Radiative Quenching of Hydrogen Atoms in 2 Dimensions

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Abstract

ABSTRACT

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CHAPTER 0

INTRODUCTION

MOTIVATION

Because the quantum mechanics is now 'old' and established theory, there has been a push towards applying the quantum mechanics to the more and more complex systems. In addition, there has been a push to apply quantum mechanical principles to processes where physics intersects with other disciplines.

Two of those disciplines are an Information Theory and material science.

Within Information Theory framework, promising route to quantum information processing [46] is via the manipulation of the internal states of ions and atoms. Within the new materials framework, there is a great stride in creating new 2D materials, with great promises. [26] In order to facilitate that emergent technology it is imperative that we understand, at a fundamental level, the processes that govern the behavior of matter at the atomic level. In this thesis we will explore the interactions of ions with neutral matter. Those topics include radiative quenching, non-radiative and radiative charge transfer reactions as well as the manipulation and control of atomic matter by external fields.

The quantitative calculations have greatly been helped with the advancement in computing technology, since it is now possible to solve the differential equation relatively quickly and using computing equipment which is widely accessible. However applying only approximative methods and using only numerical methods to solve differential equations may not be sufficient in number of cases. While the numerical methods will always provide a result, they do not provide much of an insight into the behavior of a quantum system. Also, unless one is very careful, the various numerical errors tend to accumulate, and it that case the result is neither insightful nor correct. So the analytic solution is almost always desirable. Although for the moderately complex system the closed form analytic solution is usually impossible to obtain, it is still desirable to have the exact analytic solution and fall back to the approximations and numerical methods only as a last step.

The statement above is generally true and applicable to every project and solution. So in this problem we tried to find the analytical solution and fall back on the numerical computation only as a last step. So while the Quantum Mechanics can be applied to any physical system, relative to this thesis we see two major applications: new 2 dimensional materials and quantum computing.

New Materials

Applying quantum mechanics to more complex systems brought us electronics components, lasers, high speed telecommunications, new diagnostic technologies in medicine, new materials, and in general, new applications are being researched.

After it discovery, at the beginning of this century, the quantum mechanics have been applied to more and more complex system. One of its application has been understanding the properties of materials. From the understanding of the properties of the materials, came the icreation of the new materials, using the quantum mechanical principles. And 2D materials were investigated fairly early

in the 2th century.

Graphene and Assumed Impossibility of 2D Materials

Initially, it was argued by Landau and Peierls [22] [32] that 2D materials cannot exist. The argument was that the displacement of atoms due to the thermal fluctuations would be an order or the atomic distance, at any finite temperature [22, 32]. Thus 2D material would melt at any temperature higher that $0K$.

There is even stronger statement against the 2D materials, in the form of Mermin-Wagner-Hohenberg (MWH) theorem [17] [28]. In these papers the authors show that 2D systems. with short-range interactions are unstable, and cannot exist. Starting with the thermodynamics argument, for the system to be stable, its free energy must be bounded from below and convex (upwards). This way we (the system) can minimize the energy for the ground state. Higher order fluctuations are now finite, and the system is stable. The MWH argument is that, in 2D systems, the fluctuations around the ordered state (lattice in 2D case) decorrelate over the large distances, thus destroying the large scale order.

Therefore, for a while it seems that the only 2D materials considered were a molecular films, which would form on the surface of solids. From Dash [20], the 2D materials exist as a thin film either on surface on the boundaries of the 3D materials.

The other kind research in 2 dimensional systems was motivated by the need to simplify the theoretical investigations. Often, simpler 1 or 2 dimensional conceptual models are used to analyze the physical phenomena. From that simpler model, a 3 dimensional model is than treated as the same, just more mathematically complex system. following those arguments, the application of quantum mechanics in 2 dimension was initially done as an analysis of the surface phenomena. [19].

However, despite those arguments, it has been speculated that 2D materials are possible [20]. The situation has changed dramatically in 2004 when it turns out that 2D materials can indeed exist [4]. The first 2D material, graphene was created [5] at the university of Manchester.

+So the Graphene does not contradict the Mermin et all. theorem, but it does circumvent it [1]. In Graphene thermal oscillation produce ripples, or bending of the graphene sheet.Also graphehe behaves like an ellastic membrane. That allows phonon to propagate in 2 dimensions,and couple the in plane stretching to the transverse fluctuations out of the plane. This mediates a long range interaction, thereby circumventing Mermin-Wagner

The 2D materials have qualitatively different topological properties [11]. Moreover, these properties do not depend on the type of microscopic interactions between particles. While this subject is beyond the scope of this thesis, it does show that the field of 2D materials has excellent potential for both fundamental research and applications. For the material to exhibit 3D properties, it has been shown [30] that when material has as low as 10 layers, its properties are approaching the 3D limit.

Interestingly, following [4] it seems that 2D materials have another set of interesting properties, in the regions where particles in 2D behave relativistically. Usually, in condensed mater system, the ordinary Schroedinger equation is sufficient to describe all the electronic properties of the material. In Graphene, the electrons themselves behave somewhat relativistically, moving with velocities of $\approx 10^6 m/s$. While this is still 300 times slower than the speed of light, it is still much faster that the electron velocities in a classical conductor, which are the order of $10^{(-4)}m/s$.

However the interaction of conducting electrons n Graphene with the periodic potential of the graphene lattice gives rise to new quasi-particles, which behave as massless Dirac's fermions. These quasi-particles, even at low energies, can only be described by the Dirac's equation in 2+1 dimen-

sions. Therefore it might be interesting to redo the same calculation as we did, but solving the Dirac's equation for the system of quasi-particles similar to an Hydrogen ion. There are many other interesting properties of Graphene [4], such as its QED like electronic spectrum, electron tunneling, and so on. The other interesting consequence of the QED like electron spectrum is the possibility of experimentally studying QED in curved space, by controllable bending of a graphene sheet. This can offer a possibility to address a certain class of cosmological problems.

Now, after the discovery of Graphene, there has been an extensive study regarding the new 2D materials. and the research has really picked up. Now there are number of new 2D materials being discovered. The main application in in the direction nanotubes and of 2D semiconductors. While nanotubes are made of graphene, they are not equivalent and depending on the application Graphene (as a sheet) is sometimes superior, sometimes inferior and sometimes completely different.

As far as the electronics, the hope that the Graphene can be used to build active electronic components, such as diodes, transistors (FET) and such. Alternatively due to its conductivity, Graphene can be used as a conductor, in both electronic components but also in the batteries. Graphene itself is a zero gap semiconductor. The unique opportunity in 2D semiconductors is that in 3D semiconductor electronic states are not buried deep inside the material. In 2D semiconductors, the electronic states are on the surface. The more interesting application of 2D electronics are the LED elements in 2D [36]. The research in electronics is closely related to the research of new 2D materials. For example Graphene itself is not compatible with Silicon. But there is a new material, Black Phosphorus, which is both compatible with Silicon and it posses a band gap, which also makes it able to detect light. TODO: more here

2D Electronics

One application of the 2D materials is their use in electronic devices [44], [45]. This is driven by the demand for the higher performance and lower consumption in electronic devices.

Topological Quantum Computing

Applying quantum mechanical principles in engineering disciplines, such as computer science [14] promises to bring us the much qualitatively more powerful quantum computer. This computer may possibly able to solve problems currently intractable by classical digital computers. Currently it is not clear whether the quantum computer will be able to solve NP problems. TODO: (Add citation). Now all problems in the NP class can be transformed into each other in polynomial time to each other TODO add citation, therefore finding a polynomial time solution for one of them would amount to having a polynomial time solution to the all problems in NP class. So the goal is rather worthy.

Currently, there are not final word on the subject yet. While most authors lean to the opinion that the quantum computer may not be fundamentally more powerful than the classical one, there are schemes [3] which would allow quantum computer to solve NP problems. As an related example the Schor's algorithm [40] can provably solve integer factorization in a polynomial time, as opposed to the best classical algorithm (quadratic sieve), which works in sub-exponential time [33]. Unfortunately, the integer factorization problem does not belong to the class of NP problems.

Even if the NP problems remain intractable, just the possibility that, according to Feynman [14], quantum computer can be used to simulate the quantum processes, will in itself be a step forward in modeling the physical properties and processes. In addition quantum computers may offer some

other benefits in terms of space, energy consumptions. TODO" add citation.

What relates the new 2D materials and the quantum computing architecture, is the concept of topological quantum computing [37]. While, in principle, there are no theoretical objections to building a quantum computer, there are serious issues encountered in practice TODO: add citations. Currently these problems are not solved and the quantum computers currently in existence are still unable to overcome them TODO: add citations. It seems that the topological approach promises an actually physically realizable quantum computer [34, 38]. And

Anyons

Anyons are the quasiparticles which occur only in 2D systems and whose quantum statistics in neither Fermionic nor Bosonic [25]. This has been proved [49], and the arbitrary statistics is valid only in 2 dimensions [47]. After exchanging two identical particles, the wave function gains an arbitrary phase factor $\Psi = e^{i\theta}\Psi$, where $\theta = 2\pi\nu^s$. This is in contrast the 3 dimensional world, where exchange of two particles gains either phase factor π or 0, for Fermions and Bosons respectively.

There are two kinds of Anyons, Abelian and non-Abelian. The Abelian anyons have been reliably detected in the Fractional Quantum Hall Effect. [24]. While the computation with Abelian anyones is theoretically possible [50], considerably more attention has been paid to the non-Abelian anyons. There are several possibilities for realizing non-abelian statistics experimentally: 1. a two-dimensional electron gas in a large magnetic field (the fractional quantum Hall effect); 2. rapidly rotating Bose-Einstein condensates 3. frustrated magnets.

Non-abelian anyons have not been detected yet, but most of the research have been focused on them as they could offer some interesting applications, most notably fault tolerant Topological Quantum Computing. [27]. But since the Anyons are only observed in 2D topologies, one must start from the

7

2D materials.

0.0.1 Excitons and Trions

The other interesting and relatively simple system is the Exciton, which represents a bound state of a whole and a electron in a solid state material, and allows the transport of energy without transport of an electric charge. There are two types of Excitons:

1. Frenkel exciton which is found in organic molecular crystals [15] with binding energy of $1eV$ and radius of $10\mathring{A}$ and 2. Wannier exciton, found in in semiconductors [48] with binding energy of $1meV$ and radius of $100\mathring{A}$

Exciton have been observed in 2D materials [21, 41] and also as 2D Excitons in 3D materials. The promise here is that these kind of quasiparticles can help create a new kind of electronic components, typically opto-electronics.

