}{\hbar}\Delta t} e^{i\frac{\hat{T}}{\hbar}\Delta t} = \tag{48}$$

$$e^{-i\frac{\hat{T}}{\hbar}\Delta t} e^{i\frac{\hat{T}}{\hbar}\Delta t} = \mathbb{1} \quad \Rightarrow \tag{49}$$

$$\hat{U}^{\dagger} = \hat{U}^{-1} \tag{50}$$

It is interesting to compare our resulting time evolution operator in equation (47) with our first naïve attempt to decompose the operator in (39)[7]. They are quite similar!

$$e^{-i\frac{(\hat{T}+\hat{V})}{\hbar}\Delta t} = e^{-i\frac{\hat{T}}{\hbar}\Delta t} e^{-i\frac{\hat{V}}{\hbar}\Delta t} + O(\Delta t^3) \tag{51}$$

—

Immanuel Kant pointed out that there are some things that you can neither learn nor figure out. Knowledge that is hard-wired in our brain from birth. The concepts of space and time for instance. So for a human mind the experience of the world will always be through that lens, regardless of the actual nature of the world.

In this light I find it a bit unsettling that space and time provides the fundament for so many of our mathematical descriptions of the world. Quantum Mechanics makes it worse by incorporating some concepts that seem to disregard – or perhaps transcend – the ideas of space and time, like the instantaneous collapse of a spatially extended wave function.

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[7] The negligible error from grouping operators is disregarded in equation (51).

3.4 Using the evolution operator on a two state system

In section 3.3 we found the expression for the split operator that we want to use.

$$\hat{U} = e^{-i\frac{\hat{T}}{\hbar}\Delta t} e^{-i\frac{\hat{V}}{\hbar}\Delta t} \tag{52}$$

We now insert expressions for the kinetic energy operator $\hat{T}$ and the potential energy energy operator $\hat{V}$ of the two state system. From section 2.2 we had that

$$\hat{T} = \begin{bmatrix} \hat{p}^2/2m & 0 \\ 0 & \hat{p}^2/2m \end{bmatrix} \tag{53}$$

$$\hat{V} = \begin{bmatrix} V_{11}(\hat{x}) & V_c(\hat{x}) \\ V_c(\hat{x}) & V_{22}(\hat{x}) \end{bmatrix} \tag{54}$$

Both exponentials in (52) need some discussion. Let us begin with the kinetic energy.

3.4.1 Time evolution due to kinetic energy

As shown in appendix A.1, taking an exponential of a diagonal matrix is the same as that diagonal matrix of exponentials. So the kinetic energy in (52) will be easy to express as a matrix, inserting the diagonal matrix of $\hat{T}$ from (53).

$$e^{-i\frac{\hat{T}}{\hbar}\Delta t} = \begin{bmatrix} e^{-i\frac{\hat{p}^2}{2\hbar m}\Delta t} & 0 \\ 0 & e^{-i\frac{\hat{p}^2}{2\hbar m}\Delta t} \end{bmatrix} \tag{55}$$

Done! Only one remark. We have to decide what to do with the fact that there still is an operator $\hat{p}$ in an exponential. We could try to use the most common representation of $\hat{p}$

$$\hat{p} = -i\hbar\frac{\partial}{\partial x} \tag{56}$$

However, we would get rather stuck. The operator in (56) applies when the wave function ψ is given in its x-representation. If we express ψ as a function of the wave number k instead ($p = \hbar k$), the $\hat{p}$ operator will simplify to just multiplication by p. The problem is then resolved by a Fourier transform of the wave function, to find its k-representation, and then simply multiply by p.

$$e^{-i\frac{\hat{T}}{\hbar}\Delta t} \left|\psi(k,t)\right\rangle = \ldots = \begin{bmatrix} e^{-i\frac{p^2}{2\hbar m}\Delta t}\ \psi_1(k,t) \\ e^{-i\frac{p^2}{2\hbar m}\Delta t}\ \psi_2(k,t) \end{bmatrix} \tag{57}$$

3.4.2 Time evolution due to potential energy

The potential energy takes some more work so let us get to it. We want to express the following operator in a useful manner.

$$e^{-i\frac{\hat{V}}{\hbar}\Delta t} \tag{58}$$

The main concern here is that the matrix for $\hat{V}$ is not diagonal.

$$\hat{V} = \begin{bmatrix} V_{11}(\hat{x}) & V_c(\hat{x}) \\ V_c(\hat{x}) & V_{22}(\hat{x}) \end{bmatrix} \tag{59}$$

Therefore we cannot directly use the same method as in the previous section 3.4.1. We could find a set of eigenvectors for the matrix $\hat{V}$ – a different set for every x-value – and then express our vector of wave functions in that basis. Then the matrix $\hat{U}$ would be diagonal.

$$\hat{V} = \hat{Q}\hat{U}\hat{Q}^{-1} \tag{60}$$

However, here we will concern ourself with a different approach, finding an analytical solution to expressing (58) as a matrix.[8]

When dealing with a 2×2 matrix it is possible to find an analytical solution by employing some clever strategies[9]. Since (58) is a complex valued 2×2 matrix it is a good starting point to pick some basis to express such matrices in. One such basis is the Pauli matrices joined with the unity matrix. Using complex coefficients these will span the whole space of 2×2 complex valued matrices.

$$\mathbb{1} = \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} \qquad \sigma_1 = \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} \qquad \sigma_2 = \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix} \qquad \sigma_3 = \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \tag{61}$$

Let us go for a mathematical excursion, and start by rewriting (59) in the basis of (61).

$$\begin{bmatrix} V_{11} & V_c \\ V_c & V_{22} \end{bmatrix} = \ldots = \frac{V_{11} + V_{22}}{2}\mathbb{1} + V_c\sigma_1 + \frac{V_{11} - V_{22}}{2}\sigma_3 \tag{62}$$

We want to put the whole expression (62) in an exponential, and preferably deal with each term separately, but we need to be careful. The Pauli matrices do not commute and thus we cannot deal with each of the last two terms on their own[10]. Luckily anything commutes with the identity operator $\mathbb{1}$, so we can at least split up the expression once.

$$e^{-i\frac{\hat{V}}{\hbar}\Delta t} = e^{-\frac{i\Delta t}{\hbar}\frac{V_{11}+V_{22}}{2}\mathbb{1}} e^{-\frac{i\Delta t}{\hbar}\left(V_c\sigma_1 + \frac{V_{11}-V_{22}}{2}\sigma_3\right)} \tag{63}$$

Dealing with the first factor in (63) is trivial since the identity matrix is diagonal.

$$e^{-\frac{i\Delta t}{\hbar}\frac{V_{11}+V_{22}}{2}\mathbb{1}} = e^{-i\frac{V_{11}+V_{22}}{2\hbar}\Delta t}\mathbb{1} \tag{64}$$

Done! And now the second factor of (63). This requires a bit more. We will be introducing the matrix vector $\vec{\boldsymbol{\sigma}}$, and define a scalar vector $\vec{\boldsymbol{\alpha}}$.

$$\vec{\boldsymbol{\sigma}} := \begin{bmatrix} \sigma_1 \\ \sigma_2 \\ \sigma_3 \end{bmatrix} \qquad \vec{\boldsymbol{\alpha}} := \frac{1}{\hbar}\begin{bmatrix} V_c \\ 0 \\ \frac{V_{11}-V_{22}}{2} \end{bmatrix} \tag{65}$$

It might seem that $\vec{\boldsymbol{\alpha}}$ is a bit arbitrary, but it is carefully chosen in order to rewrite the second factor in (63).

$$e^{-\frac{i\Delta t}{\hbar}\left(V_c\sigma_1 + \frac{V_{11}-V_{22}}{2}\sigma_3\right)} = e^{-i\Delta t\vec{\boldsymbol{\alpha}}\vec{\boldsymbol{\sigma}}} \tag{66}$$

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[8] Both the diagonalizing approach and the analytical solution have been tested in code and shown to give the same result, within an error of the order of magnitude of the numerical floating point precision.

[9] It is possible to do the same for a 3×3 matrix but it gets increasingly involved.

[10] Why not? See reasoning in the beginning of section 3.3.

