



# Ligação Diatômica: Uma Abordagem Clássica e Quântica

## Diatomic Bonding: A Classical and Quantum Approaches

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### Resumo

*O presente artigo possui a intenção de mostrar as diferenças entre análises clássicas e quânticas para a molécula diatômica, focando nos aspectos das transições vibracionais, mostrando os resultados e previsões de cada método, descrevendo as soluções e comparando elas com o comportamento real, deixando claro as limitações e validades de cada método.*

**Palavras-chave:** Física. Universidade. Mecânica Quântica. Molécula Diatômica. Espectro Vibracional.

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### Abstract

*The present article has the intention of showing the difference between classical and quantum analysis for a diatomic molecule, on the aspects of vibrational transitions, showing the results and predictions of each method, describing the solutions and comparing them with the real behavior, making clear the limitations and validities of each method.*

**Keywords:** Physics. University. Quantum Mechanics. Diatomic molecule. Vibrational Spectra.

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## I. INTRODUCTION

Diatomic molecules represent a huge portion of the molecular components of the atmosphere ( $H_2$ ,  $O_2$ ,  $N_2$ , are all diatomic molecules), although they also appear on other situations as crystalline structures such as HCl. These molecules present a quite interesting behavior and their study is of essential importance to the understanding of molecular dynamics.

The molecular bonding occurs for various reasons, they might be ionic when due to the electrostatic interaction of two ions, for example the case of the HCl which is constructed from the interaction between the cation (positive ion)  $H^+$  and the anion (negative ion)  $Cl^-$ . There can also be the covalent bond, where both atoms share two valence electrons, in this case the electrons orbitals are part of both atoms, this is the case of most organic compounds ( $CH_4$  for example), in this configuration there can be a non-polar bond, where the electro negativity of both atoms is not very different and the molecule has a homogeneous charge distribution, but in the case where one atom is much more susceptible to attract electrons than other, the orbitals become closer to one atom and the molecule has an inhomogeneous charge distribution creating a polar molecule such as the water molecule ( $H_2O$ ). The metallic bond is due to the electrostatic force between conduction electrons in metals and positively charged metal ions, this type of bonding is what creates alloys such as bronze, made from copper and zinc.

There are also intermolecular bonds such as hydrogen bond, but they are not the object of study of this article and will not be discussed. The study of the diatomic molecule will begin by an analysis from the classical mechanics perspective, considering Newton's laws and equations of motion, then we take a quantum approach by the use of the Schrodinger equation and study the results in this field of physics. (PAULING, 1960)

The analysis of the system will use the techniques of already known methods that can be found on the references. Beginning first by building the shape of the potential function, then making the classical approximation and solution. Later the quantum treatment and finally the discussion of the results achieved by each method.

It is important to remember that the molecular dynamics is much more complex than the atomic description. Atomic symmetry leads to the condition that the atomic spectrum is only the result of electronic transitions. In molecules there are electronic transitions, vibrations and rotations which makes the spectrum richer and more complex (EISBERG; RESNICK, 1985). The present article focus on the vibrational modes between the atoms that make up the molecule, the electronic transitions may be described by the Molecular Orbital Theory (ATKINS, 1994).

## II. CLASSICAL APPROACH

From the classical perspective, the atoms in the molecule are confined in some potential function that we use to derive the equations of motion and calculate their energies. In this context we approximate the atoms to a particle of mass  $m$  and their movement as a well defined trajectory with well defined momentum and energy.

The potential that rules a diatomic bonding is built from some ideas

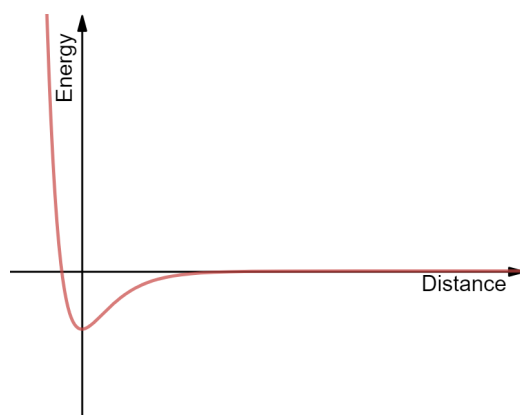
1. There's a dissociation energy in which the molecule breaks its bond and the atoms move freely, so the potential must have an asymptotic behavior for large distances,

$U(r) \rightarrow D_e$  if  $r \rightarrow \infty$ . Where  $D_e$  is the dissociation energy;

2. If the atoms become to close, the nuclear forces will push them away in a way that makes the atoms never being able to touch each other (Except in the case of nuclear fusion, but that is a different case). Therefore the potential must have a vertical asymptotic behavior for small distances,  $U(r) \rightarrow \infty$  if  $r \rightarrow r_{min}$  corresponding to the minimum distance achieved by the atoms due to nuclear forces;
3. There's some equilibrium distance  $r_0$  at lowest possible energy that the atoms try to reach (ROY, 2011).

Given these ideas we can imagine what will be the shape of the potential function that rules the diatomic bond. This shape is represented by Figure 1.

**Figure 1:** The red curve represents the shape of the potential function according to the assumptions above, the depth of the potential, that means, the lowest point of the red curve represents the dissociation energy value  $D_e$  and the  $x = 0$  axis is the equilibrium distance  $r_0$ .



## I. Harmonic oscillator

Since we know there are two forces acting on the atoms, one that attracts them as they become separated, and one that pushes, as they get very close, it is convenient to use as a first approximation the harmonic oscillator model for the vibration of the atom in a molecular diatomic bond.