Since the exciton system resembles the Hydrogen molecule, and it seems conceivable that the dynamics of $H2^+$ molecule is qualitatively similar and could be applied to the excitons systems as well.

The similar system is a Trion, which consists of either 2 electrons and a hole, or 2 holes and an electron, therefore resembling the hydrogen molecule.

Future Applications and Speculations

While the applications of the 2D materials above are certainly interesting, creating an exact analytical model of such material is extremely complex. Even with todays computing machinery, the wave equations for many bodies quantum system are unsolvable, even numerically. Equations for many

bodies systems may formally be created by extending equations for a one or two bodies systems. But as soon as one tries that, one realizes that the complexity of such equations increases enormously, and than assumptions made for a small systems are not valid any more. In this author's opinion, moving from a simple system to an order of magnitude more complex, requires a completely new mathematical and physical framework. Something analogous between the classical mechanics and thermodynamics.

Outline

While all the applications of the 2D materials above are certainly interesting and promising, it is doubtful that there is going to be an exact analytical model of the above systems. So, we turn our attention to the Hydrogen atom and molecule, which have provided, throughout history of physics, a starting point which we can analyze and use the results to predict the behavior of the more complex systems.

In this thesis we will focus on solving the simplest molecular system, namely Hydrogen Molecular Ion H_2^+ in 2 dimensions (2D in the further text), and solving such system in 2D exactly. In chapter 1 we will show that applying our method to the already solved and well known H_2^+ in 3D yields the same results. Then in chapter 2 we will follow the already well established procedure [9] to analytically solve the H_2^+. After providing an analytical solution, we will fall back to the numerical methods, in order to calculate the energy levels, and the potential curves,. In chapter 3 we use the results obtained to calculate the dynamics of such system, namely the Radiate Association process. In chapter 4 we again use the same results to calculate the Radiate Charge Transfer.

All this brings us to the next chapter, where we examine the Bates' paper and re-calculate the electron energies for Hydrogen Molecular Ion in 3D, by using different and arguably simpler approach.

chapterExisting Non-Relativistic Solution of the Hydrogen Molecular Ion in 3 Spatial Dimensions

In this chapter we review the method of Bates et al [9], and successfully reproduce the results, by finding the lowest eigenvalue of the H_2^+ system.

The subsequent studies and textbooks on the H_2^+ systems, rely on the Bates results. So any new approach for solving H_2^+ should be able to replicate the Bates' results exactly. TODO: Find experimental confirmation of the bates paper

Unfortunately there does not exist a closed form solution to the differential equation obtained after transforming the system to elliptical coordinates. So one must resort to using the numerical calculations to obtain the eigenvalues. The papers by Bates et all [9] [8] do not provide the numerical code used to obtain the solution. The paper states that they used the expanded fractions method, and it appears that they terminated the expansion at some point, after obtaining the desired precision. There are no details in the paper how they determined that the desired precision was achieved, whether the precision (and number of terms in the expansion) depended on the value of parameters, and so on. So basically the paper does not provide any details as to how the computation was performed.

The Hydrogen Molecule Ion, and similar systems, (HeH^+) represent the simplest molecular system to which we can apply the full quantum mechanical treatment. It is actually the only molecule for which we can solve the electronic Schroedinger equation exactly, although the solution does not exist in the closed form, but rather as an infinite series. The seminal study on Hydrogen Molecular Ion has been done by Bates et all [9] [8]. It has been studied extensively since then, and its solution is part of the molecular quantum theory textbooks (TODO add reference to Slater).

As it is customary, we will be using Hartree Atomic Units, in all equations. In this system the nu-

merical values of the following fundamental constants are 1:

$$m = e = \hbar = \frac{1}{4\pi\epsilon_0} = 1 \quad \text{and } \alpha = \frac{e^2}{4\pi\epsilon_0 \hbar c} \approx \frac{1}{137} \tag{1}$$

The only place where we specifically are not using Atomic units will be the following derivation, where we do transformation of the molecular Hamiltonian into a Jacobian coordinate system. Since some terms will contain reduced mass, we want to keep the units intact.

0.0.2 Description

The starting point is the Schrodinger equation for the hydrogen molecular ion. In this analysis we assume the stationary, non-relativistic case, and we neglect spin degrees of freedom. Following these assumptions the Schrodinger equation for such a system is given by:

$$\hat{H}' \psi (\mathbf{R}, \mathbf{x}) = E \, \psi (\mathbf{R}, \mathbf{x}) \tag{2}$$

$\hat{H}'$ represents total Hamiltonian and $\psi (\mathbf{R}, \mathbf{x})$ is the wavefunction describing the motion of the nuclei, with coordinate $\mathbf{R}$ and electrons with coordinate $\mathbf{x}$. Of course, since we are considering a molecular ion, the $\mathbf{x}$ is a coordinate of a single electron.

The Hydrogen Molecular Ion H_2^+ is composed of 2 protons and a single electron. Thus, because we are neglecting relativistic effects and spin, its Hamiltonian is given as:

$$\hat{H} = \hat{T}_n + \hat{T}_e + \hat{V}_{en} + \hat{V}_{nn} \tag{3}$$

The terms in the Hamiltonian are as follows:

$$\hat{T}_n = -\frac{\hbar^2}{2M}\sum_{i=1}^{2}\nabla_{R_i}^2 = -\frac{1}{2M}\sum_{i=1}^{2}\hat{P}_i^2 \tag{4}$$

represents the kinetic energy (operators) of the 2 protons in the molecule.

$$\hat{T}_e = -\frac{\hbar^2}{2m}\nabla_x^2 = -\frac{1}{2m}\hat{p}^2 \tag{5}$$

represents the kinetic energy (operators) of the single electron, and

$$\hat{V}_{en} = -\sum_{i=1}^{2}|\mathbf{R}_i - \mathbf{x}| \tag{6}$$

represents the potential energy (operators) between the electron and the nuclei, i.e. the total Coulomb electron - nuclei attraction.

$$\hat{V}_{nn} = \frac{e^2}{|\mathbf{R}_1 - \mathbf{R}_2|} \tag{7}$$

represents the potential energy (operators) between the nuclei - the total Coulomb proton - proton repulsion. The second term in the equation above represents the operator expression, in the atomic units (1).

In the equations above, the $\mathbf{R}_i$, $i = 1, 2$ and M represents the coordinates and mass of the nuclei (protons) respectively, and $\mathbf{x}$ and m are the coordinates and mass of the electron, respectively. The coordinates are defined with respect to a common origin, in a space fixed frame.

In classical mechanics, it is customary to separate the motion of the center of mass from the motion of the point particles. A similar approach can be applied for the quantum case. We show in appendix A that the motion of the center of mass will be a plane wave, which posses a well defined momentum and which is not square integrable. That makes the position of the center of mass equally probable in the hole space, which agrees with the Heisenberg uncertainty principle.

So we can solve for $\chi(\mathbf{R})$ to obtain:

$$\chi(\mathbf{R}) = \frac{1}{(2\pi\hbar)^{3/2}} e^{\frac{i}{\hbar}} \tag{8}$$

Therefore, we proceed to transform the Hamiltonian into a Jacobian coordinate system, following [6]. The outcome of this procedure will be the transformation of the wave function as $\psi(\mathbf{R}_i, \mathbf{r}) \rightarrow \psi(\mathbf{R}_{CM}, \mathbf{R}, \mathbf{r})$ where the $\mathbf{R}_{CM}$ is the coordinate of the center of the mass, R is the distance between nuclei and $\mathbf{r}$ is an electron coordinate. We choose the coordinates as:

$$\mathbf{R}_{CM} = \frac{M\,\mathbf{R}_1 + M\,\mathbf{R}_2 + m\,\mathbf{x}}{2M + m}$$

$$\mathbf{R} = \mathbf{R}_1 - \mathbf{R}_2 \tag{9}$$

$$\mathbf{r} = \mathbf{x} - \frac{\mathbf{R}_1 + \mathbf{R}_2}{2}$$

Now following [6], [13], we obtain the expression of the molecular Hamiltonian in the new coordi-
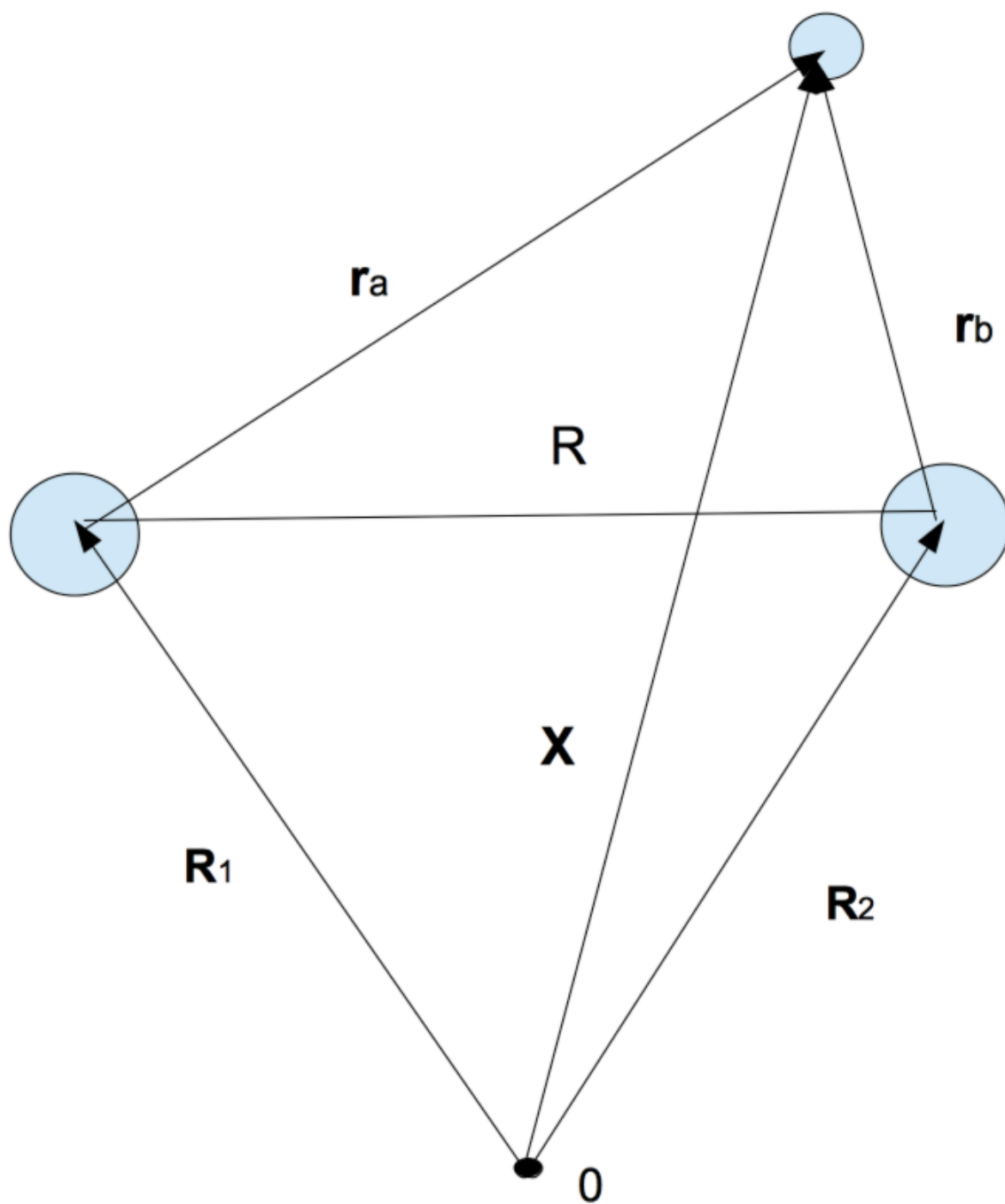
Figure 1: H2 Ion