In order to tell what kind of object the resulting exponential in equation (66) is, we express it as the series expansion.

$$e^{-i\Delta t\vec{\boldsymbol{\alpha}}\vec{\boldsymbol{\sigma}}} = \mathbb{1} - i\Delta t\vec{\boldsymbol{\alpha}}\vec{\boldsymbol{\sigma}} - \frac{(\Delta t\vec{\boldsymbol{\alpha}}\vec{\boldsymbol{\sigma}})^2}{2!} - i\frac{(\Delta t\vec{\boldsymbol{\alpha}}\vec{\boldsymbol{\sigma}})^3}{3!} + \frac{(\Delta t\vec{\boldsymbol{\alpha}}\vec{\boldsymbol{\sigma}})^4}{4!} + \dots \tag{67}$$

In section A.2 of the appendix it is shown how these terms can be simplfied.

$$(\vec{\boldsymbol{\alpha}}\vec{\boldsymbol{\sigma}})^2 = \alpha^2\mathbb{1} \quad , \quad \alpha := |\vec{\boldsymbol{\alpha}}| \tag{68}$$

Using the definition of $\vec{\boldsymbol{\alpha}}$ from equation (65), we can determine its magnitude.

$$\alpha = \frac{1}{\hbar}\sqrt{V_c^2 + \frac{(V_{11} - V_{22})^2}{4}} \tag{69}$$

With (68) and (69), we can simplify the series in (67).

$$e^{-i\Delta t\vec{\boldsymbol{\alpha}}\vec{\boldsymbol{\sigma}}} = \mathbb{1} - i\Delta t\vec{\boldsymbol{\alpha}}\vec{\boldsymbol{\sigma}} - \Delta t^2\frac{\alpha^2}{2!}\mathbb{1} - i\Delta t^3\frac{\alpha^2\vec{\boldsymbol{\alpha}}\vec{\boldsymbol{\sigma}}}{3!} + \Delta t^4\frac{\alpha^4}{4!}\mathbb{1} + \dots \tag{70}$$

By multiplying each term including $\vec{\boldsymbol{\alpha}}\vec{\boldsymbol{\sigma}}$ with α/α, and then compare this expansion with the familiar series expansions of $\sin(x)$ and $\cos(x)$, we can conclude the following.

$$e^{-i\Delta t\vec{\boldsymbol{\alpha}}\vec{\boldsymbol{\sigma}}} = \cos(\alpha\Delta t)\mathbb{1} - i\frac{\sin(\alpha\Delta t)}{\alpha}\vec{\boldsymbol{\alpha}}\vec{\boldsymbol{\sigma}} \tag{71}$$

Using our definitions for $\vec{\boldsymbol{\sigma}}$ and $\vec{\boldsymbol{\alpha}}$ we can finally write down a matrix representation.

$$e^{-\frac{i\Delta t}{\hbar}\left(V_c\sigma_1 + \frac{V_{11}-V_{22}}{2}\sigma_3\right)} = \dots =$$

$$\begin{bmatrix} \cos(\alpha\Delta t) - i\frac{V_{11}-V_{22}}{2\alpha}\sin(\alpha\Delta t) & -i\frac{V_c}{\alpha}\sin(\alpha\Delta t) \\ -i\frac{V_c}{\alpha}\sin(\alpha\Delta t) & \cos(\alpha\Delta t) + i\frac{V_{11}-V_{22}}{2\alpha}\sin(\alpha\Delta t) \end{bmatrix} \tag{72}$$

Then it is time to put it all together using the results in equation (64) and (72), and we have found our time evolution operator for the potential.

$$e^{-i\frac{\hat{V}}{\hbar}\Delta t} =$$

$$e^{-i\frac{V_{11}+V_{22}}{2\hbar}\Delta t}\begin{bmatrix} \cos(\alpha\Delta t) - i\frac{V_{11}-V_{22}}{2\alpha}\sin(\alpha\Delta t) & -i\frac{V_c}{\alpha}\sin(\alpha\Delta t) \\ -i\frac{V_c}{\alpha}\sin(\alpha\Delta t) & \cos(\alpha\Delta t) + i\frac{V_{11}-V_{22}}{2\alpha}\sin(\alpha\Delta t) \end{bmatrix} \tag{73}$$

This looks a bit hefty, but the good news is that everything in this expression is possible to recreate in code. Remember that every amplitude V in (73) is actually a function of the $\hat{x}$-operator. So in order to apply this to a wave function ψ, it should be in its x-representation. This is different from what we concluded in section 3.4.1, where we needed the k-representation. The Fourier transform comes to the rescue!

4 Constructing the model in code

4.1 Normalization of the wave function

Quantum mechanics require the wave function to stay normalized as the system develops in time. So if ψ is some wave function of, for instance, position and time the following must hold.

$$\langle\psi|\psi\rangle = \int |\psi(x,t)|^2 dx = 1 \qquad \forall\ t \tag{74}$$

Unfortunately in numerical models there is no such luxury as integrating over all space. In this model space is defined over a limited region, and the model uses cyclic space – which means that if any part of the wave function exits to the right of the interval it will re-enter on the left. Such state of affairs is not really acceptable! The wave function – as a function of x – is describing the expected distance between two particles, and the interval begins at $x = 0$ and ends at some $x = x_{max}$. Physically there is of course nothing connecting an arbitrary maximum distance x_{max} to having no distance between the particles. The solution to the problem is to make sure that the wave function never gets close to the boundaries of the interval, and this is done with different techniques for each endpoint.

At $x = 0$ both potentials used in the model grows really large. In fact they become large enough to keep the wave function so small at the boundary that there is effectively no leakage this way. See illustration of the system in figure 7 on page 6!

The situation is worse at the endpoint $x = x_{max}$. The model describes a molecule that can dissociate, so even though the Morse potential increases, the dissociative potential decreases and will attract wave function towards $x = x_{max}$. The solution here is to employ a complex potential. It is possible to show – but not shown here – that the norm of a wave function, propagating in an imaginary potential, will not be constant. If we choose the right sign of the imaginary component the norm will decrease, and the potential will start to "absorb" the wave function. Therefore we create some increasing imaginary potential at large x values – preferably using something like an arctangent function – and any part of the wave function entering into this region will vanish.

Unfortunately this means that our requirement for the wave function to stay normalized is no longer fulfilled. Luckily, in this model there is an elegant interpretation for this. The norm of the remaining wave function can be interpreted as the probability for the molecule to remain stable.

4.2 Using MatLab

MatLab was chosen as the platform for building the numerical model. Even though there are other more low level languages that have the potential for greater speed then MatLab, it was an ideal choice for this project simply because MatLab is very quick and straightforward to use when creating computer programs. Plotting and displaying data require very little effort, and the programming language supports creating good design patterns with object oriented programming.

4.3 General structure of the code

A design pattern that uses object oriented programming was employed to attain a good structure in the code. Figure 10 shows a simple illustration of the most important objects that are used for creating the model.

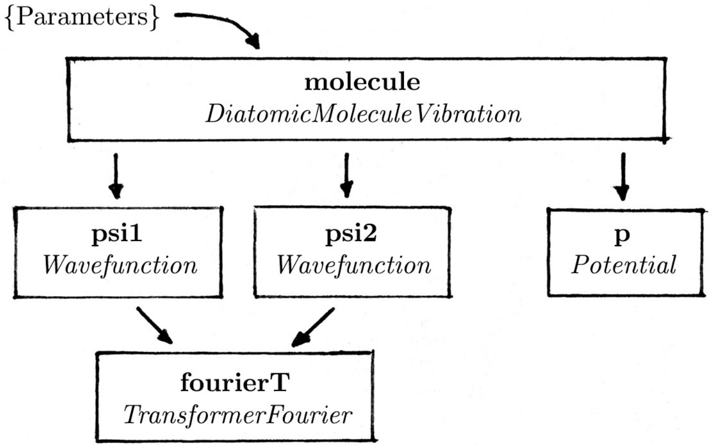

Figure 10: Schematic overview of the central objects in the code.

The main object in the model, named `molecule` – an instance of the class `DiatomicMoleculeVibration` – is created with some initial parameters that determines the properties of the system. This object then contains the functions suitable for running optimisation algorithms (section 4.4), calculating various quantities, and propagating the system in time using the split operator method (section 3.3). The object `molecule` creates two instances – named `psi1` and `psi2` – of `Wavefunction` (compare to equation (1) on page 3). `Wavefunction` is essentially a class that defines an improved and extended array for the wave function values. Whenever possible, wave function manipulations are built as methods on `Wavefunction`, but some manipulations on the data – in particular pertaining to the time evolution – has to be executed from `molecule`. For that reason `Wavefunction` allows for manipulation of the wave function data directly, going against a general idea of encapsulation. However manipulations that are possible to encapsulate – for instance the Fourier transform which has to be executed whenever time evolution is carried out, in either momentum or position space – are of course properly encapsulated. To gain the ability to do a Fourier transform, `psi1` and `psi2` both acquire a pointer to the singleton object `fourierT`, an object that at its core employs the *fast fourier transform* method that is native to MatLab, to transform wave functions between the position representation and the momentum representation.

The main object `molecule` also includes an object `p`, that is an instance of `Potential`. This object contains the matrix of arrays to store - and if necessary manipulate - the potentials introduced in equation (3) on page 5.

4.4 Optimization – Creating a custom algorithm

To find the desired meta-stable behaviour, a numerical optimization over several parameters will be conducted (further details in section 5.1 and 5.2.1). There are a couple of different optimization tools built into MatLab, and the following have been investigated to find a good candidate for this particular optimisation task: *patternsearch*, *genetic algorithms*, *particle swarm*, *multistart* using `fmincon()` and *simulated annealing* (all descried on-line, in the MatLab documentation).