Considering the potential function of a harmonic oscillator

$$U(r) = \frac{k}{2}(r - r_0)^2 \quad (1)$$

and making the substitution

$$x = r - r_0$$

which means to consider the distance  $x$  as the distance of the atom from the equilibrium point, we end up with

$$U(x) = \frac{k}{2}x^2 \quad (2)$$

where  $k$  is the “spring constant” of the bond. Another consideration to be made is that of the reduced mass, used to simplify the problem from the motion of two atoms to the one of one atom with a mass equivalent to a single atom moving and the second stopped. The reduced mass of the system is simply given by

$$\mu = \frac{m_1 m_2}{m_1 + m_2} \quad (3)$$

This way we construct the differential equation of motion, according to Newton’s law

$$\mu \frac{d^2 x}{dt^2} = -\frac{dU}{dx} = -kx \quad (4)$$

making  $\omega^2 = k/\mu$

$$\frac{d^2 x}{dt^2} = -\omega^2 x \quad (5)$$

The equation has a well know solution given by

$$x(t) = A \cdot \cos(\omega t) + B \cdot \sin(\omega t) \quad (6)$$

Now we assume that at  $t = 0$  the particle is passing through the equilibrium point, so  $r = r_0 \Rightarrow x = 0$ .

$$x(0) = A \cdot \cos(0) + B \cdot \sin(0) = 0 \quad (7)$$

$$A = 0$$

Then, the solution is actually

$$x(t) = B \cdot \sin(\omega t)$$

where  $\omega$  represents the oscillation frequency of the atoms in the molecule. Then the atoms have an oscillatory motion with a defined frequency around an equilibrium point. Now, in order to find the energy associated with the movement of the particle, we simply use the well known equation for the total energy of a system.

$$E = T + V \quad (8)$$

$$E = \frac{\mu v^2}{2} + \frac{kx^2}{2} \quad (9)$$

We calculate  $v$  simply by

$$v = \frac{dx}{dt} = B\omega \cdot \cos(\omega t)$$

With that expression for  $v$ , the energy becomes

$$E = \frac{\mu}{2} B^2 \omega^2 \cos^2(\omega t) + \frac{k}{2} B^2 \sin^2(\omega t)$$

$$E = \frac{\mu B^2 \omega^2}{2} \cos^2(\omega t) + \frac{\mu B^2 \omega^2}{2} \sin^2(\omega t)$$

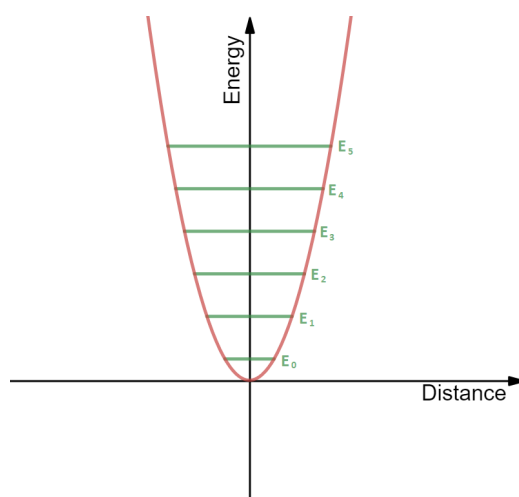
$$E = \frac{\mu B^2 \omega^2}{2} \tag{10}$$

By equation 10, we can isolate  $B$  and get a full equation of motion in terms only of physical quantities.

$$x(t) = \sqrt{\frac{2E}{\mu\omega^2}} \cdot \sin(\omega t) \tag{11}$$

According to this model the atoms move in defined trajectories depending on their energy, mass and angular frequency. The higher the energy, the higher the amplitude of the movement, what makes sense if we analyse the graphic of the potential energy  $U$  for some constant values of  $E$  according to figure 2.

**Figure 2:** In red, the potential function for the harmonic oscillator and in green five fixed values for energy  $E$ , one can verify relation between energy and amplitude, higher energies implies in largers oscillatory amplitudes.



## II. Morse oscillator

Unfortunately, the harmonic oscillator does not correspond to a real representation of the potential function for a diatomic bond due to it's asymptotic behavior, which leads to a non-harmonic vibration at higher energies. A better function that describes the potential is given by the Morse potential function. Which is a phenomenological potential suggested in 1929 to describe the attraction and repulsion forces in the atomic structure. Although the rules mentioned in the beginning of the article are very generic to construct the potential of interaction between two atoms in a diatomic bond, the Morse potential fits the needs mentioned in a much better way than the harmonic oscillator (SLATER, 1963).

$$U_m = D_e((1 - e^{-ax})^2 - 1) \tag{12}$$

Where  $a$  is a coupling factor that dictate the intensity of the curve of the potential felt by the atom. Equation (12) has a more realistic behavior as we can see evaluating the limits at infinity.

$$\lim_{x \rightarrow -\infty} D_e((1 - e^{-ax})^2 - 1) = \infty \quad (13)$$

$$\lim_{x \rightarrow \infty} D_e((1 - e^{-ax})^2 - 1) = 0 \quad (14)$$

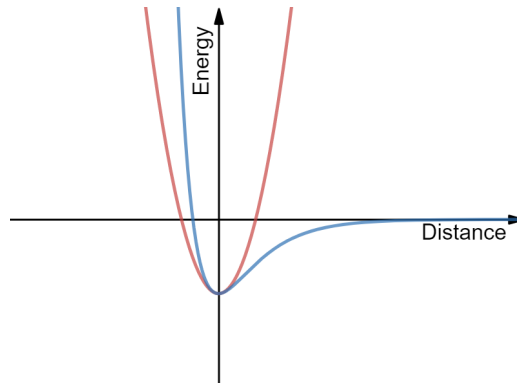
The result from the limits give us the behavior we wanted to construct, as the particles move away from each other, the potential tends to zero (14) and as one of them moves to close to the other, the potential increases indefinitely (13).

Notice that the constant  $D_e$  is exactly the depth of the potential (15). Which physically means the dissociation energy of the molecule

$$U_m(0) = U_m(r = r_0) = -D_e \quad (15)$$

In comparison with the harmonic oscillator, it may be possible to verify that the harmonic potential works as a good approximation for lower energies (Figure 3).