nates,

$$H' = T_{CM} + T_{KE} + H_{AD} \quad \text{where}$$

$$T_{CM} = -\frac{1}{2(2M+m)}\nabla_{CM}^2$$

represents the motion of the center of the mass and can be separated from the total energy of the nuclei.

$$T_{KE} = -\frac{1}{2\mu}\nabla_R^2$$

represents the relative motion of the nuclei, and $\mu = \dfrac{M}{2}$ is a reduced mass of the 'bare' nuclei

(10)

and

$$H_{AD} = -\frac{1}{2m}\nabla_r^2 - \frac{1}{4M}\nabla_r^2 + \frac{1}{|R|} - \frac{1}{|r+R/2|} - \frac{1}{|r-R/2|}$$

(11)

represents the adiabatic Hamiltonian.

The second term in the expression for the H_{AD} represents the mass polarization term, and due to the $M \gg m$, it can be neglected. It represents the movement of the electron as the center of the mass is moving. However, the center of the mass is moving much slower than the electron, due to the mass difference, and thus justifies neglecting this term. TODO: Check mass polarizatin

Now we get for the Schrodinger equation:

$$T_{KE}\psi(\mathbf{R},\mathbf{r}) + H_{AD}\psi(\mathbf{R},\mathbf{r}) = E\,\psi(\mathbf{R},\mathbf{r})$$

(12)

where E is the internal energy of the nuclei - electron system. To develop a working theory we use

Born-Oppenheimer approximation. In it we solve for the electronic Hamiltonian in the Coulomb field of the nuclei, where the nuclei are assumed to be stationary with respect to inertial frame. In this case, the electronic Hamiltonian is the H_{AD} from (11). We neglect the mass polarization term and express the electronic Hamiltonian as:

$$H_{AD} = T_e + V_{NN} + V_{Ne} \quad \text{or}$$

$$H_{AD} = \frac{1}{2m}\nabla_r^2 + \frac{1}{|R|} - \frac{1}{|r + R/2|} - \frac{1}{|r - R/2|}$$

(13)

The Born-Oppenheimer approximation neglects the motion of the nuclei when describing the electron motion in a molecule. The physical basis for the approximation is the fact that the $m_p \approx 1836 m_e$, where m_p and m_e are the proton's and electron's mass respectively. Because of this mass difference, protons move much slower than the electrons. In addition, due to their opposite charges, there is an attractive Coulomb force between proton and electron. But the magnitude of the acceleration is inversely proportional to the mass, so the acceleration of the electron is large and the acceleration of the proton is small.

So at this step, we neglect the nuclear kinetic energy, effectively rendering the nuclei immobile. Following [42] we then solve for the motion of an electron in the Coulomb field of the nuclei, which leads to a following Schrodinger equation:

$$\left[-\frac{1}{2}\nabla_r^2 + V(\mathbf{R};\mathbf{r}) \right] u(\mathbf{R};\mathbf{r}) = E(\mathbf{R})u(\mathbf{R};\mathbf{r})$$

(14)

Now the equation (14) is the Schrodinger equation for the electron only, moving in the potential

$V(\mathbf{R}; \mathbf{r})$ with the coordinate $\mathbf{r}$. The electron's wavefunction $u(\mathbf{R}, \mathbf{r})$ and the energy $E(\mathbf{R}$ both depend on the position of the nuclei $\mathbf{R}$ as a parameter. The last step in Born-Oppenheimer approximation is to solve the Schrodinger equation for the nuclei, using the above calculated $E(\mathbf{R})$ as a potential energy, which leads to a following equation.

$$\left[-\frac{1}{2}\nabla_R^2 + E(\mathbf{R}) \right] v(\mathbf{R}) = \epsilon v(\mathbf{R}) \tag{15}$$

Once these operations are carried, the Born-Oppenheimer approximation states that the energy ϵ is a good approximation of the energy levels of the exact Schrodinger equation (2) As a result, the total molecular wave function is separated into the electronic and the nuclear wavefunction.

$$\psi(\mathbf{R}, \mathbf{r}) = u(\mathbf{R}; \mathbf{r})v(\mathbf{R}) \tag{16}$$

In addition, each electronic eigenvalue $E_n(R)$ will give a rise to the electronic surface, known as Born-Oppenheimer surfaces. Therefore the full internuclear potential will be given as $V_{NN}(R) + E_n(R)$.

One could proceed further for the complete treatment of the Born-Oppenheimer approximation, for example dealing with the Born-Oppenheimer diagonal correction [39], but it will go beyond the scope of this thesis .

So at this moment, using BO approximation we have a Schrodinger equation for the electron, orbiting the two nuclei (each consisting of a single proton). Note that in the further text the ψ will denote the function $u(\mathbf{R}; \mathbf{r})$, since it is customary to denote the wave function as ψ. On somewhat unrelated note, the universe of functions, used in physics is quite a big larger than the Greek and Latin alphabet combined. Perhaps it is time to branch out and starti considering languages like San-

skrit or Hebrew as source of symbols for various physical quantities.

0.0.3 Replicating the Solution

Following the seminal papers by Bates et. all. [9] [8], we can re-express the equation 1.1 as:

$$\left(-\frac{1}{2}\nabla^2 - \frac{1}{r_a} - \frac{1}{r_b}\right)\psi = E\,\psi \tag{17}$$

where $r_a = \left|\mathbf{r} - \frac{1}{2}\mathbf{R}\right|$ and $r_b = \left|\mathbf{r} + \frac{1}{2}\mathbf{R}\right|$ are distances of the electron from the nuclei.

Due to the cylindrical symmetry of the problem, we choose the elliptical coordinates. In the [9], the authors chose the confocal elliptic co-ordinates, which transforms the coordinates r_a and r_b from (17) into:

$$r_a = \frac{R}{2}(\lambda + \mu)\,, \quad r_a = \frac{R}{2}(\lambda - \mu) \tag{18}$$

After applying the coordinate transformations (18) into the equation (17), we obtain another partial differential equations [9]:

$$\frac{d}{d\lambda}\left\{(\lambda^2 - 1)\frac{d\psi}{d\lambda}\right\} + \frac{d}{d\mu}\left\{(1 - \mu^2)\frac{d\psi}{d\mu}\right\} + \left\{\frac{1}{\lambda^2 - 1} + \frac{1}{1 - \mu^2}\right\}\frac{d^2\psi}{d\phi^2} + \left\{\frac{1}{4}R^2 E(\lambda^2 - \mu^2) + 2R\lambda\right\}\psi = 0 \tag{19}$$

We assume that the solution is the product of the functions of the single variable, λ, μ, ϕ. Under

this assumption the solution can written as:

$$\psi(\lambda, \mu, \phi) = L(\lambda)M(\mu)e^{im\phi} \quad \text{where is} \quad p^2 = -\frac{1}{4}R^2E \qquad (20)$$

In this equation the L, M are the functions of their respective coordinates, and m is an integer, either positive or negative. The next step is to insert the ansatz (20) into the Eq (19) . After some algebra, one observes that the equation (19) separates into the system of two ordinary, coupled differential equations. an

$$\frac{d}{d\mu}\left\{(1-\mu^2)\frac{dM}{d\mu}\right\} + \left\{-A + p^2\mu^2 - \frac{m^2}{1-\mu^2}\right\}M = 0 \qquad (21)$$

$$\frac{d}{d\lambda}\left\{(\lambda^2-1)\frac{dL}{d\lambda}\right\} + \left\{A + 2R\lambda - p^2\lambda^2 - \frac{m^2}{\lambda^2-1}\right\}L = 0 \qquad (22)$$

Following the method given by Bates et al., [9], we assume the solution to equation (21) expressed as the series of associated Legendre polynomials. Following the same methid, the solution to the equation (22) is also expressed to be the power series. In [9], Bates et al. obtain two set of continued fraction [9, eq:14-17] and follow method of Stratton [43] in solving equation (22).

In [9], Bates et al. state that they used the method of successive approximation to found the coefficients in the seriers. It was tacitly assumed that the successive approximation themselves converge. The approximation is terminated either when the desired precision is achieved of when the certain number of approximation is met. However the details of the numerical calculation are not provided in the paper.

We chose to follow somewhat different approach. Following Zygelman TOOD: Add citation, We

expressed equations (21),(22) as a matrix eigenvalue problem. Since it is a Sturm-Liouville problem, or more precisely a system of 2 Sturm-Liouville problems, our approach is fundamentally the same approach as taken by Bates. but it is more practical, as it can better accommodate the existing numerical software. There exist excellent numerical packages [23] for computing the matrix eigenvalues, and they greatly simplify the actual computation. The system (21),(22) of the two ODEs then depend on the two parameters, total energy E, and the separation constant A. The problem is reduced to finding those values of E and A for which the solution to the differential equation satisfy the requisite boundary conditions.