The best algorithm turned out to be simulated annealing. However, none of the investigated algorithms were very well suited for the task. All of them seemed to operate on a principle of quickly finding one local minima without really *exploring the space*[11] of parameters. Simulated annealing did some exploration, however it was often focused in areas of the space that clearly were not going to give any interesting result – like calculating a lot of points in some corner of the space where the value of the function clearly would not assume any extremum – and sometimes the algorithm could ignore investigating areas where promising function values had previously been found.

It is worth noting, even though the best local extremum (that could be found) is very important, it might not be the most interesting point, since there are other considerations for this particular optimization task. For instance, the best extremum might correspond to a system that is not very satisfactory as a real physical system. If the space contains multiple local extrema it would be useful to evaluate them manually, after the optimization has finished, and thus the algorithm should preferably produce several local extremum points instead of just one.

The conclusion of these considerations was that it would be beneficial to create a custom optimization algorithm suited to the premises of the problem. This was done, and the result was an algorithm built around an iterative process and a set of heuristical scoring principles.

Iterative process in custom algorithm

1. Begin by randomly select a large number of potential points in a constrained space of parameters.
2. Evaluate each point from a set of heuristical rules that assigns a numerical score to each point.
3. Select a few of the highest scoring points and discard the rest.
4. Calculate the function value at the few selected points.
5. Based on points calculated so far, evaluate small subspaces of the entire space to see if any region qualifies as a good place to search for a minima.
6. If any region qualifies a potential local minima run `fmincon()` in this small subspace to find and store a single point as a local minimum.
7. Iterate back to 1.

---

[11] *Exploring the space* refers to a behaviour of avoiding to leave large areas of the space empty of function evaluations.

One challenge worth discussing is the rules for assigning a score to each potential point. This is where the heuristical evaluations enter. In general, the algorithm rewards any potential point that is either far from previously calculated points, or close to any previous point that has some extreme value. This prevents clusters of points where no extreme function value has been found, and encourages both exploration of the space and clustering where extreme values previously have been found.

Is is worth noting that this algorithm became significantly slower than the inherent algorithms of MatLab. However, this is not a problem for this particular optimization task. Since calculating the value of a single point, in general, takes about a second (the algorithm required some fraction of a second), the speed of the algorithm was less important than having an algorithm that selects points with due care. Avoiding to calculate any redundant or poorly selected points is the main concern for this task.

Figure 12 on page 26 illustrates an optimisation in a 2-dimensional space of parameters, with the third dimension as the function value. Note that points cluster where the value of the function assumes an extremum (the bright blue dots) and otherwise they are rather evenly spread out over the space.

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"If you know an answer to something – as a scientist – it's a really nice thing to find it, particularly when you're starting something new."

– Joy Hirsch

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5 Results and discussions

5.1 Replicating results from earlier paper

An important goal of this thesis was to reproduce an earlier result from the paper *Molecular quantum wavepacket revivals in coupled electronic states* by D. Wang, Å. Larson, H. O. Karlsson and T. Hansson [2].

In this paper investigations are carried out in two different kinds of coupled systems. The first is a system with two attractive potentials (corresponding to a stable system), and the second is a system where one potential is repulsive (corresponding to an unstable system). It is the latter – illustrated in figure 11 – that has been replicated here. Particular parameters are presented as associated with a metastable state. The goal of the replication is to run the same optimization and find this state.

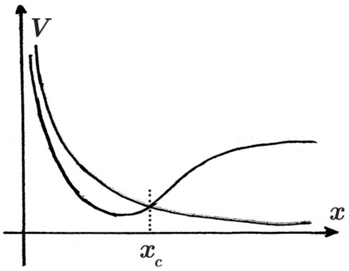


Figure 11: Illustration of the potentials V_{11} (attractive Morse potential) and V_{22} (repulsive potential) used in the original paper.

The system is described by the Schrödinger equation for a two state system, discussed in section 2 (specifically section 2.3).

$$i\hbar\frac{\partial}{\partial t}\begin{bmatrix}\psi_1\\ \psi_2\end{bmatrix}=\begin{bmatrix}\hat{p}^2/2m+V_{11}(\hat{x}) & V_c(\hat{x})\\ V_c(\hat{x}) & \hat{p}^2/2m+V_{22}(\hat{x})\end{bmatrix}\begin{bmatrix}\psi_1\\ \psi_2\end{bmatrix}\tag{75}$$

A number of parameters are used to specify the system properties, potentials and initial condition. Note that they are all expressed in *atomic units* [10].

Potentials are specified by the following equations and parameters:

$$V_{11}=D_{11}\left(1-e^{-\beta_{11}(x-x_{11})}\right)^2+E_{11}\tag{76}$$

$$V_{22}=D_{22}\,e^{-\frac{x-x_{22}}{\beta_{22}}}+E_{22}\tag{77}$$

$$V_{21}=V_{12}=D_{21}\,e^{-\beta_{21}(x-x_{21})^2}\tag{78}$$

Table 1: Values used in potentials (atomic units)

n	E_n	D_n	β_n	x_n
11	0	0.03185	0.63235	4.07549
22	*(optimized)*	8.07567	0.060226	-0.18568
21		*(optimized)*	0.484000	*(calculated)*

The mass used in the replication is identical to that in the paper, i.e the reduced molecular mass of the Rb_2 (expressed in atomic units).

$$m = \mu = 42.7339 \cdot 1822.88842 \tag{79}$$

A relatively narrow Gaussian wave packet is placed in the stable potential to the right of the coupling area – i.e. to the right of x_c in figure 11. The initial wave function is specified by the following functions and parameters.

$$\begin{bmatrix} \psi_1 \\ \psi_2 \end{bmatrix} = \begin{bmatrix} (2\pi\sigma^2)^{\frac{1}{4}} e^{-\frac{(x-x_0)^2}{4\sigma^2}} \\ 0 \end{bmatrix} \tag{80}$$

Table 2: Values used in initial wave function (atomic units)

σ	x_0
0.0772	6.000

The spatial grid uses 4096 points, as does the momentum grid. The time step (discussed in section 3.3) used for time evolution of the wave function is not explicitly defined in the paper [2], but investigating a piece of code underlying the results in the paper, a value could be recovered: $\Delta t \simeq 41$. To be on the safe side a smaller time step (a fifth of the time step in the paper) $\Delta t \simeq 8.2$ was used. (Times are expressed in atomic units.)

To optimize the system for meta-stable behaviour a *function for optimization* is created. It takes any desired system parameters as inputs, and outputs a value that is close to 0 if the system is close to having the desired properties, and increases to 2 if the system is far from desired properties.

$$f_{op}(\{\text{system parameters}\}) = [0, 2] \tag{81}$$

Calculating the value of this function incorporates two system properties that each has a desired value. The first part is to optimize for a *wave function splitting ratio*: $\eta \simeq 0.5$ – meaning that during the first *classical period*[12], as the wave function has gone through the region of the coupling, the stable and the dissociative state will be about equally populated. Figure 8 on page 6 illustrates this situation. To evaluate this behaviour, under the appropriate time interval the maximum value of the norm of ψ_2 (the second electronic state, see equation (1) on page 3) is calculated. However, it is not a requirement that η is exactly 0.5. We want to allow for some deviations that should only effect f_{op} to a small degree. Using the following formula for calculating the first part – f_{op1} – will insure a slow increase of f_{op1} as η deviates from 0.5.

$$f_{op1} = |2\,(\eta - 0.5)\,|^4 \tag{82}$$

The second part f_{op2} is the most central feature – the meta-stable behaviour. After one classical period T_1, as the bulk of the wave function returns to the initial position, and the autocorrelation $R(T_1)$ should then be as close to 1 as

---

[12] A classical period is defined as the time it takes from $t = 0$ to the time when the autocorrelation function reaches its first maximum.

possible. This is because when the autocorrelation is close to 1, most of the wave function is populating the *stable* Morse potential, so the process is simultaneously optimising for autocorrelation and meta-stable behaviour. Figure 7 on page 6 illustrates the initial condition that we want to get as close to as possible after one classical period T_1. Since f_{op} is required (by MatLab) to approach its minimum value for the desired behaviour, the following function for f_{op2} will suit our purposes.

$$f_{op2} = 1 - R(T_1) = 1 - \left| \int \psi_1^*(x, T_1)\psi_1^*(x, 0)dx \right| \tag{83}$$

The total function for optimization is formed by taking the sum of the parts.

$$f_{op} = f_{op1} + f_{op2} \tag{84}$$

Running the custom optimization algorithm (section 4.4) on f_{op}, varying the two parameters E_n and D_n, and plotting the points in a 3D space, gave the plot in figure 12.