**Figure 3:** The harmonic potential (red) in comparison with the Morse potential (blue).



By series expansion of the Morse potential around  $r_0$ , which corresponds to  $x = 0$ , term of the harmonic oscillator appears as expected.

$$U_m \approx -D_e + U' \cdot x + \frac{1}{2!}U'' \cdot x^2 + \frac{1}{3!}U''' \cdot x^3 \dots \quad (16)$$

The first three terms of the expansion are:

$$U_m \approx 2D_e a^2 \frac{x^2}{2} - D_e \quad (17)$$

which corresponds to the harmonic oscillator with a zero potential energy at  $D_e$  and  $k = 2D_e a^2$ , so

$$a = \sqrt{\frac{k}{2D_e}} \quad (18)$$

The harmonic oscillator is a first approximation to the Morse oscillator, what makes it a nice approximation to the molecular behavior at energies close to the bottom, in other words, when the molecule is close to the lowest possible energy. But now we study a more general case with the Morse oscillator. Again, we want to derive the potential function in order to obtain the differential equation of motion for a particle in this case.

$$F = -\frac{dU_m}{dx} = -\frac{d}{dx}D_e((1 - e^{-ax})^2 - 1) \quad (19)$$

$$F = -2D_e a(e^{-ax} - e^{-2ax}) \quad (20)$$

The differential equation for the movement in this situation becomes:

$$\frac{d^2x}{dt^2} + \frac{2D_e a}{\mu}(e^{-ax} - e^{-2ax}) = 0 \quad (21)$$

using  $\alpha = 4D_e a / \mu$ .

$$\frac{d^2x}{dt^2} + \frac{\alpha}{2}(e^{-ax} - e^{-2ax}) = 0 \quad (22)$$

$$\frac{d^2x}{dt^2} + \sum_{n=1}^2 \frac{\alpha}{2}(-1)^n \cdot e^{-a(3-n)x} = 0 \quad (23)$$

A quick inspection of the equation 23 leads to the conclusion that we can rewrite it as

$$\frac{d}{dt} \left[ \frac{1}{2} \left( \frac{dx}{dt} \right)^2 - \sum_{n=1}^2 \frac{\alpha(-1)^n}{2(3-n)a} e^{-a(3-n)x} \right] = 0 \quad (24)$$

To verify it's validity, it is only needed to apply the time derivative to the terms inside the keys. We can directly integrate the equation with respect to  $t$  to get:

$$\left( \frac{dx}{dt} \right)^2 - \sum_{n=1}^2 \frac{\alpha(-1)^n}{(3-n)a} e^{-a(3-n)x} = \epsilon \quad (25)$$

Where  $\epsilon$  is a integration constant. In order to find the value of  $\epsilon$ , notice that the second term in the equation 25 can be rewritten as

$$\sum_{n=1}^2 \frac{\alpha(-1)^n}{(3-n)a} e^{-a(3-n)x} = -\frac{\alpha}{2a} e^{-2ax} + \frac{\alpha}{a} e^{-ax} \quad (26)$$

Substituting the value of  $\alpha$

$$\begin{aligned} \sum_{n=1}^2 \frac{\alpha(-1)^n}{(3-n)a} e^{-a(3-n)x} &= -\frac{2D_e}{\mu} e^{-2ax} + \frac{4D_e}{\mu} e^{-ax} = \\ &= \frac{2D_e}{\mu} (2e^{-ax} - e^{-2ax}) = \\ &= -\frac{2}{\mu} U_m \end{aligned} \quad (27)$$

So, if we multiply all the terms by  $\mu/2$  we get exactly the sum of kinetic energy and potential energy, it is possible to find  $\epsilon$ .

$$\epsilon = \frac{2E}{\mu} \quad (28)$$

Therefore, we can rewrite the equation 25 as

$$\left(\frac{dx}{dt}\right)^2 = \epsilon - \frac{\alpha}{2a} e^{-2ax} + \frac{\alpha}{a} e^{-ax} \quad (29)$$

Making  $y = e^{ax}$  in a way so  $dy = ae^{ax} dx = -ay dx$ , then separating the  $t$  part from the  $x$  part we rewrite it as

$$\frac{1}{a} \int_{y_0}^y \frac{dy}{\sqrt{\epsilon y^2 + \frac{\alpha}{a} y - \frac{\alpha}{2a}}} = t - t_0 \quad (30)$$

Where  $t_0$  is the initial time related to the position  $x_0$ , or  $y_0$  as an equivalent, we can set  $x_0 = 0$  so  $t_0 = 0$  and then we get the equation as

$$\frac{1}{a} \int_1^y \frac{dy'}{\sqrt{\epsilon y'^2 + \frac{\alpha}{a} y' - \frac{\alpha}{2a}}} = t \quad (31)$$

The solution for this integral depends on the value of  $\epsilon$ , so it also depends on the value for the energy. Since there will be different integrals for  $\epsilon > 0$ ,  $\epsilon = 0$  and  $\epsilon < 0$ , we calculate each case separately and analyse the results for the equations of motion. In the section of discussion we compare the results obtained from this potential to the ones obtained from the harmonic potential.

For the first situation, let's consider  $E = 0 \Rightarrow \epsilon = 0$  (the exact value of the dissociation energy for the molecule), the  $y^2$  term vanishes and we can make the substitution  $u = \frac{\alpha}{a} y' - \frac{\alpha}{2a}$  and so  $du = (\alpha/a) \cdot dy'$ . The integral becomes

$$\frac{1}{\alpha} \int_1^y \frac{dy'}{\sqrt{u}} = t \quad (32)$$



With solution

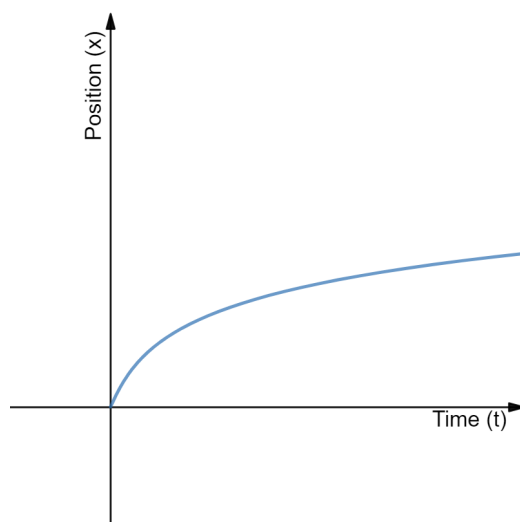
$$x(t) = \frac{1}{a} \ln \left( \frac{1}{2} + \frac{D_e a^2}{\mu} \left( t + \frac{2}{\alpha} \sqrt{\frac{\alpha}{a} - \frac{\alpha}{2a}} \right)^2 \right) \quad (33)$$

Which can be simplified to

$$x(t) = \frac{1}{a} \ln \left( \frac{1}{2} + \frac{D_e a^2}{\mu} \left( t + \sqrt{\frac{2}{\alpha a}} \right)^2 \right) \quad (34)$$

The solution shows that the particle starts the oscillatory motion but then escapes it, since it has exactly the energy necessary to dissociate from the potential, the trajectory as a function of time is show bellow by figure 4.