We express both function $M(\mu)$ and $L(\lambda)$ using the set of orthogonal functions which satisfy the boundary conditions. We then follow the method of Frobenius. Once we replace the assumed solution into the equation and after some algebra, we obtain effectively two uncoupled, infinite systems of equations, where the unknowns are the coefficients in the solution series. The solution vector depends on the two parametes, p, which is the function of energy and A which is the separation constant.

The next step is rather simple. For functions $M(\mu)$ and $L(\lambda)$, we need to find the functional dependency of the parameters p and A, so that solution exists. The intersections of the two curves $p_1 = f(A_1)$ and $p_2 = g(A_2)$ provides the value of p and A when the condition for the solutions exists. The desired precision is obtained by choosing the size number of terms in the series.

The renaming issue is that even with the modern fast computers and optimized numerical libraries [23], calculating eigenvalues is a slow process. The complexity of the QR decomposition algorithm is $O(n^3)$, and TODO: Add reference the best algorithm has the complexity of $O(n^\omega, 2 < \omega \leq 3$.

0.0.4 SERIES EXPANSIONS AND EIGENVALUE DETERMINANT

Here we describe in details the method describe in the previous section.

L EQUATION

Start with:

$$\frac{d}{d\lambda}\left\{(\lambda^2-1)\frac{d\Lambda}{d\lambda}\right\} + \left\{A - p^2\lambda^2 + 2R\lambda\right\}\Lambda = 0 \Rightarrow$$

$$(\lambda^2-1)\frac{d^2\Lambda}{d\lambda^2} + 2\lambda\frac{d\Lambda}{d\lambda} + \left\{A - p^2\lambda^2 + 2R\lambda\right\}\Lambda = 0 \tag{23}$$

For practical reasons we first shift the L equation b $x = \lambda - 1$ to obtain:

$$\frac{d}{dx}\left\{x(x+2)\frac{d\Lambda}{dx}\right\} + \left\{-p^2\,x^2 + (-2p^2 + 2R)x - p^2 + 2R + A\right\}\Lambda = 0$$

$$x(x+2)\frac{d^2\Lambda}{dx^2} + (2x+2)\frac{d\Lambda}{dx} + \left\{-p^2\,x^2 + (-2p^2 + 2R)x - p^2 + 2R + A\right\}\Lambda = 0 \tag{24}$$

Now we assume that the solution exists and that it can be represented as the sum of Laguerre polynomials:

$$\Lambda(x) = e^{-px}\sum_{n=0}^{\infty} c_n\, L_n(x) \tag{25}$$

Inserting the ansatz (25) into (24), applying the properties of Laguerre's polynomial some algebra we

obtain.

$$
- 2p \sum_{n=0}^{\infty} c_n \, n(2n+1) L_n + 2p \sum_{n=0}^{\infty} c_{n+1} \, n(n+1) L_{n+1} + 2p \sum_{n=0}^{\infty} c_{n-1} \, n^2 L_{n-1}+
$$

$$
+ (2p-1) \sum_{n=0}^{\infty} c_{n-1} n(2n-1) L_{n-1} - (2p-1) \sum_{n=0}^{\infty} c_n n^2 L_n-
$$

$$
- (2p-1) \sum_{n=0}^{\infty} c_{n-2} n(n-1) L_{n-2} + (-2p+2R) \sum_{n=0}^{\infty} c_n (2n+1) L_n-
$$

$$
- (-2p+2R) \sum_{n=0}^{\infty} c_{n+1} (n+1) L_{n+1} - (-2p+2R) \sum_{n=0}^{\infty} c_{n-1} n L_{n-1}+
$$

$$
+ (-4p+1) \sum_{n=0}^{\infty} c_n \, n \, L_n + (4p+1) \sum_{n=0}^{\infty} c_{n-1} \, n \, L_{n-1}+
$$

$$
+ (-2p - p^2 + 2R + A) \sum_{n=0}^{\infty} c_n \, L_n = 0
$$

(26)

The next step is to multiply the equation (26) with $e^{-x} L_m(x)$ and integrate from 0 to ∞ using the orthogonality property of the Laguerre's polynomials: $\int_0^{\infty} dx \, e^{-x} L_n(x) L_m(x) = \delta_{mn}$ to obtain

the recurrence equations for the unknown coefficients c_n

$$- 2p\, n(2n + 1)c_n + 2p\, n(n + 1)c_{n+1} + 2p\, n^2 c_{n-1} + (2p - 1)n(2n - 1)c_{n-1} -$$

$$- (2p - 1)n^2 c_n - (2p - 1)n(n - 1)c_{n-2} + (-2p + 2R)(2n + 1)c_n -$$

$$\tag{27}$$

$$- (-2p + 2R)(n + 1)c_{n+1} - (-2p + 2R)nc_{n-1} + (-4p + 1)\, n\, c_n +$$

$$+ (4p + 1)\, n\, c_{n-1} + (-2p - p^2 + 2R + A), c_n = 0$$

This expression (27) is a system of linear equations, where the unknowns are the coefficients c_n. The coefficients multiplying the unknowns c_n in (27) form the band matrix.

M Equation

We the same approach for the M equation.

$$\frac{d}{d\,\mu} \left\{ (1 - \mu^2)\, \frac{d\,M}{d\,\mu} \right\} + \left(-A + p^2\mu^2 \right) M(\mu) = 0 \tag{28}$$

We express the $M(\mu)$ as the series of Legendre polynomials.

$$M(\mu) = \sum_{n=0}^{\infty} f_n\, P_n(\mu) \tag{29}$$

where

$$\int_{-1}^{1} P_m(x)P_n(x)dx = \frac{2}{2m + 1}\delta_{m,n} \tag{30}$$

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Substituting (29) into (28), multiplying by $P_m(\mu)$, and integrating from -1 to 1 we obtain

$$\sum_{n=0}^{\infty} \left\{ - \int_1^1 P_m(\mu)n(n+1)P_n(\mu)d\mu - A \int_1^1 P_m(\mu)P_n(\mu)d\mu + \right.$$

$$\left. + p^2 \int_1^1 P_m(\mu)\mu^2 P_n(\mu)d\mu \right\} = 0 \quad \text{or} \tag{31}$$

$$\sum_{n=0}^{\infty} \left\{ \frac{-2}{2n+1}n(n+1)\delta_{m,n} - A\frac{2}{2n+1}\delta_{m,n} + p^2 \int_1^1 P_m(\mu)\mu^2 P_n(\mu)d\mu \right\} = 0$$

Taking advantage of the orthogonality of Legendre Polynomials (30), we obtain a system of linear equations, where the coefficients form a band matrix.

$$\sum_{n=0}^{\infty} \left\{ \frac{-2n(n+1)}{2n+1}\delta_{m,n} - A\frac{2}{2n+1}\delta_{m,n} + \right.$$

$$+ p^2 \frac{2}{2n+1} \left[\frac{(n+1)^2}{(2n+1)(2n+3)} + \frac{n^2}{(2n+1)(2n-1)} \right] \delta_{m,n} + \tag{32}$$

$$\left. p^2 \frac{2(n+1)(n+2)}{(2n+1)(2n+3)(2n+5)}\delta_{m,n+2} + p^2 \frac{2\,n(n-1)}{(2n+1)(2n-1)(2n-3)}\delta_{m,n-2} \right\} = 0$$

NUMERICAL CALCULATION

Equations (27) and (32) constitute the couple system of linear equation. Each series is parametrized by 2 parameters, p and A, as well as the parameter R, the distance between nuclei. We select the values of R as shown in table 1.1. We tacitly assume that the series (25) (28) converge, moreover, we assume that they converge uniformly. Therefore, we truncate the series at some index $i = K, chosentoachievethedesiredaccuracy..$ So now the coefficient matrices are dimensions $K \times K$ and each matrix has K eigenvalues, and the lowest eigenvalue corresponds to the lowest

value of p, thus to the lowest energy.

In next step, for each value of R, we calculate the eigenvalues, sort them, and pick the lowest (or the i-th one from the bottom), and view them as functions $A = A(p)$. So for each of the equations (27) and (32), we choose the interval $[0, 2 * R]$ and divide it into N points $p_i, i = 1..N$. For each point, we calculate, sort and pick desired the eigenvalue of the matrix M (L). That way we obtain two functions $A_M = A_M(p)$ and $A_L = A_L(p)$, evaluated at points p_i. We interpolate these two functions, using Wolfram's Mathematica 3-rd order Spline interpolation. As a side note, for a small subset of values R we used the higher order Spline interpolation but we were unable to observe the difference in the results obtained. The intersection of these two curves in the value of p for which both $M(\mu)$ and $L(\lambda)$ equations have results satisfying the boundary conditions. Now repeat for the next value of R.

After all this exercise, we get the function $E = E(R)$, from (14) which is the electron energy in the BO approximation. Adding the potential energy between nuclei is $V(R) = 1/R$, we obtain the potential energy curve. The paper by Bates does not explicitly use this curve to calculate the vibrational energies, but we will, in our 2D case.

For illustration purposes we present some of the results below.