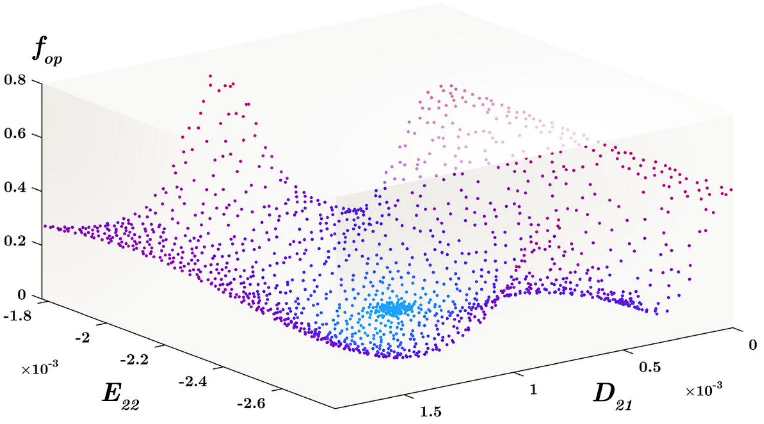


Figure 12: Optimization around the point where an extremum is declared to be. Bright blue points have a lower (more desired) value and purple and red have higher (less desired) value.

In the paper the position of the minima is found at:

$$E'_{22} = -0.00228 \tag{85}$$

$$D'_{21} = 0.000907 \tag{86}$$

This investigation has found the minimizing parameters to be:

$$E_{22} = -0.002279 \tag{87}$$

$$D_{21} = 0.0008812 \tag{88}$$

On the scale of the plot in figure 12 the two points are possible to separate, but they both clearly lie within the area of the local minimum – where the derivative is very small – and thus the auto correlation $R(T_1)$ does not vary much between the points. When comparing the autocorrelation of the two points using this model the result is:

$$R'(T_1) = 0.966 \tag{89}$$

$$R(T_1) = 0.976 \tag{90}$$

Note that though the values E'_{22} and D'_{21} were stated in the paper, there was no explicit reference to the value of the auto correlation, thus both R and R' are calculated using the same model.

5.1.1 Discussion about the replication results

Comparing the values in equations (85) – (88), there is a small but noticeable discrepancy. However, there are several reasons that enables this discrepancy without interpreting it as an indication of problems with the model. On the contrary, when optimizing over various spaces it is evident that extremum points are not very abundant in the space of parameters, thus finding a local extremum on top of where it should be is a strong indication that the numerical model is accurate.

Possible reasons for the small discrepancy include:

1. The most obvious problem is that it is not clear how the optimization for the wave function splitting ratio $\eta \simeq 0.5$ is carried out in the original paper. There might have been a smaller or bigger tolerance for deviations around 0.5 that moves the position of the extremum for f_{op}.
2. The number of significant figures that are presented in the paper is limited. It is possible that the sum of rounding errors of the parameters in table 1 and 2 create a slightly different model than was originally used.
3. The method used to calculate the position of the coupling – x_{21} in equation (78) – are slightly different in the two models, and other investigations have indicated a small numerical discrepancy in x_{21}.

In general though, the results are very promising and a clear indication that the model works the way it should.

5.2 Interaction-free measurement with electromagnetic field

The central purpose of the work in this thesis is to investigate the effects of attempting an interaction-free measurement on the vibrational state of a metastable diatomic molecule. In practical terms this means trying to measure where the particle is after the wave function has split up in a superposition of following two different paths in the potentials. This situation is illustrated in figure 8 on page 6, and discussed in detail in that section.

The means by which we wish to measure the path is to gently entangle the state of the molecule with the state of an electromagnetic field, in order to make the measurement on the field, instead of the molecule.

The claim is that there is no such thing as a free lunch. If we try to entangle the state of the molecule with the field, the latter will contain some information about the state of the molecule, but this will also disrupt the meta-stable state, and the molecule will break apart. The more entanglement (i.e. information) we wish to have the more we will disturb the molecule, and it will dissociate quicker.

The model for the dispersive interaction with the electromagnetic field is described and derived in section 2.5.

$$i\hbar\frac{\partial}{\partial t}\begin{bmatrix}\psi_1\\\psi_2\end{bmatrix}=\begin{bmatrix}\hat{p}^2/2m+V_{11}(\hat{x}) & V_c(\hat{x})\\ V_c(\hat{x}) & \hat{p}^2/2m+V_{22}(\hat{x})-\hbar\frac{g^2n}{\delta}\end{bmatrix}\begin{bmatrix}\psi_1\\\psi_2\end{bmatrix}\qquad(91)$$

The unique part is the term added to the second potential, $\hbar g^2n/\delta$. This is the disturbance that the electromagnetic field is creating in the system. (Throughout this thesis atomic units are used, which means $\hbar=1$.) The factor g^2/δ is the strength of the interaction between the field and the atom, and the factor n is the number of photons in the field. Note that n will have some distribution around $\langle n\rangle$, and not a single value (discussed in section 2.5). In separate calculations, both g^2/δ and $\langle n\rangle$ have been varied while keeping the other constant to observe the relationship between entanglement and dissociation. The two cases are discussed in detail below.

The method for measuring the entanglement between the molecule and the field – using density operators and the von Neuman entropy – is described in section 2.6.

5.2.1 Investigation I – Finding parameters for a meta-stable state

The meta-stable state described in previous paper, and replicated in section 5.1, is not very useful for this entanglement investigation. Those parameters describe a coupling V_c between the electronic states that is too wide, which means the wave packet will never really travel outside of the region of the coupling. Having a superposition of states and the wave packets outside the region (illustrated in figure 8 on page 6) was crucial, and thus a new set of parameters – describing a meta-stable molecule with more desirable features – had to be found.

Using the custom optimization algorithm, described in section 4.4, and the same optimization function f_{op} as described in section 5.1, to optimize over four parameters – E_{22}, D_{21}, β_{21} and x_0 – revealed a suitable local extremum for the parameters in table 3, and the initial system that is described by these parameters is visualized in figure 13.

Table 3: Parameters specifying potentials and initial wave function (atomic units)

n	E_n	D_n	β_n	x_n	σ	x_0
11	0	0.03185	0.63235	4.07549	0.0772	5.529
22	0.004641	8.07567	0.060226	-0.18568		
21		0.0006837	8.613	*(calculated)*		

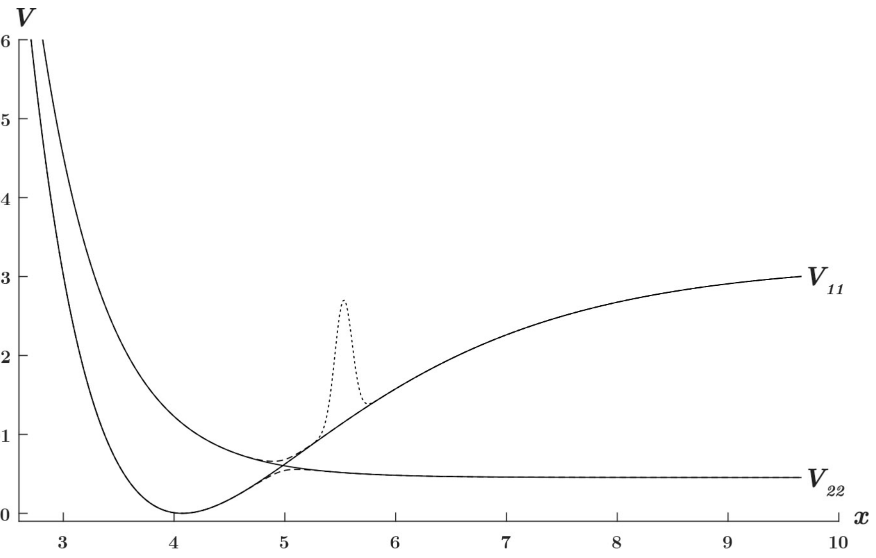


Figure 13: Plot of the potentials used to model the meta-stable behaviour. Solid curves are diabatic potentials. Dashed curves are adiabatic potentials signifying the region of the coupling. The dotted curve is an illustration of the initial wave function as a probability density.

5.2.2 Investigation II – Large scale behaviour of energy corrections

The objective of this first investigation is to get a broad sense of the behaviour as the term g^2n/δ varies. A wide range of systems are modelled with different values for the energy corrections, and the autocorrelation after one classical period ($t = T_1$) is recorded. A high autocorrelation after one classical period means better molecular stability.

The result of this investigation is shown in figure 14, and from this it is obvious that the maxima in autocorrelation that was optimized for is not the only maxima we are dealing with.

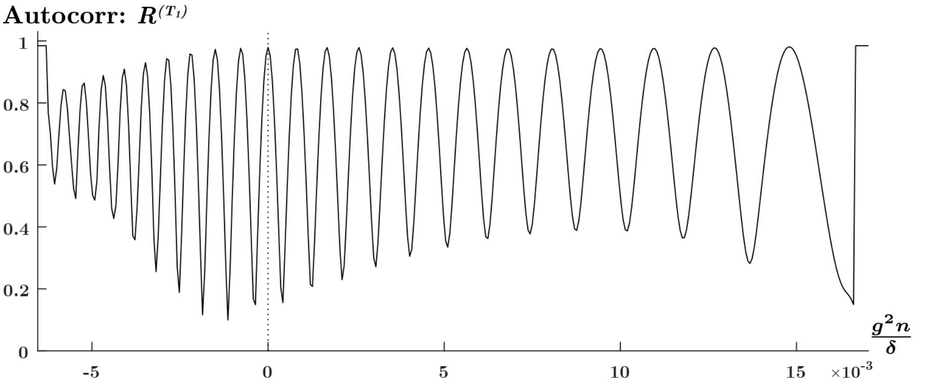


Figure 14: Autocorrelation of $|\Psi\rangle$ after one classical period (i.e. $t = T_1$) as the strength of the energy correction varies.