**Figure 4:** Position of a particle in the Morse potential with energy  $E = 0$  as a function of time.



Now we look at the case where  $E > 0 \Rightarrow \epsilon > 0$ . In order to solve the integral in this situation we need to substitute the values for  $\alpha$ ,  $\epsilon$  and factor the resulting polynomial equation, after that we apply integration by parts and make some substitution of variables to get the result, the step-by-step process is shown in (BARBOZA et al., 2007). The result gives the equation as

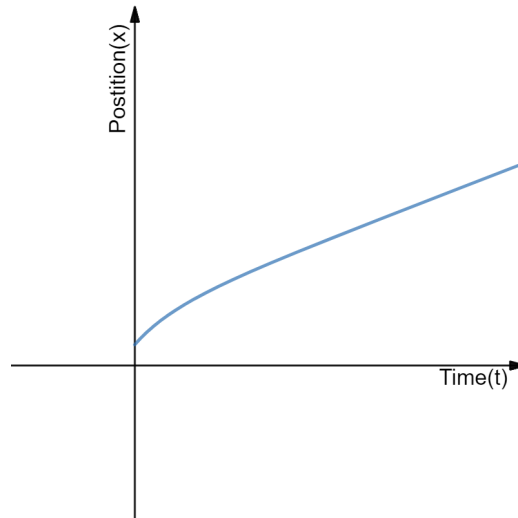
$$x(t) = \frac{1}{a} \ln \left[ \frac{D_e}{E} \left( \sqrt{\frac{E + D_e}{D_e}} \cosh \left( \sqrt{\frac{2E}{\mu}} a(t + \beta) \right) - 1 \right) \right] \quad (35)$$

where

$$\beta = \frac{2}{\alpha} \sqrt{\frac{\alpha}{a} - \frac{\alpha}{2a}} = \sqrt{\frac{2}{\alpha a}}$$

In this situation the particle almost doesn't feel attraction to the potential and it's motion is very close to a straight line, as shown in Figure 5

**Figure 5:** Position of a particle in the Morse potential with energy  $E > 0$  as a function of time.

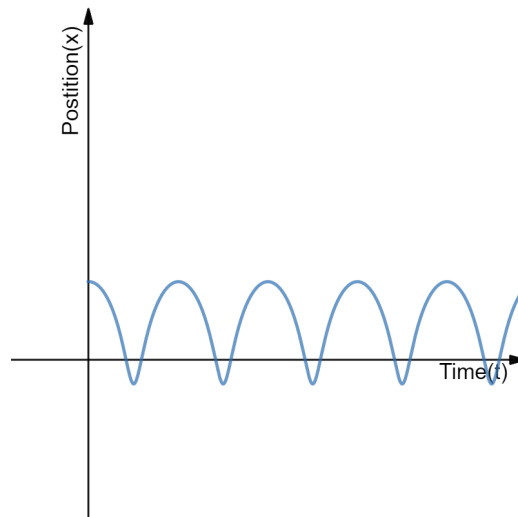


Finally we take a look at the case where  $E < 0 \Rightarrow \epsilon < 0$ , again we won't solve the integral step by step, instead we look only at the result.

$$x(t) = \frac{1}{a} \ln \left[ -\frac{D_e}{E} \left[ 1 - \sqrt{\frac{E + D_e}{D_e}} \cos \left( \sqrt{\frac{-2}{E\mu}} D_e a (t + \beta) \right) \right] \right] \quad (36)$$

In this final case, the particle has a confined movement, oscillatory but not harmonic as we see in Figure 6.

**Figure 6:** Position of a particle in the Morse potential with energy  $E < 0$  as a function of time.



Finally we conclude that in the case of a particle (atom) in the Morse potential, the equation of motion will depend on the energy and the trajectory may or may not be an oscillatory motion. We finish the study of the diatomic molecule in the classical mechanical perspective and now we pass to the quantum treatment where we will consider the quantization effects.

### III. QUANTUM APPROACH

Now the quantum treatment for the problem will be studied, starting again by the same approximation of the harmonic oscillator, but this time considering the quantum effects, then we pass to the Morse oscillator. In a quantum view, the atoms don't have a defined trajectory, hence, there will be no equation of motion such as in the classical consideration, instead there is going to be a wave function that represents the amplitude of probability density wave inside the potential, also the quantum states of the atoms and their respective energies. We will derive our results from the Schrodinger equation, just like we used Newton's equations for the classical approach.

Fortunately, the shape of the potential functions will not change from the classical to the quantum approach, only the behavior of the particles inside them.

#### I. Quantum harmonic oscillator

For our first approximation, we will consider again the harmonic oscillator, but this time in a quantum treatment. We are also interested in solving the Schrodinger equation for the nucleus, which can be separated from the equation for the electrons by the Born-Oppenheimer approximation (WOOLLEY; SUTCLIFFE, 1977), resulting in a single Schrodinger equation describing the nuclear movement of the molecule. As we have discussed above, the potential energy will be the same and so the Schrodinger equation for this problem is

$$-\frac{\hbar^2}{2\mu} \frac{d^2\psi}{dx^2} + \frac{k}{2} x^2 \psi = E\psi \quad (37)$$

We write  $k = \mu\omega^2$  and multiply everything by  $2\mu/\hbar^2$  to get a simplified form of equation 37.

$$-\frac{d^2\psi}{dx^2} + \frac{\mu^2\omega^2}{\hbar^2} x^2 \psi = \frac{2\mu E}{\hbar^2} \psi \quad (38)$$

For simplicity we put

$$\alpha = \frac{\mu\omega}{\hbar}$$

$$\epsilon = \frac{2\mu E}{\hbar^2}$$

Leaving the equation in the form

$$\frac{d^2\psi}{dx^2} + (\epsilon - \alpha^2 x^2) \psi = 0 \quad (39)$$

Introducing now the new variable  $u = \sqrt{\alpha}x$  and applying the derivatives to it, we are

left with a non-dimensional form of the differential equation 39.