Plot of the ground state energies $E(R)$ and $E(R) + V(R)$ where $V(R) = \frac{1}{R}$ represents the potential energy of the nuclei.
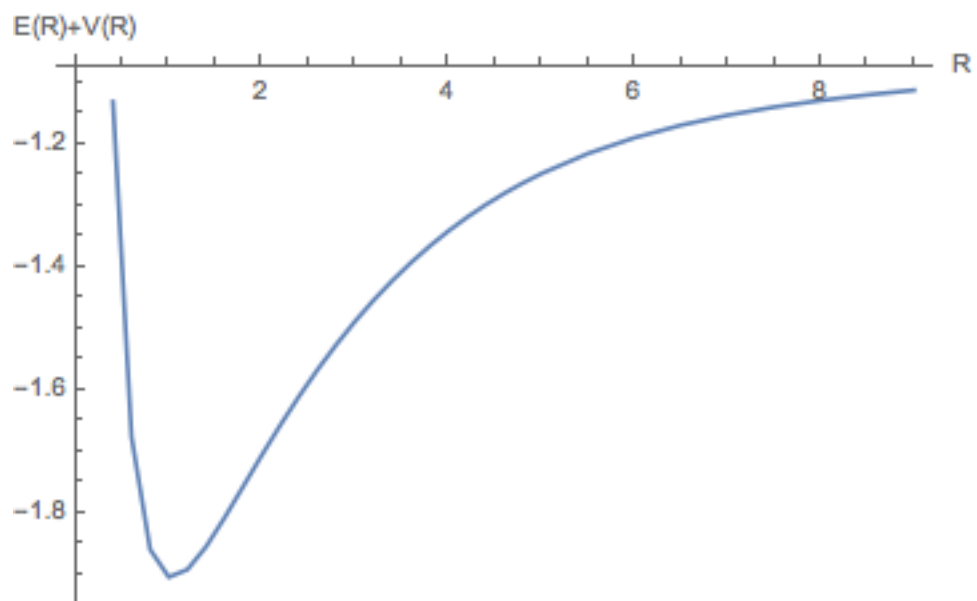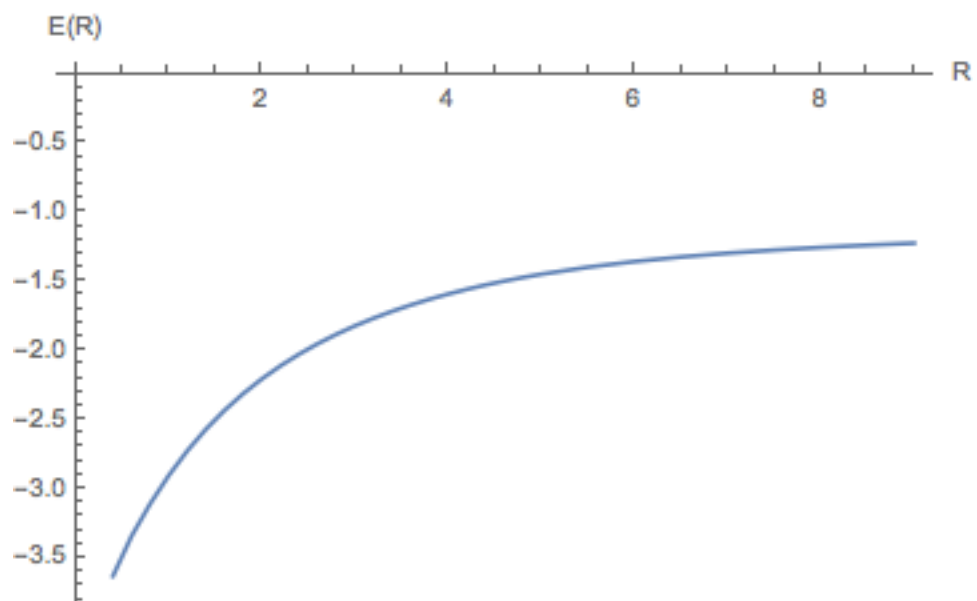
Electron energy as an eigenvalue of the equations (27) and (32).

Total energy, calculated by adding the potential energy of the nuclei $V(R) = 1/R$.

Electron energy as an eigenvalue of the equations (27) and (32).

Table comparing the eigen energies obtain using our method vs method applied by Bates et al. We

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chose a subset of values to indicate the overall trend.

afterpage

Table 1: Electron Energy, $1s\sigma_g$ state

R	-E(R) (Bates)	-E(R) (out method)
0.4	3.60157	3.632200
0.6	3.34301	3.3429676
0.8	3.10895	3.1089586
1.0	2.90356	2.9035720
1.2	2.72461	2.7246154
1.4	2.56853	2.5685373
1.6	2.43186	2.4318740
1.8	2.31162	2.3116176
2.0	2.20525	2.2052681
2.2	2.11076	2.1107695
2.4	2.02642	2.0264405
2.6	1.95090	1.9508966
2.8	1.88299	1.8829977
3.0	1.82178	1.8217919
3.2	1.76647	1.7664850
3.4	1.71639	1.7164029
3.6	1.67097	1.6709739
3.8	1.62971	1.6297050
4.0	1.59216	1.5921695
4.2	1.55799	1.5579948
4.4	1.52685	1.5268516
4.6	1.49844	1.4984480
4.8	1.47252	1.472523
5.0	1.44884	1.448840

Non-Relativistic Solution of the Hydrogen Molecular Ion in 2 Spatial Dimensions

1.0.1 Existing solutions

We apply the method used in the 3D case of the H_2^+ ion to find the solution in 2 dimensions. The problem itself is analogous to the 3D problem, but leads to the Mathieu's function like solution for the radial problem.

TODO: Move after There are not too many papers dealing with solving the H_2^+ but here is some relevant, and recent work in this problem. [31]. TODO: Add more citations. As with other work in this problem, the paper relies on the work done by Bates et all. [9]. The solution in [31] agrees well with our solution TODO: Verify. There are other solutions, but they rely on the approximative methods, and should be considered inferior to the analytical solution, we provide here.

Following the 3D case, we rely on Born-Oppenheimer (BO) approximation, in order to provide an analytical solution. The justification for using the BO approximation applies to the 2D problem as well, since the masses of the nuclei and electron(s) remain unchanged.

Following the same BO approximation as in Chapter 1, and using atomic units, the Schrodinger equation for the H_2^+ molecules is given by equation (1.1) below. The geometry of the 2D problem leads to choosing the elliptical coordinates as well, with two coordinates, μ and λ.

$$\left(-\frac{1}{2}\nabla^2 - \frac{1}{r_a} - \frac{1}{r_b}\right)\psi = E\,\psi \tag{1.1}$$

The equation (1.1) is superficially similar to the equation (17) and the diagram 1, but in this case, the r_a and r_b are vectors in 2 dimensions.

The electron wavefunction depends on only 3 quantum numbers, principal quantum number n, angular quantum number l and spin s. Again we ignore the spin degrees of freedom,considering the electron to be the regular 3 dimensional particles, where only its orbit is restricted to 2 dimensions. Therefore the spin magnetic moment of the electron is not affected by the 2D restriction and the spin vector can point in any direction in 3D space. Also the orbit can have different shapes, thus there remains the need for an orbital quantum number. However, there can be one one orientation of the orbit, thus we do not consider the magnetic quantum number. This reasoning agrees with The solution of the electron wavefunction to the hydrogen atom in 2 dimensions [51] where electron wavefunction solution only depends on the principal and orbital quantum numbers.

TODO: Add references and more text

1.0.2   Exact solution of the H_2^+ electronic Hamiltonian

The goal is to provide the exact solution to the wavefunction of the H_2^+ electron, for a given definition of exact. However even for this, relatively simple problem, it is impossible to find a closed form solution. So the solution is exact, in a sense that it can be done to an arbitrary precision.
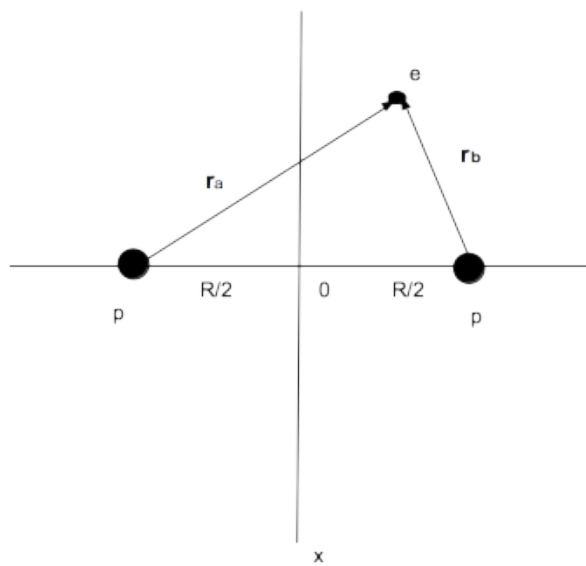
Figure 1.1: H2 Ion in 2D

As illustrated by the figure 1.1, we express equation (1.1) in the elliptical coordinates, and by setting the x axis to be perpendicular to the internuclear axis, we have the nuclei at: $y = \pm\frac{R}{2}$, R being the distance between nuclei. So in 2D elliptic coordinates, λ, μ we have

$$\lambda = (r_a + r_b)/R; \qquad \mu = (r_a - r_b)/R$$

$$\text{where } \lambda \in [1, \infty], \qquad \mu \in [-1, 1] \qquad \text{and} \tag{1.2}$$

$$r_a = \frac{R}{2}(\lambda + \mu) \qquad r_b = \frac{R}{2}(\lambda - \mu)$$

We assume that the total electronic wavefunction can be written as the product of two functions:

$$\psi(\lambda, \mu) = F(\mu)G(\lambda) \tag{1.3}$$

This way the original equation separates into two ODEs:

$$(\lambda^2 - 1)\frac{d^2}{d\lambda^2}G(\lambda) + \lambda\frac{d}{d\lambda}G(\lambda) + \left(A + \frac{E\,R^2}{2}\lambda^2 + 2R\lambda\right)G(\lambda) = 0 \tag{1.4}$$

$$(1 - \mu^2)\frac{d^2}{d\mu^2}F(\mu) - \mu\frac{d}{d\mu}F(\mu) + \left(-A - \frac{E\,R^2}{2}\mu^2\right)F(\mu) = 0 \tag{1.5}$$

where

$$p^2 = -\frac{E\,R^2}{2} \tag{1.6}$$

A is the separation constant. To eliminate the singularities, and following [31] we introduce two new

functions:

$$F(\mu) = (1 - \mu^2)^{k/2} M(\mu)$$

$$G(\lambda) = (\lambda^2 - 1)^{k/2} L(\lambda)$$

(1.7)

to obtain

$$\frac{d\,F}{d\mu} = (1 - \mu^2)^{k/2}\frac{d\,M}{d\mu} - k\mu(1 - \mu^2)^{k/2-1} M(\mu)$$

$$\frac{d^2\,F}{d\mu^2} = (1 - \mu^2)^{k/2}\frac{d^2\,M}{d\mu^2} - 21Gk\mu(1 - \mu^2)^{k/2-1}\frac{d\,M}{d\mu} +$$

$$+ \left[2\left(\frac{k}{2} - 1\right)k\mu^2\left(1 - \mu^2\right)^{k/2-2} - k(1 - \mu^2)^{k/2-1}\right]M$$