These restorations of stability as the influence of the electromagnetic field changes can – with some hand-waving – be explained in terms of the phase of the wave function (though only the component travelling in the state with the energy correction) turning a multiple of 2π, ending up where it began, and recreating the original interference.

At the ends of the spectrum the autocorrelation goes sharply to a value close to 1, a behaviour that has a simple explanation: The electromagnetic field is shifting the energy of the second electronic state (illustrated by V_{22} in figure 13), and at some point we have shifted the potential so much that there is no longer an intersection between the curves, and the coupling between the electronic states vanishes. The wave packet is then suddenly travelling in a single potential and the autocorrelation increases sharply.

5.2.3 Investigation III – Varying $\langle n \rangle$

As discussed at the end of section 2.5, the model will not use an electromagnetic field with a specific number of photons. Instead, we have a probability density that follows a Poisson distribution around some $\langle n \rangle$.

The purpose of this investigation is to show that increased entanglement causes the autocorrelation to decline, and the molecule to dissociate quicker. We can imagine that in the neighbourhood of any of the peaks in figure 14, the behaviour of the system will resemble the behaviour without disturbance. Thus to efficiently find a behaviour where we can expect entanglement will increase over time, the value of g^2/δ is chosen to be low enough that when varying the values of $\langle n \rangle$ (within a reasonable range), we will only operate in an interval over the slope next to the peak corresponding to zero correction. Choosing g^2/δ quite small is also a physically reasonable choice, since it is not likely that an electromagnetic field with a large detuning would have a great impact on the dynamics of the molecule, and in an experimental situation, we can also imagine that, there will be some degree of control over the magnitude of g^2/δ by varying the detuning δ to either positive or negative values. So a suitable value is chosen.

$$g^2/\delta = -5.000 \cdot 10^{-06} \tag{92}$$

Separate calculations are made for 7 different distributions around mean values $\langle n \rangle_k$. These distributions over $|n\rangle$ are plotted in figure 15 together with the autocorrelation of $|\Psi\rangle$ after the time of one classical period.

$$\langle n \rangle = \{5, 10, 15, 20, 25, 30, 35\} \tag{93}$$

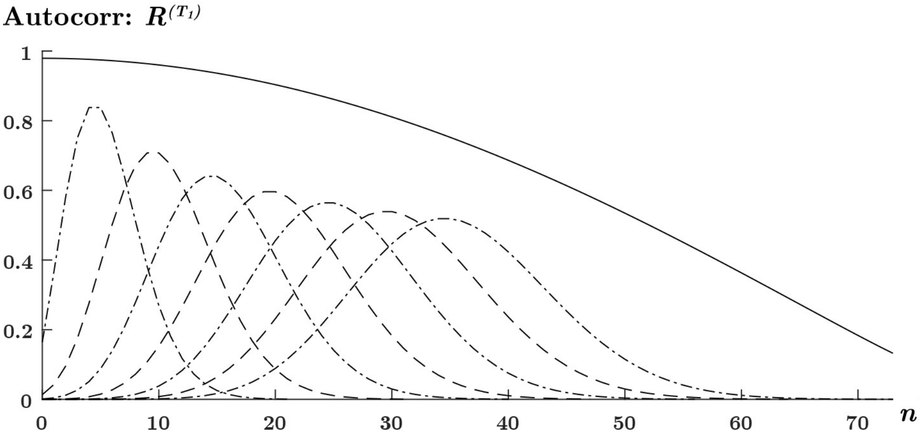


Figure 15: The solid line shows the autocorrelation of $|\Psi\rangle$ after one classical period (i.e. $t = T_1$). Dashed curves illustrates the seven distributions over n for which entanglement and autocorrelation later are calculated.

For each distribution of the field over n, entanglement S_{vN}, and the autocorrelation R, are both calculated as a function of time. Thus, for every distribution displayed in figure 15 we get two curves. What we expect to see is that the sharper the entanglement increases the quicker the autocorrelation decreases. And that is indeed the observed result, shown in figure 16.

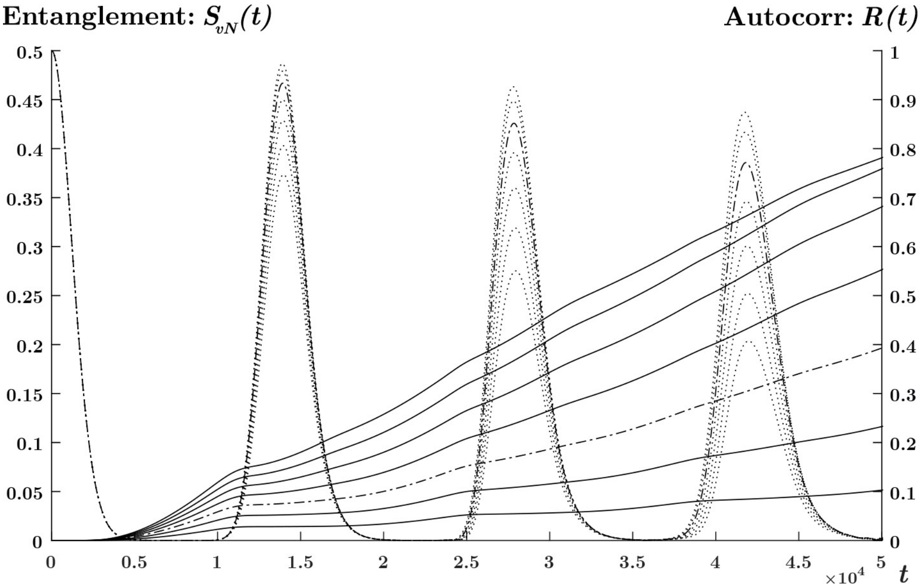


Figure 16: The solid lines are the von Neumann entropies (i.e. entanglement) as functions of time, with their scale to the left. The dotted peaks are the autocorrelations as functions of time, and their scale is to the right. Each dotted line has a corresponding solid line. This correspondence is illustrated with the two dashed curves.

Each solid curve (entanglement) corresponds to a dotted curve (autocorrelation), and the solid curve that has the smallest slope corresponds to the highest autocorrelation (both are from the calculation where $\langle n \rangle = 5$) and so on all the way up to the steepest entanglement slope (the calculation where $\langle n \rangle = 35$) that corresponds to the lowest curve for autocorrelation. The third line (for $\langle n \rangle = 15$) is printed dashed for both entanglement and autocorrelation to emphasize the correspondence between the curves.

Note however, something is starting to happen with the sharpest rising entanglement curve after the third classical period. Its slope declines a bit and it is approaching the curve below it. Plotting the entanglement curves over a larger time interval – about 15 classical periods – reveals a secondary pattern, as seen in figure 17.

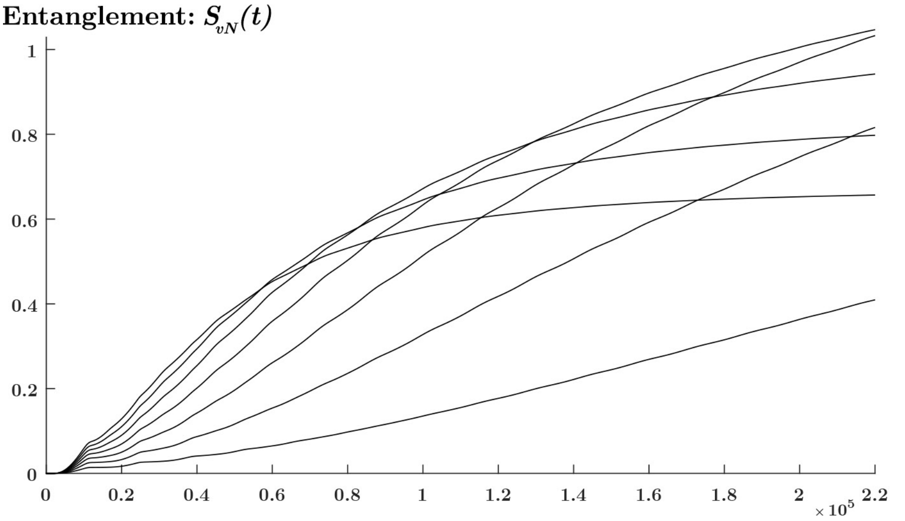


Figure 17: Von Neumann entropies (i.e. entanglement) as a function of time, spanning about 15 classical periods.