$$\alpha \frac{d^2\psi}{du^2} + (\epsilon - \alpha u^2)\psi = 0 \quad (40)$$

$$\frac{d^2\psi}{du^2} + \left(\frac{\epsilon}{\alpha} - u^2\right)\psi = 0 \quad (41)$$

To continue the solution it is useful to make use of the asymptotic analysis, in which we examine the behavior of the equation for an extreme, in this case we want to look at  $u \rightarrow \infty$ . In this situation, the  $\epsilon/\alpha$  term becomes really small compared to the others and can be neglected, giving us

$$\frac{d^2\psi}{du^2} = u^2\psi \quad (42)$$

$$\psi(u) = A \cdot e^{-\frac{u^2}{2}} \quad (43)$$

With this we know that the complete solution cannot be larger than  $e^{-\frac{u^2}{2}}$ , otherwise the asymptotic behavior won't be obeyed. We have the complete solution given as

$$\psi(u) = A \cdot e^{-\frac{u^2}{2}} \cdot H(u) \quad (44)$$

Getting this value for  $\psi$  and making the derivatives, we get the equation written as

$$A \cdot e^{-\frac{u^2}{2}} \left( -H + u^2H - 2u \frac{dH}{du} + \frac{d^2H}{du^2} + \frac{\epsilon}{\alpha}H - u^2H \right) = 0 \quad (45)$$

$$\frac{d^2H}{du^2} - 2u \frac{dH}{du} + \left(\frac{\epsilon}{\alpha} - 1\right)H = 0 \quad (46)$$

To solve the equation 46, we use the method of power series

$$H(u) = \sum_{l=0}^{\infty} C_l \cdot u^l$$

If we derivate this assumption and place it back into 46, we end up with a equation involving sums and equal to 0, for that the terms inside the sum must be zero. And we are left with the recurrence relation

$$C_{l+2} = -\frac{\frac{\epsilon}{\alpha} - 1 - 2l}{(l+1)(l+2)} C_l \quad (47)$$

Calculating some values for C it becomes clear that they are all written in terms of  $C_0$  and  $C_1$  in the relation

$$H(u) = C_0 \left( 1 + \frac{C_2}{C_0}u^2 + \frac{C_4}{C_2} \frac{C_2}{C_0}u^4 + \dots \right) + C_1 \left( u + \frac{C_3}{C_1}u^3 + \dots \right) \quad (48)$$

The solution may be enhanced by making the calculation

$$\frac{C_{l+2}}{C_l} \approx \frac{2l}{l^2} = \frac{2}{l}$$

and comparing this expression with the expression for series expansion of  $e^{u^2}$

$$e^{u^2} \approx 1 + u^2 + \frac{u^4}{2!} + \frac{u^6}{3!} + \dots + \frac{u^l}{(l/2)!}$$

For a big  $l$  the expression for  $H(u)$  becomes

$$H(u) = C_0 \cdot K e^{u^2} + C_1 \cdot K' u e^{u^2} \quad (49)$$

But this goes to infinity when  $u \rightarrow \infty$  and as we have seen, the solution cannot do that, so the series must stop at a certain point. Stating that the top term of the recurrence relation goes to 0, so

$$\frac{\epsilon}{\alpha} = 2n + 1 \quad (50)$$

And then, when  $l = n$ ,  $C_{n+2} = 0$ , and the series stops at the  $n^{th}$  term, becoming a polynomial equation called Hermite polynomials. The complete solution for the quantum harmonic oscillator is given in terms of these polynomials.

$$\psi_n(u) = A_n \cdot e^{-\frac{u^2}{2}} H_n(u) \quad (51)$$

To find the value of the constant  $A_n$  we use the normalization condition

$$\int_{-\infty}^{\infty} \psi(x) \cdot \psi^*(x) dx = 1 \quad (52)$$

Resulting in

$$A_n = \left( \frac{\mu\omega}{\pi\hbar} \right)^{\frac{1}{4}} \frac{1}{\sqrt{2^n n!}} \quad (53)$$

The complete solution is then

$$\psi_n(x) = \left( \frac{\mu\omega}{\pi\hbar} \right)^{\frac{1}{4}} \frac{1}{\sqrt{2^n n!}} e^{-\frac{\mu\omega x^2}{\hbar^2}} \cdot H_n \left( \sqrt{\frac{\mu\omega}{\hbar}} x \right) \quad (54)$$

The energies allowed in the oscillator can be found by the relation 50, which is rewritten as

$$\frac{2\mu E}{\hbar^2} \frac{\hbar}{\mu\omega} = \frac{2E}{\hbar\omega} = 2n + 1 \quad (55)$$

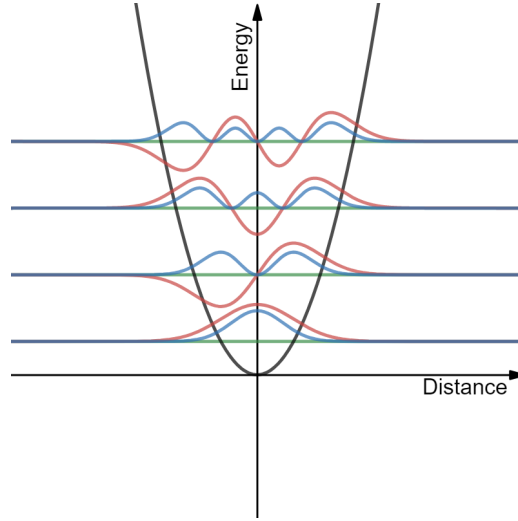
$$E_n = \left( n + \frac{1}{2} \right) \hbar\omega \quad (56)$$

The quantum harmonic oscillator has discrete values of energy and it is not defined by a trajectory but instead by a probability of finding the atoms at some point given by

$$P(x) = |\psi(x)|^2$$

The next figure (7) shows the wave functions  $\psi_0, \psi_1, \psi_2, \psi_3$  and the corresponding probabilities on top of the energy level for each state.

**Figure 7:** Green lines represent the energy levels for the oscillator, the red curves represent the wave functions and the blue curves the corresponding probabilities of finding the atom.