(1.8)

$$\frac{d\,G}{d\lambda} = (\lambda^2 - 1)^{k/2}\frac{d\,L}{d\lambda} + k\lambda(\lambda^2 - 1)^{k/2-1} L(\lambda)$$

$$\frac{d^2\,G}{d\lambda^2} = (\lambda^2 - 1)^{k/2}\frac{d^2\,L}{d\lambda^2} + 2k\lambda(\lambda^2 - 1)^{k/2-1}\frac{d\,L}{d\lambda} +$$

$$+ \left[2\left(\frac{k}{2} - 1\right)k\mu^2\left(\lambda^2 - 1\right)^{k/2-2} - k(\lambda^2 - 1)^{k/2-1}\right]L$$

(1.9)

Plug in:

$$(1 - \mu^2)(1 - \mu^2)^{k/2}\frac{d^2\,M}{d\mu^2} - (1 - \mu^2)2k\mu(1 - \mu^2)^{k/2-1}\frac{d\,M}{d\mu} +$$

$$+ (1 - \mu^2)\left[2\left(\frac{k}{2} - 1\right)k\mu^2\left(1 - \mu^2\right)^{k/2-2} - k(1 - \mu^2)^{k/2-1}\right]M -$$

$$- \mu(1 - \mu^2)^{k/2}\frac{d\,M}{d\mu} + k\mu^2(1 - \mu^2)^{k/2-1}M(\mu) +$$

$$+ \left(-A - \frac{E\,R^2}{2}\mu^2\right)(1 - \mu^2)^{k/2}M(\mu) = 0$$

(1.10)

Or dividing by $(1 - \mu^2)^{k/2}$:

$$(1 - \mu^2)\frac{d^2\,M}{d\mu^2} - (2k + 1)\mu\frac{d\,M}{d\mu} + \left[A - \frac{E\,R^2}{2}\mu^2 + k(k - 1)\frac{\mu^2}{1 - \mu^2} - k\right]M = 0 \quad (1.11)$$

And for the other equation, plug in:

$$(\lambda^2 - 1)(\lambda^2 - 1)^{k/2}\frac{d^2\,L}{d\lambda^2} + (\lambda^2 - 1)2k\lambda(\lambda^2 - 1)^{k/2-1}\frac{d\,L}{d\lambda} +$$

$$+ \left[2\left(\frac{k}{2} - 1\right)k\lambda^2\left(\lambda^2 - 1\right)^{k/2-2} - k(\lambda^2 - 1)^{k/2-1}\right](\lambda^2 - 1)L +$$

$$+ \lambda(\lambda^2 - 1)^{k/2}\frac{d\,L}{d\lambda} + k\lambda^2(\lambda^2 - 1)^{k/2-1}L(\lambda) +$$

$$+ \left(A + \frac{E\,R^2}{2}\lambda^2 + 2R\lambda\right)(\lambda^2 - 1)^{k/2}L(\lambda) = 0$$

(1.12)

Or dividing by $(\lambda^2 - 1)^{k/2}$:

$$(\lambda^2 - 1)\frac{d^2\,L}{d\lambda^2} + (2k + 1)\lambda\frac{d\,L}{d\lambda} + \left[A + \frac{E\,R^2}{2}\lambda^2 + 2R\lambda - k + k(k - 1)\frac{\lambda^2}{\lambda^2 - 1}\right]L = 0$$

(1.13)

To make both $M(\mu)$ and $L(\lambda)$ non singular at $\mu, \lambda = 1$ we must have the $k = 0, 1$. So the equations reduces to:

$$(1 - \mu^2)\frac{d^2 M}{d\mu^2} - (2k + 1)\mu\frac{d M}{d\mu} + \left[A - \frac{E R^2}{2}\mu^2 - k\right] M(\mu) = 0 \qquad (1.14)$$

$$(\lambda^2 - 1)\frac{d^2 L}{d\lambda^2} + (2k + 1)\lambda\frac{d L}{d\lambda} + \left[A + \frac{E R^2}{2}\lambda^2 + 2R\lambda - k\right] L(\lambda) = 0 \qquad (1.15)$$

Effectively the choice of parameter k determines the parity of the solution. At this point we set:

$$p^2 = -\frac{ER^2}{2} \qquad (1.16)$$

And proceed with solving each equation separately:

M EQUATION

Using the substition $\mu = \cos x$ we get the other form of the equation:

$$M''(x) - 2kM'(x) + \left[A - k + \frac{p^2}{2} + \frac{p^2}{2}\mu^2 \cos(2x)\right] M(x) = 0 \qquad (1.17)$$

The equation (1.17) is a form of a angular Mathieu's equation [29], thus we look for the solution in

the form of:

$$M(\mu) = \sum_{n=1}^{\infty} a_n e^{i2nx} \tag{1.18}$$

The solution depends on the chosen boundary conditions. The angular Mathieu's equation admits an even and odd solution, with respect to the origin. The parity of the solution is chosen depending on the boundary conditions for a particular problem. Therefore

For the even case, the boundary condition is

$$M(\mu = 1) = M(\mu = -1) = 1 \, ; \; \Rightarrow M'(0) = M'\left(\frac{\pi}{2}\right) = 0 \Rightarrow \tag{1.19}$$

The solution is then in the form

$$M(\mu) = \sum_{n=1}^{\infty} a_n \cos(n\,\mu)$$

And for the odd case, take the boundary conditions:

$$M(\mu = 1) = 1 \, ; \; M(\mu = -1) = -1 \, ; \; \Rightarrow M(0) = M'\left(\frac{\pi}{2}\right) = 0 \Rightarrow \tag{1.20}$$

The solution is then in the form:

$$M(\mu) = \sum_{n=1}^{\infty} a_n \sin\left[(2n+1)\,\mu\right] \tag{1.21}$$

From now on, the solution to the equation for $M(\mu)$ (1.17) is straightforward. Set the boundary conditions, and express $M(\mu)$ in the series of sine or cosine functions.

L Equation

$$(\lambda^2 - 1)\frac{d^2 L}{d\lambda^2} + (2k + 1)\lambda\frac{d L}{d\lambda} + \left[A + \frac{E R^2}{2}\lambda^2 + 2R\lambda - k\right] L(\lambda) = 0 \qquad (1.22)$$

The equation for the $L(\lambda)$ looks similar to the radial (modified) Mathieu equation, but unfortunately, it is not. However it is possible that the solution could be found using the same technique as for the radial equation, by expressing the solution as a series of functions. For the radial equation, the solution may exists int the form of the sum of Bessel functions [16]. TODO: verify,

We observe that both equations for the function $M(\mu)$ and $L(\lambda)$ are related to the Mathieu's equations. In general the Mathieu's equation represents the standing wave on an elliptical drum, (2D space), and the solution for the Schroedinger equation is in general a standing wave, in 2D in this case.

For the equation (1.22) one could proceed by following the radial Mathieu's equations approach. One way to solve the Radial Mathieu's equation is by using the series of hyperbolic functions, obtained from the solution of angular Mathieu's equation using the substitution $\eta = i\xi$. But that this approach in numerically unstable and hard to compute [16]. There is another approach, using the product of Bessel Functions [16]

We took a different approach to solving the equation (1.22), namely look for the solution in the form of the series of orthogonal functions. This approach has some challenges, since there are number of functions orthogonal on a finite interval, and one can choose the one which fits the problem the best. On an infinite interval, such as $\lambda = [1, \infty]$ the choice is somewhat limited. The Laguerre's

polynomial seemed like a suitable choice, as they form an orthogonal set on the infinite interval. So we look for the solution in the form:

$$L(\lambda) = e^{-p\lambda} \sum_{n=0}^{\infty} c_n \, L_n(\lambda) \tag{1.23}$$

Where $L_n(\lambda)$ are Laguerre polynomials. They have several interesting properties, which can be found in [2].

Towards the solution

So using the solutions above, the next step is to find the eigenvalues A, p, of the equations (1.14) and (1.22) for the values of $k = 0, 1$. Using the series above, for each equation, we find function $A_i(p)$ for which the solution exists. The intersection of the two functions $A_i(p)$ is the value of p common for both equations (1.14) (1.22). This procedure translates into the matrix eigenvalues problem, following the steps below.

For the even M equation, we insert the solution (1.19) in the equation eqFinal, multiply by $\cos(2m\,x)$,

$m = 0, 1, 2, ...$ and integrate. Since the basis functions in the series are orthogonal we obtain:

$$\sum_{n=0}^{\infty} c_k \left\{ -4n^2 \int_{-\pi/2}^{\pi/2} \cos(2mx)\cos(2nx)dx + \left[\frac{p^2}{2} + k\right] \int_{-\pi/2}^{\pi/2} \cos(2mx)\cos(2nx)dx + \right.$$

$$\left. + \left[\frac{p^2}{2} + k\right] \int_{-\pi/2}^{\pi/2} \cos(2x)\cos(2mx)\cos(2nx)dx \right\} =$$

$$= A \int_{-\pi/2}^{\pi/2} \cos(2mx)\cos(2nx)dx \implies$$

$$(1.24)$$

or

$$\frac{p^2}{2}\pi\,\delta_{0,0} + \left[\frac{p^2}{2} + k\right]\frac{\pi}{2}\delta_{0,1} + \left[\frac{p^2}{2} + k\right]\frac{\pi}{2}\delta_{1,0} + \sum_{m=1}^{\infty}\sum_{n=1}^{\infty}\left(-4n^2 + \frac{p^2}{2}\right)\frac{\pi}{2}\delta_{m,n} +$$

$$+ \left[\frac{p^2}{2} + k\right]\frac{\pi}{4}\delta_{m,n+1} + \left[\frac{p^2}{2} + k\right]\frac{\pi}{4}\delta_{m,n-1} = A\pi\,\delta_{0,0} + \sum_{m=1}^{\infty}\sum_{n=1}^{\infty} A\frac{\pi}{2}\delta_{m,n} \implies$$

$$p^2\delta_{0,0} + \left[\frac{p^2}{2} + k\right]\delta_{0,1} + \left[\frac{p^2}{2} + k\right]\delta_{1,0} + \sum_{m=1}^{\infty}\sum_{n=1}^{\infty}\left\{ -4k^2\,\delta_{m,n} + \frac{p^2}{2}\,\delta_{m,n} + \left[\frac{p^2}{4} + k\right]\delta_{m,n\pm1} \right\} =$$

$$= 2A + \sum_{m=1}^{\infty}\sum_{n=1}^{\infty} A\,\delta_{m,n}$$

$$(1.25)$$

For the odd case, inseert the equation (1.21) in the equation eqFinal, multiply by $\sin[(2m+1)\,x]$,