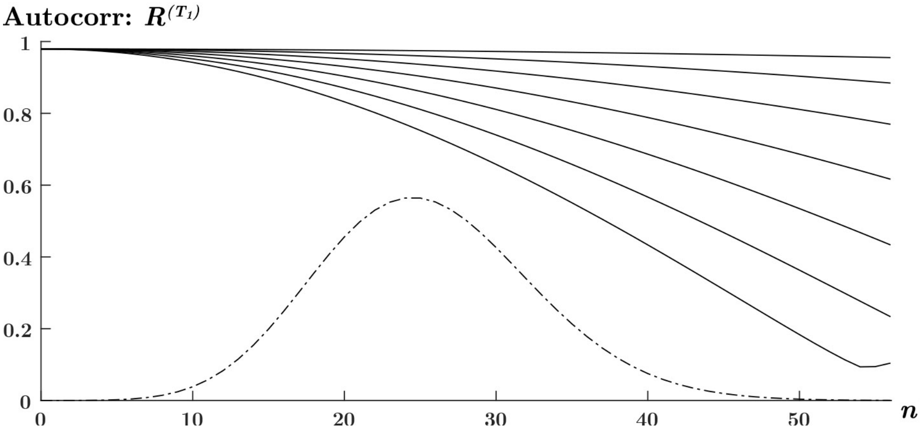
5.2.4 Discussion about the halting increase of entanglement

The declining of the steepest curves in figure 17 can be understood when you consider the properties of the system, at least if we accept a few waving hands in our arguments. A sharper increase in entanglement is connected to a larger portion of the wave function ”leaking out” to the right of the curve crossing of the second electronic state (illustrated by V_{22} in figure 13 on page 29), and in this region the wave function will behave much like a freely moving particle (the molecule has dissociated). The fact that this state has small corrections for different values of n will not differentiate the overall behaviour very much. Thus, as the wave function starts travelling more like a free particle, there is no process by which it is possible to keep increasing entanglement, and the amount of entanglement stays almost constant. Or in other words, as soon as probability leaves the region for the coupling, the field can no longer measure ”which path” the molecule is traversing (V_{11} or V_{22}), and thereby not attain the information that causes the increase in entanglement.

5.2.5 Investigation IV – Varying g^2/δ

In the previous investigation $\langle n\rangle$ was varied, which corresponds to a system that is a good model for a real physical system – changing $\langle n\rangle$ is just analogous to changing the intensity of the electromagnetic field. However as $\langle n\rangle$ increases, so does the size of the truncated density matrix that have been used to calculate the amount of entanglement, and we get a greater number of eigenvalues to add up for the von Neumann entropy. In order to confirm that this difference would not play any role, we compare the result in section 5.2.3 with a calculation that instead vary the strength of the coupling between the electromagnetic field and the atom, i.e. g^2/δ, while keeping the intensity of the field constant. In other words we use the same number for $\langle n\rangle$ – in this case $\langle n\rangle = 25$ – and we vary g^2/δ instead. Compare this method illustrated in figure 18 with the previous method illustrated in figure 15.

$$\frac{g^2}{\delta} = -\{1.000,\ 2.000,\ 3.000,\ 4.000,\ 5.000,\ 6.000,\ 7.000\}\cdot 10^{-6} \tag{94}$$



Autocorr: $R^{(T_1)}$

Figure 18: The solid lines shows the different autocorrelation after one classical period as functions of n. Each line has a different value of g^2/δ. The dashed curve illustrates the constant photon distribution that is used in all seven calculations.

Similar to investigation III – for each value of g^2/δ, entanglement S_{vN} and the autocorrelation R, are calculated as a function of time. Thus in this investigation, for every solid curve displayed in figure 18, we will get two corresponding curves for entanglement and autocorrelation. We still expect to see that the sharper the entanglement increases the quicker the autocorrelation decreases. And the observed result is indeed consistent with expectations!

In figure 19, each solid curve (entanglement) corresponds to a dotted curve (autocorrelation), and the solid curve that has the smallest slope corresponds to the highest autocorrelation, and so on to the steepest entanglement slope that corresponds to the lowest curve for autocorrelation (just like in investigation III). The third curve is again printed dashed for both entanglement and autocorrelation to emphasize the correspondence between the curves.

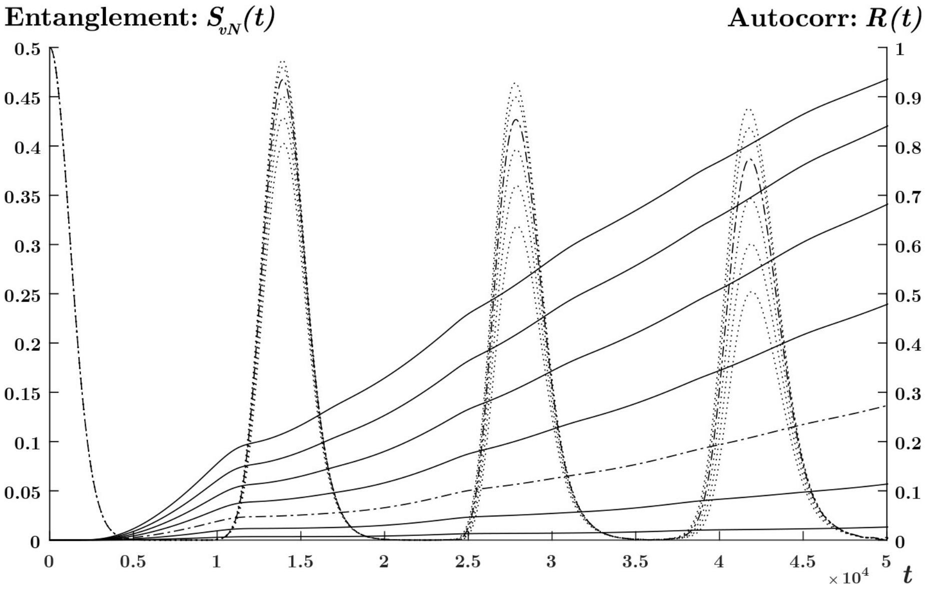


Figure 19: The solid lines are the von Neumann entropies (i.e. entanglement) as a function of time, with its scale to the left. The dotted peaks are the autocorrelation calculated as function of time, its scale is to the right. Each dotted line has a corresponding solid line. This correspondence is illustrated with the dashed line.

Again, plotting the entanglement curves over a larger time interval – also about 15 classical periods – in figure 20, reveals a very similar pattern as the previous investigation.

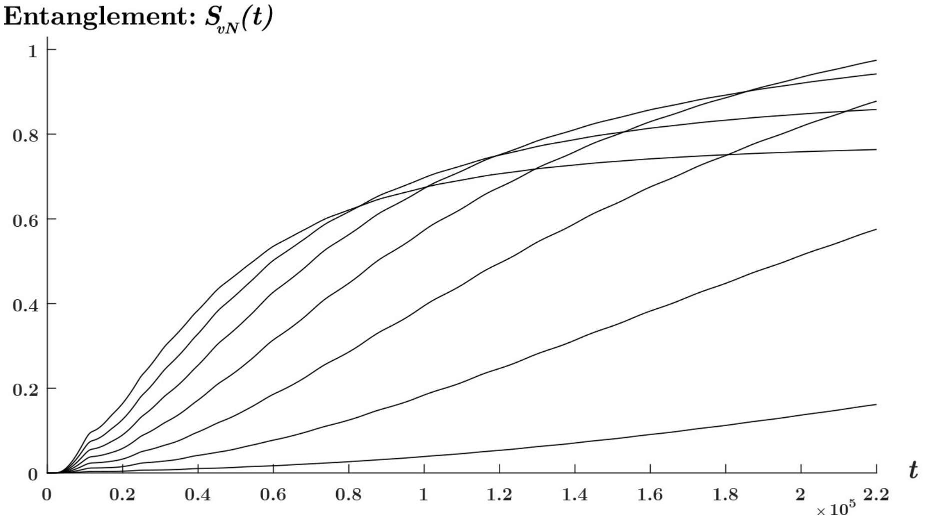


Figure 20: Von Neumann entropies (i.e. entanglement) as a function of time, spanning about 15 classical periods.

There are small differences in the shape of the curves (on larger time scales), comparing figure 17 to figure 20. For instance, the sharpest rising entanglement in this investigation reaches a higher plateau than the one from the previous investigation. However such deviations are not surprising since the two cases are in fact calculated by different procedures.

5.2.6 Discussion about the results

This numerical model indeed supports that increasing entanglement correlates with increasing risk for dissociating the meta-stable molecule. However, in these calculations we observe one behaviour that is more unexpected. The entanglement stopped growing after a few periods (shown in figure 17 and 20), and this phenomenon happens sooner for a more rapidly dissociating molecule. However, the behaviour can be understood as a effect of the system, and is discussed in section 5.2.4.

6 Conclusions

This thesis set out to study the particular phenomenon of meta-stability that can occur in diatomic molecules. In order to fulfil this objective, various subject matters have been studied and utilized. Quantum mechanics theory and modelling (section 2), a few quantum field theory concepts (section 2.5 and appendix A.4), numerical methods applied to the time evolution operator (section 3), general programming principles as well as specific MatLab characteristics and some heuristical problem solving (section 4), and last some foundational mathematical concepts (appendix A.1, A.2 and A.3).