With this result we can calculate the difference of energy between two states inside the oscillator

$$E_m - E_n = \hbar\omega \left( m + \frac{1}{2} \right) - \hbar\omega \left( n + \frac{1}{2} \right) \quad (57)$$

$$E_m - E_n = \hbar\omega(m - n) \quad (58)$$

If  $m = n + 1$

$$\Delta E = \hbar\omega \quad (59)$$

## II. Quantum Morse Oscillator

At this point we start to make a better assumption of the behavior of an atom in a diatomic bond by using the Morse oscillator in its quantum mechanical formulation. Again, the potential energy is the same as the classical one, but the phenomena are different as we shall see.

$$U_m(x) = D_e((1 - e^{-ax})^2 - 1) \quad (60)$$

The Schrodinger equation takes the form

$$-\frac{\hbar^2}{2\mu} \frac{d^2\psi}{dx^2} + D_e((1 - e^{-ax})^2 - 1)\psi = E\psi \quad (61)$$

we can also rewrite the potential and leave the equation as

$$\frac{d^2\psi}{dx^2} - \frac{2\mu D_e}{\hbar^2} e^{-2ax} \psi + \frac{4\mu D_e}{\hbar^2} e^{-ax} \psi + \frac{2\mu E}{\hbar^2} \psi = 0 \quad (62)$$

Where now we introduce the new variable to leave the equation non dimensional (CHEN, 2004)

$$y = k \cdot e^{-ax}$$

where

$$k = \frac{2\sqrt{2\mu D_e}}{\hbar a}$$

Also calling

$$\beta^2 = -\frac{2\mu E}{\hbar^2}$$

Making the derivatives  $d^2/dx^2$  in terms of  $d/dy$  and  $d^2/dy^2$  using the chain rule we get the equation rewritten as

$$a^2 y^2 \frac{d^2\psi}{dy^2} + a^2 y \frac{d\psi}{dy} - \frac{2\mu D_e}{\hbar^2 k^2} y^2 \psi + \frac{4\mu D_e}{\hbar^2 k} y \psi - \beta^2 \psi = 0 \quad (63)$$

Dividing everything by  $a^2$  and remembering the value of  $k$ , we simplify the equation to

$$y^2 \frac{d^2\psi}{dy^2} + y \frac{d\psi}{dy} - \frac{y^2}{4} \psi + \frac{k}{2} y \psi - \frac{\beta^2}{a^2} \psi = 0 \quad (64)$$

And making an asymptotic analysis for  $y \rightarrow 0$  we get a solution in the form  $\psi(y) = y^\beta / a$  and for  $y \rightarrow \infty$ ,  $\psi(y) = e^{-y/2}$ . So the complete solution must be a multiplication of these two functions times a third function that adjusts the "middle part" of the function, something that goes to 1 in both extremes.

$$\psi(y) = y^{\frac{\beta}{a}} e^{-\frac{y}{2}} F(y) \quad (65)$$

Again, making the derivatives of  $\psi$  with respect to  $y$ , and placing the results of these derivatives in the differential equation we get an equation for  $F(y)$ .

$$\frac{d\psi}{dy} = \left( \beta y^{\frac{\beta}{a}-1} e^{-\frac{y}{2}} - \frac{e^{-\frac{y}{2}}}{2} y^\beta \right) F(y) + y^\beta e^{-\frac{y}{2}} \frac{dF}{dy} \quad (66)$$

$$\frac{d^2\psi}{dy^2} = \frac{d}{dy} \left( \frac{d\psi}{dy} \right)$$

$$\frac{d^2\psi}{dy^2} = \frac{d}{dy} \left[ \left( \beta y^{\frac{\beta}{a}-1} e^{-\frac{y}{2}} - \frac{e^{-\frac{y}{2}}}{2} y^\beta \right) F(y) + y^\beta e^{-\frac{y}{2}} \frac{dF}{dy} \right] \quad (67)$$

The differential equation for  $F$  becomes, after all the manipulations,

$$y \frac{d^2 F}{dy^2} + (2\beta + 1 - y) \frac{dF}{dy} + \left( \frac{k}{4} - \frac{1}{2} - \frac{\beta}{a} \right) F(y) = 0 \quad (68)$$

Which we can apply the some method of power series solution as used in the harmonic oscillator and find that the solution for this differential equation is the generalized Laguerre function. Defined by

$$y \cdot F'' + (\alpha + 1 - y)F' + nF = 0 \quad (69)$$

$$L_n^\alpha(x) = \frac{x^{-\alpha} e^x}{n!} \frac{d^n}{dx^n} (e^{-x} x^{n+\alpha}) \quad (70)$$

In this situation  $\alpha = 2\beta$  and  $n = k/4 - 1/2 - \beta/a$ . So, the complete wave function for the Morse oscillator is

$$\psi(y) = N_n \cdot y^{\frac{k}{2} - n - \frac{1}{2}} e^{-\frac{y}{2}} L_n^{k-2n-1}(y) \quad (71)$$

Where  $N_n$  is a normalization constant found by the normalization condition.

$$N_n = \left( \frac{an!(k-2n-1)}{\Gamma(k-n)} \right)^{1/2} \quad (72)$$

Another result we can take out of the derivations for the Morse potential is the possible energies for this case which are found to be

$$E_n = -D_e \left[ 1 - \frac{a\hbar}{\sqrt{2\mu D_e}} \left( n + \frac{1}{2} \right) \right]^2 \quad (73)$$

The first interesting thing we can notice at this allowed energy equation is that the spacing between two levels of energy is not constant as in the harmonic oscillator case, the spacing becomes smaller as the level increases, we can find the amount of energy to go from a initial state  $n$  to a final state  $m$  simply by making the difference of the two

$$\Delta E_{mn} = E_m - E_n = (n^2 - m^2) \frac{a^2 \hbar^2}{2\mu} + (n - m) \left( \frac{a^2 \hbar^2}{4\mu} - a\hbar \sqrt{\frac{2D_e}{\mu}} \right) \quad (74)$$

Notice that this quantity decreases with the increase of  $m$ , in order to find the energy necessary to go from one state to the next we simply put  $m = n + 1$  and get

$$\Delta E = a\hbar \sqrt{\frac{2D_e}{\mu}} - (n + 1) \frac{a^2 \hbar^2}{\mu} \quad (75)$$

The other interesting result is that it has a limited quantity of allowed energies. It has some maximum  $n$ , that if we try to put a larger  $n$ , we get a negative or zero energy. This would correspond to the dissociation energy of the molecule, physically speaking, if the energy exceeds the maximum  $n$ , the molecule dissociates, what means that the particles



escape the potential well.