$m = 0, 1, 2, 3...$ and integrate (again exploiting the orthogonality of the basis functions):

$$\sum_{n=0}^{\infty} c_k - (2n+1)^2 \int_{-\pi/2}^{\pi/2} \sin[(2m+1)x]\sin[(2n+1)x]dx + \left[\frac{p^2}{2}+k\right]\int_{-\pi/2}^{\pi/2}\sin[(2m+1)x]\sin[(2n+1)x]dx+$$

$$+\left[\frac{p^2}{2}+k\right]\int_{-\pi/2}^{\pi/2}\cos(2x)\sin[(2m+1)x]\sin[(2k+1)x]dx = A\int_{-\pi/2}^{\pi/2}\sin[(2m+1)x]\sin[(2k+1)x]dx \implies$$

$$(1.26)$$

$$\left[-\frac{\pi}{2}+\frac{\pi}{2}\frac{p^2}{2}-\frac{\pi}{4}\frac{p^2}{2}\right]\delta_{0,0} + \frac{\pi}{4}\left[\frac{p^2}{2}+k\right]\delta_{0,1} + \left[\frac{\pi}{4}+k\right]\frac{p^2}{2}\delta_{1,0}+$$

$$+\sum_{m=1}^{\infty}\sum_{n=1}^{\infty}\left[-(2n+1)^2+\frac{p^2}{2}\right]\frac{\pi}{2}\delta_{m,n} + \left[\frac{p^2}{2}+k\right]\frac{\pi}{4}\delta_{m,n\pm 1} = \qquad (1.27)$$

$$= A\frac{\pi}{2}\delta_{0,0} + A\frac{\pi}{2}\sum_{m=1}^{\infty}\sum_{n=1}^{\infty}\delta_{m,n} \implies$$

$$\left(-1+\frac{p^2}{4}\right)\delta_{0,0} + \left[\frac{p^2}{4}+k\right]\delta_{0,1} + \left[\frac{p^2}{4}+k\right]\delta_{1,0}+$$

$$+\sum_{m=1}^{\infty}\sum_{n=1}^{\infty}\left(-(2n+1)^2+\frac{p^2}{2}\right)\delta_{m,n} + \left[\frac{p^2}{4}+k\right]\delta_{m,n\pm 1} = \qquad (1.28)$$

$$= A\delta_{0,0} + A\sum_{m=1}^{\infty}\sum_{n=1}^{\infty}\delta_{m,n}$$

For the L equation, first by shifting the origin $x = \lambda - 1$ and by using various properties of Laguerre

polynomials and its derivatives [2] we obtain.

$$\sum_{n=0}^{\infty} c_n \left\{ \sum_{i=0}^{n-1} L_i(x) + \right.$$

$$+ \left[-2pn(2n+1) - (2p-1)n^2 - 4pn + (2R-p)(2n+1) - p^2 - p + 2R \right] L_n +$$

$$+ \left[2pn(n+1) - (2R-p)(n+1) \right] L_{n+1} +$$

$$+ \left[2pn^2 + (2p-1)n(2n-1) + (4p-2)n - (2R-p)n \right] L_{n-1} -$$

$$\left. - \left[(2p-1)n(n-1) \right] L_{n-2} \right\} \tag{1.29}$$

Now multiply by $L_m(x)$ and use the orthogonality of Laguerre's polynomials.

$$\int_0^\infty \sum_{n=0}^{\infty} c_n \sum_{m=0}^{\infty} L_m(x) \left\{ \sum_{i=0}^{n-1} L_i(x) + \right.$$

$$+ \left[-2pn(2n+1) - (2p-1)n^2 - 4pn + (2R-p)(2n+1) - p^2 - p + 2R \right] L_n +$$

$$+ \left[2pn(n+1) - (2R-p)(n+1) \right] L_{n+1} +$$

$$+ \left[2pn^2 + (2p-1)n(2n-1) + (4p-2)n - (2R-p)n \right] L_{n-1} -$$

$$\left. - \left[(2p-1)n(n-1) \right] L_{n-2} \right\} \tag{1.30}$$

The result is an "almost" lower triangular matrix, called Hessenberg matrix.

The rest of the work is numerical. Since our goal is to obtain the function $E(R)$ we choose the suitable values of R as in table 1.1 . For each value of R we divide with the interval $p \in [0, 2 * R]$ into the n points. For each value of p we calculate store the eigenvalues for equation for $M(\mu)$ and $L(\lambda)$. Finding matrix eigenvalues is a common operation is a number of fields, and good numerical algorithms and libraries are available, such as [23]. Regardless, finding eigenvalues is a relative slow operation, with the complexity $O(n^\omega), 2 < \omega \leq 3$, [23] n being the size of the matrix. Eigenvalues for matrices up to 100×100, i.e. limiting the sums above to 100 elements can be found using Wolfram Mathematica, within a reasonable time. However for $n \geq 100$ the time needed increases as n^3 TODO verify and the Mathematica becomes unusable. For $n = 1000$, i.e 1000×1000 matrices I used the Fortran Gnu compiler and Lapack [23] libraries. The Lapack libraries are both accurate and fast, and it took about 30 minutes to find an eigenvalue on Apple Macbook Pro, with 16GB ram and Intel I7 processor at 2.2 GHz.

In comparison, the results obtain by using Wolfram Mathematica for $n = 100$ and results using Lapack for $n = 1000$ agree up to a part in 10^{-3}.

Once the eigenvalues are calculated we have two functions $A_i(p)$ for each of the equations. Interpolate and find the value of p for which the curves intersect. From the value of p we obtain the eigenenergy $E = E(R)$ using equation (1.6).

TODO: Check stability, i.e obtain a and q from A and p.

1.0.3   Plots, Tables, etc...

Table depicting the calculated energies of the electron for the ground state (even and odd) and first and second excited state: (TODO: wording, captions) . Also TODO: note that it does not work for small R (needs more points). All numbers are in atomic units.

Table 1.1: Ground State, Even Energies

R	p	A	E
.2	-1	-1	-1
.4	0.6482991	0.215659	-5.2536
.6	0.8968546	0.422304	-4.4686
.8	1.1214876	0.677779	-3.93042
1.0	1.3311023	0.982007	-3.54367
1.2	1.5312058	1.33809	-3.25638
1.4	1.7254930	1.75074	-3.03809
1.6	1.9165547	2.22543	-2.86967
1.8	2.1062223	2.76777	-2.73838
2.0	2.2957553	3.38297	-2.63525
2.2	2.4859626	4.07548	-2.55372
2.4	2.6772997	4.84875	-2.48887
2.6	2.8699576	5.70516	-2.4368
2.8	3.0639450	6.64611	-2.39484
3.0	3.2591587	7.67222	-2.36047
3.2	3.4554388	8.78351	-2.33204
3.4	3.6526076	9.97968	-2.30823
3.6	3.8504933	11.2602	-2.28801
3.8	4.0489429	12.6244	-2.27063
4.0	4.2478273	14.0717	-2.2555
4.2	4.4470414	15.6016	-2.2422
4.4	4.6465020	17.2136	-2.23037
4.6	4.8461448	18.9072	-2.21977
4.8	5.0459206	20.6821	-2.21018
5.0	5.2457926	22.5380	-2.20147
5.5	5.7457302	27.5309	-2.18271
6.0	6.2458815	33.0265	-2.16726
6.5	6.7460376	39.0236	-2.15427
7.0	7.2462380	45.5215	-2.14318
7.5	7.7464325	52.5198	-2.13359
8.0	8.2466140	60.0184	2.12521
8.5	8.7467810	68.0173	-2.11782
9.0	9.2469337	76.5162	-2.11125

R	p	A	E
9.5	9.7470735	85.5153	-2.10538
10.0	10.247201	95.0145	-2.1001
10.5	10.747319	105.014	-2.09533
11.0	11.247427	115.513	-2.09099
11.5	11.747527	126.513	-2.08702
12.0	12.247620	138.012	-2.08339
12.5	12.747706	150.012	-2.08005
13.0	13.247787	162.511	-2.07697
13.5	13.747862	175.511	-2.07411
14.0	14.247932	189.010	-2.07147
14.5	14.747997	203.010	-2.06899
15.0	15.248059	217.510	-2.06669
15.5	15.748117	232.509	-2.06454
16.0	16.248172	248.009	-2.06252
16.5	16.748223	264.009	-2.06063
17.0	17.248272	280.508	-2.05884
17.5	17.748318	297.508	-2.05716
18.0	18.248362	315.008	-2.05557
18.5	18.748404	333.008	-2.05407
19.0	19.248443	351.508	-2.05265
19.5	19.748481	370.507	-2.05129
20.0	20.248517	390.007	-2.05001
20.5	20.748551	410.007	-2.04879
21.0	21.248584	430.507	-2.04763
21.5	21.748615	451.507	-2.04652
22.0	22.248645	473.006	-2.04546
22.5	22.748673	495.006	-2.04445
23.0	23.248701	517.506	-2.04349
23.5	23.748727	540.506	-2.04256
24.0	24.248753	564.006	-2.04167
24.5	24.748777	588.006	-2.04082
25.0	25.248800	612.506	-2.04001

Table 1.2: Ground State, Odd Energies

R	p	A	E
0.2	0.2002000	-0.989967	-2.004
0.4	0.2899422	-0.978928	-1.05083
0.6	0.4698674	-0.944425	-1.22653
0.8	0.6583497	-0.890176	-1.35445
1.	0.83893725	-0.820177	-1.40763
1.2	1.0072282	-0.738337	-1.40904
1.4	1.1637570	-0.647105	-1.38197
1.6	1.3101216	-0.547923	-1.34095
1.8	1.4478995	-0.441659	-1.29408
2.	1.57842277	-0.328846	-1.24571
2.2	1.7027722	-0.209819	-1.19811
2.4	1.8218201	-0.084788	-1.15244
2.6	1.9362735	0.0461182	-1.10922
2.8	2.0467105	0.182823	-1.06863
3.	2.15360935	0.325285	-1.03067
3.2	2.2573686	0.473487	-0.995256
3.4	2.3583242	0.627428	-0.962231
3.6	2.4567615	0.787117	-0.931432
3.8	2.5529247	0.952568	-0.90269
4.	2.64702425	1.1238	-0.875842
4.2	2.7392425	1.30082	-0.850731
4.4	2.8297387	1.48366	-0.827213
4.6	2.9186522	1.67232	-0.805154
4.8	3.0061054	1.86681	-0.784433
5.	3.09220669	2.06715	-0.764939
5.5	3.3021488	2.59351	-0.720938
6.	3.50544693	3.15618	-0.682675
6.5	3.7030358	3.75479	-0.649111
7.	3.89563406	4.38877	-0.619427
7.5	4.083801	5.05737	-0.592975
8.	4.2679801	5.7597	-0.569239
8.5	4.448525	6.49477	-0.547803
9.0	4.62572696	7.26153	-0.528329