As a first test for the program, that was built on these principles, the results from an earlier paper were successfully replicated (section 5.1). There was a small discrepancy between the paper and the results, but this discrepancy is not surprising considering the level of detail the original paper provided. A discussion of this discrepancy, and a bullet list of reasons, can be found in section 5.1.1.

When the first test proved successful, the work steered towards investigating a hypothesis about using interaction-free measurement on the meta-stable molecule (described in section 2.5 and 2.6, and results presented in section 5.2). The goal was to show that while interaction-free measurement can obtain some information about the electronic state of the molecule, the more information we want, the more we will disturb the molecule and destroy the meta-stable characteristic. The conclusion is that the results from the numerical model indeed supports the hypothesis. Though it is worth noting that in the process we encountered a somewhat unexpected phenomena where the entanglement stops increasing, and levels off, after a certain time (shown in figure 17 and 20). However, this effect can be understood as a consequence of the system, and it is discussed in section 5.2.4.

Future prospects, for the line of work in this thesis, would be to evaluate how realistic the various choices of parameters are for any real physical system in an experimental situation that is feasible to recreate. The interesting question would be, how frequently can the processes described in this thesis be expected to occur in nature?

7 References

For some sections in the thesis report no reference to source material is provided. In those cases the theory has been laid out in lectures by Jonas Larson and Åsa Larson, and the details have been expanded on by the thesis author.

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A Appendix

A.1 Rewriting the exponential of a diagonal matrix

Using the series definition of the exponential function, we can find a suitable definition to what the exponential of a matrix should look like, and derive a useful relation if the matrix is diagonal. If x is a number, the exponential function has the following definition:

$$e^x := 1 + x + \frac{x^2}{2!} + \frac{x^3}{3!} + \frac{x^4}{4!} + \ldots = \sum_{k=0}^{\infty} \frac{x^k}{k!} \tag{95}$$

Thus we use the same pattern to define the exponential of a matrix A.

$$e^A := \mathbb{1} + A + \frac{A^2}{2!} + \frac{A^3}{3!} + \frac{A^4}{4!} + \ldots = \sum_{k=0}^{\infty} \frac{A^k}{k!} \tag{96}$$

From this we can see that e^A is itself a matrix. Further, in order for this definition to make sense A is required to be a square matrix (let it be $n \times n$), and e^A is then of the same dimensions as A. However, we have to sort out if we have convergence for each element in the matrix e^A. That discussion is here left to the curious reader to continue, but it is indeed possible to show that we have convergence.

So, what about when A is diagonal?

$$A := \begin{bmatrix} a_1 & & & \\ & a_2 & & \\ & & \ddots & \\ & & & a_n \end{bmatrix} \tag{97}$$

Following the ordinary rules for matrix multiplication we can clearly see that a product between to diagonal matrices is just taking the product of each element on the diagonal.

$$AA = \begin{bmatrix} a_1 & & & \\ & a_2 & & \\ & & \ddots & \\ & & & a_n \end{bmatrix} \begin{bmatrix} a_1 & & & \\ & a_2 & & \\ & & \ddots & \\ & & & a_n \end{bmatrix} = \begin{bmatrix} a_1^2 & & & \\ & a_2^2 & & \\ & & \ddots & \\ & & & a_n^2 \end{bmatrix} \tag{98}$$

And from this it is clear how the pattern continues.

$$A^k = \begin{bmatrix} a_1^k & & & \\ & a_2^k & & \\ & & \ddots & \\ & & & a_n^k \end{bmatrix} \tag{99}$$

We are now ready to finish this line of reasoning. Taking the definition in (96) and using the results from (99), we see that the infinite series of matrix multiplications becomes infinite series of ordinary number multiplication on the diagonal.

$$e^A := \sum_{k=0}^{\infty} \frac{A^k}{k!} = \begin{bmatrix} \sum \frac{a_1^k}{k!} & & & \\ & \sum \frac{a_2^k}{k!} & & \\ & & \ddots & \\ & & & \sum \frac{a_n^k}{k!} \end{bmatrix} \tag{100}$$

And by the definition of the exponential function of an ordinary number in (95), we can replace the series in the matrix and conclude.

$$e^A = \begin{bmatrix} e^{a_1} & & & \\ & e^{a_2} & & \\ & & \ddots & \\ & & & e^{a_n} \end{bmatrix} \tag{101}$$

Q.E.D.

A.2 Simplify expression with repeated Pauli matrices

We want to show that the relation used in section 3.4.2 holds.

$$(\vec{\boldsymbol{\alpha}}\vec{\boldsymbol{\sigma}})^2 = |\alpha|^2 \mathbb{1} \tag{102}$$

We begin by expressing every vector in terms of its components.

$$(\vec{\boldsymbol{\alpha}}\vec{\boldsymbol{\sigma}})^2 = (\alpha_1\sigma_1 + \alpha_2\sigma_2 + \alpha_3\sigma_3)(\alpha_1\sigma_1 + \alpha_2\sigma_2 + \alpha_3\sigma_3) = \tag{103}$$

$$\begin{gathered} \alpha_1^2\sigma_1^2 + \alpha_2^2\sigma_2^2 + \alpha_3^2\sigma_3^2 + \\ \alpha_1\alpha_2(\sigma_1\sigma_2 + \sigma_2\sigma_1) + \alpha_1\alpha_3(\sigma_1\sigma_3 + \sigma_3\sigma_1) + \alpha_2\alpha_3(\sigma_2\sigma_3 + \sigma_3\sigma_2) \end{gathered} \tag{104}$$

It is here left to the curious reader to show that the parenthesis with sigmas are all equal to 0, i.e. the Pauli matrices *anti-commute*.

$$\sigma_m\sigma_n + \sigma_n\sigma_m = 0 \quad , \quad \forall\, m \neq n \tag{105}$$

With simple exhaustion of all cases it is also straight forward to show that the squares of the Pauli matrices, in equation (104), simplifies to the unity operator.

$$\sigma_n^2 = \mathbb{1} \quad ; \quad n = \{1, 2, 3\} \tag{106}$$

Inserting the results from (105) and (106) in equation (104), we are able to conclude.

$$(\vec{\boldsymbol{\alpha}}\vec{\boldsymbol{\sigma}})^2 = \alpha_1^2\mathbb{1} + \alpha_2^2\mathbb{1} + \alpha_3^2\mathbb{1} = |\alpha|^2\mathbb{1} \tag{107}$$

Q.E.D.

A.3 Partial Trace

Reference for the section: Jens Eisert [7].

Consider a composite system made from two subsystems with corresponding Hilbert spaces $\mathcal{H}_1$ and $\mathcal{H}_2$. Then the space of the complete composite system is the tensor product.

$$\mathcal{H} = \mathcal{H}_1 \otimes \mathcal{H}_2 \tag{108}$$

Let a basis for the fist subsystem in $\mathcal{H}_1$ be $|\psi_i\rangle$, and for the second space in $\mathcal{H}_2$ we take the basis $|\phi_i\rangle$.

Taking a sum over all combinations of states in both spaces, with corresponding probability coefficients, we can create a general state of the system and form our density operator.

$$|\psi\rangle = \sum_{m,n} c_{mn} |\psi_m\rangle |\phi_n\rangle \tag{109}$$

$$\rho = |\psi\rangle \langle\psi| \tag{110}$$

Taking the partial trace over the first system then has the following definition.

$$\rho_2 = \mathrm{Tr}_1[\rho] = \sum_i \langle\psi_i| \rho |\psi_i\rangle \tag{111}$$

The resulting ρ_2 is a *reduced density operator* that has the same dimensionality as $\mathcal{H}_2$.

A.4 The Jaynes-Cummings model

Reference for the section: Göran Johansson and Thilo Bauch [5], and Marlan O. Scully and M. Suhail Zubairy [11].

The goal here is to provide a brief derivation of the so called *Jaynes-Cummings Hamiltionian* for the interaction between a two state atom and a quantized electromagnetic field. The system – a two level atom in an optical cavity with a single mode of electromagnetic radiation – is illustrated in figure 21. The angular frequency of the mode is denoted ω_c, and the frequency corresponding to the energy required to excite the atom is ω_a.

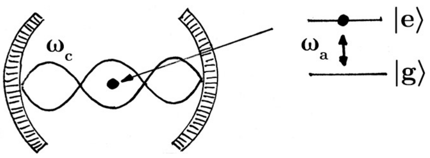

Figure 21: To the left, an illustration of a two level atom (the dot) in an optical cavity (the circular walls) with one mode of electromagnetic radiation (the waves). To the right, an illustration of the two energy levels of the atom.