In other words  $\Delta E = 0$

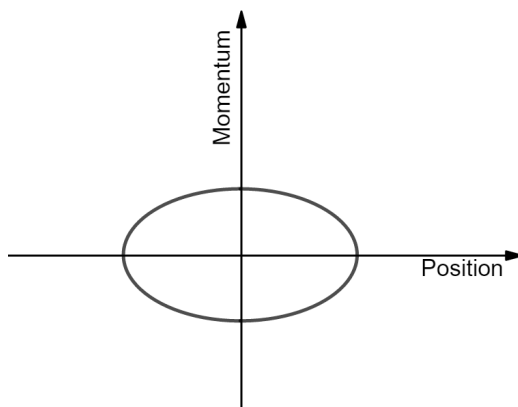
$$n < \frac{\sqrt{2\mu D_e}}{a\hbar} - 1$$

There is also the possibility of constructing the solution for the Quantum Morse Potential by an algebraic method using the so called ladder operators(DONG; LEMUS; FRANK, 2002).

#### IV. DISCUSSION

We begin the discussion of the results by looking carefully at the harmonic oscillator from the classical perspective. The first thing we notice is that the particle follows a trajectory well defined and has a well defined momentum too. This can be seen by looking at the diagram on the phase space (GOLDSTEIN; POOLE; SAFKO, 2002) for the harmonic oscillator (Figure 8)

**Figure 8:** *The trajectory of a classical harmonic oscillator in a phase space diagram, the equation is represented by an ellipse of the type  $\frac{p^2}{2\mu E} + \frac{x^2}{2E/k} = 1$ . The maximum value for  $p$  is when  $x$  is zero and it corresponds to  $\sqrt{2\mu E}$  while the maximum  $x$  is found when  $p$  is zero and it's exactly  $\sqrt{2E/k}$  just as we expect it to be.*

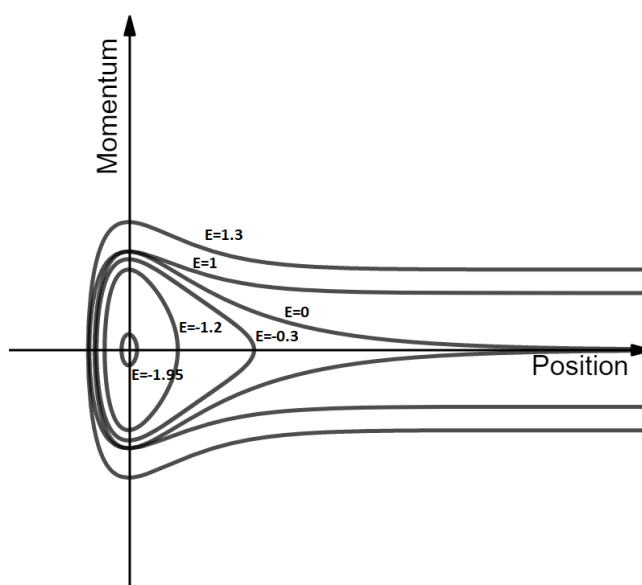


The other observable result is that the energy assumes continuous values for the particle, so there is a continuous number of trajectories that a particle can take when put inside this potential function. This result is a rough approximation, since we know that there are not an infinite number of energies for the particle because at a certain energy level, the molecule dissociates and the atoms get in a free motion. The other correction is that the amplitude of oscillation is equal to both sides, while in reality the nuclear force (repulsion) and the electromagnetic force (attraction) are not in the same magnitude with the distance, so the oscillations are not balanced.

We drive our attention now to the results from the classical Morse potential, first we see that the trajectories are not the same for the energies, there's a limitation between bounded

trajectories and free ones, although the energy assumes continuous values again, the main difference from the harmonic oscillator is exactly the asymmetry in the oscillations and the energy limit for closed trajectories. Again, we look at the phase space diagram for different values of  $E$  and look at the behavior of the particles (Figure 9)

**Figure 9:** *The trajectory of a classical Morse oscillator in a phase space diagram. The equation is written in the form of a parametric equation of position and momentum, the diagram shows that for  $E > 0$  the trajectory is open and the position goes to infinite, the molecules doesn't even make one oscillation and go further apart to infinite. For  $E = 0$  the particles's momentum tends to zero as the position goes to infinite, so this case is exactly the limit between open and closed orbits. And for  $E < 0$  the particle has a closed trajectory, anti-symmetric as we can see that the shape of the figure is not an ellipse. Finally it is possible to see that for a really small energy, close to the minimum, the shape of the figure becomes the ellipse on the harmonic oscillator case. In this graphic,  $D_e = 2$ ,  $\mu = a = 1$ .*



The physical analysis of this situation is that if the atoms are in a bounded state, the oscillations are not symmetric, showing the non-equal value for the nuclear repulsion force and the electromagnetic attraction force. When the energy is exactly the dissociation value, the amplitude of the oscillation is infinite, since the maximum distance on the movement is acquired when the velocity is zero, so the molecule breaks apart and the atoms keep slowing down reaching velocity zero on infinite. For large values of energy, the atoms come close with some specified momentum, then they are strongly repulsed by the nuclear force and leave with almost the same momentum, losing some part of it when they are still close to each other because of the breaking due to the electromagnetic force, but also gaining some more momentum when are really close to each other, before the nuclear force acts. The problem can then be imagined to be a collision of the atoms, in other words, when the energy is very big, the atoms experience a collision but do not keep on a closed trajectory.

This is a much more appropriate method, the problem now is that atoms are tiny particles described by quantum mechanics, and so we have the need for the quantum description of the system. By looking at the phase space diagram again, we notice that for low energies,

the trajectory becomes, in quite good approximation, an ellipse described by the harmonic oscillators, what means that when the energy of the molecule is very low (close to its minimum), the harmonic oscillator becomes a better description since it delivers a excellent result and becomes much more simple. Even though the quantum treatment is better, when the mass of the atoms are too big and the quantum effects become smaller and smaller, and then the classical treatment becomes more precise.