The Hamiltonian is composed of three parts, the energy of the field, the internal electronic energy of the atom, and the interaction between the field and the atom.

$$\hat{H}_{jc} = \hat{H}_{field} + \hat{H}_{atom} + \hat{H}_{int} \tag{112}$$

The field Hamiltonian is expressed in ladder operators ($\hat{a}^\dagger$ is the creation operator and $\hat{a}$ is the annihilation operator), that together count the number of excitations (i.e the number of photons) in the field.

$$\hat{H}_{field} = \hbar\omega_c \hat{a}^\dagger \hat{a} \tag{113}$$

Next, putting the energy of the atom to 0 in the centre between the electronic ground state $|g\rangle$, and the excited state $|e\rangle$, makes the atomic Hamiltonian particularly simple to express in terms of the Pauli matrix $\sigma_z = |e\rangle\langle e| - |g\rangle\langle g|$ and the atomic transition frequency ω_a.

$$\hat{H}_{atom} = \hbar\frac{\omega_a}{2}\hat{\sigma}_z \tag{114}$$

The interaction Hamiltonian is described in terms of the electric field operator $\hat{E}$, the polarisation operator $\hat{\sigma}_x$ (assuming the field is polarized in the x direction), and a coupling strength parameter g.

$$\hat{H}_{int} = \hbar g \hat{E}\hat{\sigma}_x \tag{115}$$

Under the dipole approximation – i.e. the wavelength of the electromagnetic wave is much larger than the size of the atom – the electric field operator is proportional to $\hat{a}^\dagger + \hat{a}$ (further details at page 194 in [11]) and the proportionality constant is absorbed into the coupling strength g. The polarization operator $\hat{\sigma}_x$ can be rewritten in terms of the ladder operators for the atomic system, $\hat{\sigma}_x = \hat{\sigma}_+ + \hat{\sigma}_-$. Inserting the expressions for $\hat{E}$ and $\hat{\sigma}_x$ gives us

$$\hat{H}_{int} = \hbar g \left(\hat{a}^\dagger\hat{\sigma}_+ + \hat{a}^\dagger\hat{\sigma}_- + \hat{a}\hat{\sigma}_+ + \hat{a}\hat{\sigma}_-\right) \tag{116}$$

Two of these terms ($\hat{a}^\dagger\hat{\sigma}_-$ and $\hat{a}\hat{\sigma}_+$) conserve the total number of excitations in the system. It is then possible to show that the other terms, that do not conserve the number of excitations, rotate on much shorter time scales and can thus be ignored. This is the so called *rotating wave approximation* and it will not be discussed in detail here. Using this, we can simplify the interaction part.

$$\hat{H}_{int} = \hbar g \left(\hat{a}^\dagger\hat{\sigma}_- + \hat{a}\hat{\sigma}_+\right) \tag{117}$$

Putting together the three terms from equations (113), (114), and (117), we can form the total Hamiltonian.

$$\hat{H}_{jc} = \hbar\omega_c \hat{a}^\dagger \hat{a} + \hbar\frac{\omega_a}{2}\hat{\sigma}_z + \hbar g \left(\hat{a}^\dagger\hat{\sigma}_- + \hat{a}\hat{\sigma}_+\right) \tag{118}$$

Here, the Hamiltonian depends on the frequency for the field ω_c and the atomic transition frequency ω_a. However, the behaviour of the system is in practice only dependent on the differences between these two frequencies. If they start to approach the same value, the electric field would start causing excitations in the atomic state. Thus we introduce a parameter describing the difference between the two – the so called *detuning* – $\delta := \omega_a - \omega_c$, and rewrite the Hamiltonian in terms of that.

$$\hat{H}_{jc} = \hbar\omega_c \left(\hat{a}^\dagger \hat{a} + \frac{1}{2}\hat{\sigma}_z\right) + \hbar\frac{\delta}{2}\hat{\sigma}_z + \hbar g \left(\hat{a}^\dagger\hat{\sigma}_- + \hat{a}\hat{\sigma}_+\right) \tag{119}$$

We would now wish to find a set of eigenstates for this Hamiltonian, that we can use as a basis to express the Hamiltonian as a diagonal matrix. However, there are no obvious and simple eigenstates. So instead, let us pick some easy basis, check how diagonal the matrix then becomes, and take it from there. The simplest set of states we can envision as a basis is just the number of photons – for which we use the symbol n_c (with subscript c for "cavity") – and the state of the atom – for which we use the symbol i_a (a for "atom") . Further, we let $i_a = g$ signify that the atom is in its ground state, and $i_a = e$ corresponds to an excited state. From the tensor product we can then construct the states we intend to use as a basis.

$$\{\ |n_c\,, i_a\rangle\ \} \quad , \quad n_c = 0, 1, 2, \ldots \quad , \quad i_a = e, g \tag{120}$$

Using these basis states we can create the infinite dimensional matrix representation of $\hat{H}_{jc}$, where any one element in the matrix is found by taking:

$$\hat{H}_{jc}^{(n_c m_c i_a j_a)} = \langle n_c\,, i_a|\,\hat{H}_{jc}\,|m_c\,, j_a\rangle \tag{121}$$

Then, using $\hat{H}_{jc}$ from (119) it is quite straightforward to show that any matrix element, gained from two basis vectors that represent different total number of excitations (for instance $|1\,, e\rangle$ correspond to 2 excitations, and $|50\,, g\rangle$ correspond to 50), are all zero. This means that there is no coupling between states with different number of excitations, and for any given number of excitations n we can find a 2×2 matrix, for the Hamiltonian, expressed in the basis vectors $\{\,|n\,, g\rangle\ ,\ |n{-}1\,, e\rangle\,\}$.

$$\hat{H}_{jc}^{(n)} = \begin{bmatrix} \langle n{-}1\,, e|\,\hat{H}_{jc}\,|n{-}1\,, e\rangle & \langle n{-}1\,, e|\,\hat{H}_{jc}\,|n\,, g\rangle \\ \langle n\,, g|\,\hat{H}_{jc}\,|n{-}1\,, e\rangle & \langle n\,, g|\,\hat{H}_{jc}\,|n\,, g\rangle \end{bmatrix} \Rightarrow \ldots \Rightarrow \tag{122}$$

$$\hat{H}_{jc}^{(n)} = \hbar \begin{bmatrix} (n{-}\frac{1}{2})\omega_c + \frac{\delta}{2} & \sqrt{n}\, g \\ \sqrt{n}\, g & (n{-}\frac{1}{2})\omega_c - \frac{\delta}{2} \end{bmatrix} \tag{123}$$

It is worth pointing out that the matrix for zero excitations is not a 2×2 matrix at all, but instead a 1×1 matrix. (When the atom is in its ground state and there are no field excitations the atom cannot transform into an excited state.)

$$\hat{H}_{jc}^{(0)} = -\hbar\frac{\omega_c}{2} - \hbar\frac{\delta}{2} = -\hbar\frac{\omega_a}{2} \tag{124}$$

With these expressions we can now form the entire Jaynes-Cummings Hamiltonian as a matrix of block matrices.

$$\hat{H}_{jc} = \begin{bmatrix} \hat{H}_{jc}^{(0)} & & & \\ & \hat{H}_{jc}^{(1)} & & \\ & & \hat{H}_{jc}^{(2)} & \\ & & & \ddots \end{bmatrix} \tag{125}$$

A.4.1 Jaynes-Cummings in the dispersive regime

Note that the Hamiltonian in (125) is not entirely diagonal since the matrices $\hat{H}_{jc}^{(n)}$ in (123) are not. Expressed in the eigenstates of $\{\,|n_c\,, i_a\rangle\,\}$ there is a coupling between every two states of the same number of excitations.

However, in the so called *dispersive regime*, we can diagonalise the Hamiltonian by approximative methods without having to find new eigenvectors. The dispersive regime means that the *detuning* δ is large compared to the coupling between the field and the atom g.

$$\delta := \omega_a - \omega_c \tag{126}$$

$$|\delta| \gg \sqrt{n}g \tag{127}$$

Using perturbation theory in the parameter g/δ it is possible to find a new diagonalised matrix for (123). The perturbation calculation is not shown here, but the result is.

$$\hat{H}_{jc}^{(n)} = \hbar \begin{bmatrix} (n-\frac{1}{2})\omega_c + \frac{\delta}{2} + \frac{g^2 n}{\delta} & \\ & (n-\frac{1}{2})\omega_c - \frac{\delta}{2} - \frac{g^2 n}{\delta} \end{bmatrix} \tag{128}$$

Noting that this Hamiltonian contains a constant term – i.e. $(n-1/2)\omega_c$ – for any given n, we can redefine the zero level of the energy for any system with n excitations, and remove that term.

$$\hat{H}_{jc}^{(n)} = \hbar \begin{bmatrix} \frac{\delta}{2} + \frac{g^2 n}{\delta} & \\ & -\frac{\delta}{2} - \frac{g^2 n}{\delta} \end{bmatrix} \tag{129}$$

Or we can go even further. In the dispersive regime the state when the atom is excited is never really populated, so it makes sense to define the ground state to have zero energy, and add $\delta/2$ to the diagonal terms.

$$\hat{H}_{jc}^{(n)} = \hbar \begin{bmatrix} \delta + \frac{g^2 n}{\delta} & \\ & -\frac{g^2 n}{\delta} \end{bmatrix} \tag{130}$$

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