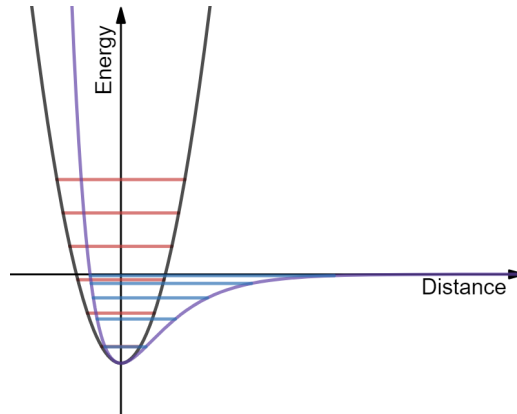
On the quantum case, as we have seen, the harmonic oscillator is the first approximation. There are many divergences between the classical and quantum results, first for the classical result we have seen that we get a well defined orbit, while for the quantum treatment we ended up with a wave function, that described the state of the particle inside the potential, by that we get the probability of finding the particle somewhere inside the system, the average values for the position and momentum along the movement. The consideration becomes quite different since now we don't have trajectories, but probabilities. We cannot know where the atoms are, but we have a higher probability of finding them somewhere. The second result is the energy, which is not continuous anymore, is discrete (quantized). The molecule can only have specified values of energy, changing from one level to another by the emission or absorption of some specified value of energy, found to be  $\Delta E = \hbar\omega$ , that result opens the space for spectroscopy, looking at the frequency of emitted or absorbed photons on a state transition, an experimental tool to look at the energies for diatomic molecules, a result that it is not possible on the classical result, since the change from one specific state to another is continuous, for example, decreasing the energy of the system would correspond to a continuous emission of radiation. While, in the quantum treatment, this quantity is discrete.

At last, we bring the discussion to the Quantum Morse Oscillator, which gives the best result between all of them. At this point it is important to state that the the Morse Potential (12) is not the only analytical curve that describes the potential energy in the vibrational aspect of molecules. First, just as the harmonic oscillator, the atoms have specified energy levels allowed inside the potential well, but the big difference now is in the spacing between the energy levels (TASELI, 1998), what changes them and their limit value. To begin with, as we have seen in the development of the solution that the space between energy levels decreases with the increase of the level, meaning that close to the dissociation point the energies are more close together, there are more states allowed when close to the dissociation point than close to the bottom of the well. The other important thing about the energy spacing is that it depends on many more factors, the size of the well, a larger well gives a larger spacing, and also the reduced mass of the system, a larger mass reduces the space between the energies, in other words, when the mass becomes larger, the system approach a continuous distribution of energy,  $\Delta E \rightarrow 0$  as  $\mu \rightarrow \infty$ , making the classical treatment where the energy is continuous more valid. Another important difference is the limit on energies, or, the presence of the breaking stage (dissociation point) of the molecule, the atoms now cannot increase their energy indefinitely, so for example, if we heat the molecule enough, it won't become more agitated for ever, it will break at some point, again, this value is changed by the increase of mass, a larger mass allows more states of energies, also a deeper potential

allows more states of energy too, as we expect in a real case.

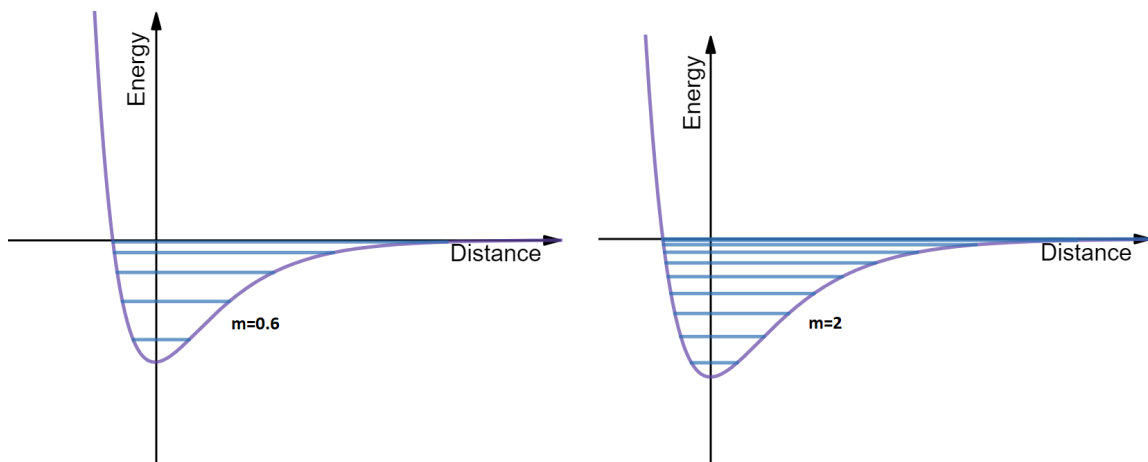
The next figure shows a comparison of the energies in the QHO(Quantum harmonic oscillator) and the QMO(Quantum Morse oscillator)

**Figure 10:** In black, the harmonic potential and in purple the Morse potential. It's possible to see that for the ground state the energy described by the QHO and the QMO is pretty much equal, the next level has a tiny difference, the next levels become quite different and the QMO respects the limit of dissociation energy while the QHO does not.



To evaluate also the effect of the mass in the behavior of the molecule, it's shown a comparison between two different values of mass in the next figure

**Figure 11:** The left graph shows the energy levels for  $\mu = 0,6$  while the right one shows for  $\mu = 2$ , showing that there are more levels allowed and with a smaller spacing between them, both graphs used the same value for the all the others parameters.



## V. CONCLUSION

The results taken from both approaches show a description inside its limitation to the behavior of a diatomic bonding. The classical approach may seem to be possible, although, one should not think that such a description is valid. The molecular behavior is only fully

described by the quantum theory and the assumptions done here are just a means for comparison between results more accurate taken from quantum theory and the ones that classical mechanics predict, which are not in accordance with reality. The development of the methods, used all the possible tools inside their limitations to achieve the most complete description as possible, from the mathematical results to their physical meaning by manners of graphs and discussion.

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