R	p	A	E
9.5	4.7998226	8.05888	-0.510544
10.0	4.971016	8.88573	-0.49422
10.5	5.139479	9.74099	-0.47917
11.0	5.305363	10.6236	-0.465238
11.5	5.468800	11.5325	-0.452292
12.0	5.629908	12.4667	-0.44022
12.5	5.788793	13.4253	-0.42893
13.0	5.945554	14.4073	-0.418339
13.5	6.100278	-0.40837	-0.408378
14.0	6.253049	16.4385	-0.398986
14.5	6.403943	17.4861	-0.39011
15.0	6.553030	18.554	-0.381709
15.5	6.700378	19.6416	-0.373736
16.0	6.846048	20.7482	-0.366159
16.5	6.990098	21.8732	-0.358946
17.0	7.132585	23.016	-0.352068
17.5	7.273559	24.1762	-0.3455
18.0	7.413071	25.3531	-0.33922
18.5	7.551165	26.5464	-0.333207
19.0	7.687887	27.7555	-0.327444
19.5	7.823278	28.98	-0.321913
20.0	7.957378	30.2195	-0.316599
20.5	8.090224	31.4735	-0.311489
21.0	8.221852	32.7418	-0.306571
21.5	8.352296	34.0239	-0.301832
22.0	8.481589	35.3195	-0.297262
22.5	8.609763	36.6282	-0.292851
23.0	8.736845	37.9498	-0.288592
23.5	8.862866	39.2839	-0.284474
24.0	8.987851	40.6303	-0.280491
24.5	9.111828	41.9886	-0.276636
25.0	9.234820	43.3586	-0.272902

Table 1.3: First Excited State, Even Energies

R	p	A	E

R	p	A	E

Table 1.4: First Excited State, Odd Energies

R	p	A	E

R	p	A	E

Table 1.5: Second Excited State, Even Energies

R	p	A	E

R	p	A	E

Table 1.6: Second Excited State, Odd Energies

R	p	A	E

R	p	A	E

chapterThe Radiative Quenching H_2 Ion Atom Collisions in 2D Space

Radiative Quenching is an interaction between two atoms (or molecules), one being in excited state and the other in 'normal ground state. The simplest such case is the collision of the two hydrogen molecules, in the process $H_2(2\,{}^2_S) + H_2(1\,{}^1_S) \to H_2(1\,{}^1_S) + H_2(1\,{}^1_S) + \hbar\omega$.

TODO: Add more

1.0.4 THEORY

In this chapter we will calculate the cross section and the emission spectra of the reaction $H(2\,{}^2_S) + H(1\,{}^1_S) \to H(1\,{}^1_S) + H(1\,{}^1_S) + \hbar\omega$, formed by the quenching of the excited H atom by the approaching H atom, in 2D dimensions. To my knowledge, there is no experimental results related to the 2D problem. There are results for the 3D case, listed in [12] and references there.

In this calculation, the atoms are confined in 2 dimensions, while the radiation is not. Therefore the photon can be emmited in any direction and the potential felt by the incoming ion is the standard Coulomb potential.

We will model this as a scattering problem, with a twist of a Born-Oppenheimer approximation. The Hamiltonian in this case will contain another term, namely the interaction of the radiation field with the electron. Following [12], in the center of the mass of the nuclei, the Hamiltonian for the system is given by:

$$H = -\frac{1}{2\mu}\nabla^2_{\mathbf{R}} + H_{el}(\mathbf{R}, \mathbf{r}) + H_{rad} + H_{int} \tag{1.31}$$

where μ is the reduced mass, $nabla_{\mathbf{R}}$ is the gradient operator for the relative nuclear motion. $H_{el}(\mathbf{R}, \mathbf{r})$ is the fixed nuclei Hamiltonian for the electron, whose coordinate are labeled by $\mathbf{r}$. H_{rad} is the Hamiltonian of the radiation field, and H_{int} is the radiation-matter coupling. Since we are dealing with the interaction of an atom with the EM radiation, it is common to use the length gauge.

Length gauge

The length gauge is a gauge transformation that replaces the vector potential for the field by the scalar potential for the quasi-static electric field [35]. In this gauge we take the Hamiltonian as: $H = \mathbf{p}^2/2m + V(\mathbf{r}) + e\mathbf{E}\mathbf{r}$. The length gauge is convenient since both the Coulomb and the external fields are represented by the scalar potentials, which are additive. In the presence of the radiation field, the length gauge is obtained by the gauge transformation of the vector potential $\mathbf{A}$, such that $\mathbf{A} \to \mathbf{A} + \nabla\chi$ where $\chi = -\mathbf{r} \cdot \mathbf{A}$.

In the length gauge, the interaction Hamiltonian is:

$$
H_{int} = -\sum_j \mathbf{r} \cdot \mathbf{E}
$$

$$
\mathbf{E} = i \sum_{k\alpha} \left(\frac{2\pi ck}{V} \right)^{1/2} \hat{\epsilon}_{k\alpha} \left(a_{k\alpha} - a_{k\alpha}^{\dagger} \right)
$$

(1.32)

where $a_{k\alpha}$ and $a_{k\alpha}^{\dagger}$ are destruction and creation operators for the photon of momentum $\hbar k$ and polarization α respectively.

Continuing with the Quenching

So if we regard this process as a transition induced by the radiation field from the $A^1\Sigma_u^+$ state to of the H_2 molecule formed by the approaching H atom, to the $X^1\Sigma_g^+$ state in which the atoms separate.

Now we write the system wave function:

$$|\Psi\rangle = F_a(\mathbf{R})\chi_a(\mathbf{R},\mathbf{r})\,|0\rangle + \sum_{k\alpha} F_{k\alpha}(\mathbf{R})\chi_b(\mathbf{R},\mathbf{r})\,|k\alpha\rangle \tag{1.33}$$

where $\chi_a(\mathbf{R},\mathbf{r})$ and $\chi_b(\mathbf{R},\mathbf{r})$ are the eigenstates of the fixed position nuclei Hamiltonian H_{el} corresponding to the $A^1\Sigma_u^+$ and $X^1\Sigma_g^+$ state in body fixed frame respectively. The $F_a(\mathbf{R})$ and $F_{k\alpha}(\mathbf{R})$ are the amplitudes for the relative nuclear motion and $|0\rangle$ and $|k\alpha\rangle$ are the kets for the photon vacuum and single photon states. The ansatz (2.3) is valid at low speed collisions, where the other channels are unaccessible. In the adiabatic approximation (i.e. ignoring the non-adiabatic effects) the amplitudes $F_a(\mathbf{R})$ and $F_{k\alpha}(\mathbf{R})$ obey the set of coupled equations:

$$\left[-\frac{1}{2\mu}\nabla_R^2 + V_a(R) - E\right]F_a(\mathbf{R}) = \sum_{k\alpha} F_{k\alpha}(\mathbf{R})U_{k\alpha}(\mathbf{R}) \tag{1.34}$$

$$\left[-\frac{1}{2\mu}\nabla_R^2 + V_b(R) + \hbar\omega - E\right]F_{k\alpha}(\mathbf{R}) = F_a(\mathbf{R})U_{k\alpha}^\dagger(\mathbf{R}) \tag{1.35}$$

where

$$U_{k\alpha}(\mathbf{R}) = -i\left[\frac{2\pi ck}{V}\right]^{1/2} D(R)\hat{\mathbf{R}}\cdot\hat{\epsilon}_{k\alpha} \tag{1.36}$$

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and $V_a(R)$, $V_b(R)$ are the potential energy curves for the $A^1\Sigma_u^+$ and $X^1\Sigma_g^+$ states respectively. $D(R)$ is the radial transitional dipole moment between them. E is the initial energy of the relative motions and ω is the angular frequency of the emitted photon.

Now to solve this. We find the Green function for the equation (2.5) which satisfies the retarted boundary conditions so that $F_{k\alpha}$ contains only outgoing waves in the limit $R \to \infty$:

$$\left[-\frac{1}{2\mu}\nabla_R^2 + V_b(R) + \hbar\omega - E \right] G^+(\mathbf{R}, \mathbf{R}') = \delta^3(\mathbf{R}, \mathbf{R}') \tag{1.37}$$

and from the equation (2.7) we get:

$$F_{k\alpha}(\mathbf{R}) = \int d^3R' G^+(\mathbf{R}, \mathbf{R}') F_a(\mathbf{R}') U_{k\alpha}^\dagger(\mathbf{R}') \tag{1.38}$$

We can express this function in the partial waves bases. Since V_b contains no bound states we get for $\mathbf{R} = \mathbf{R}(R, \theta)$:

$$G^+(\mathbf{R}, \mathbf{R}') = \frac{\pi\mu}{k_b} \sum_{l=0}^{\infty} \sqrt{\frac{1}{2\pi}} \cos(l\,\theta) \cos(l\,\theta') \times \frac{f_l(k_b R_<) g_l^+(k_b R_>)}{RR'} \tag{1.39}$$

where $P_l(\cos\theta)$ are Legendre polynomials, also $m = 0$ part of the spherical harmonics: $P_l(\cos\theta) = Y_{l0}\theta, \phi$.

The $f_l(kR)$ is a regular solution of the homogenous Schrodinger radial equation for the 2D case:

[51]:

$$\left\{ \frac{d^2}{dR^2} - \frac{l(l+1)}{R^2} - 2\mu\left[V_b(R) - V_b(\infty)\right] + k^2 \right\} f_l(kR) = 0$$

$$k \equiv \sqrt{2\mu[E - \hbar\omega - V_b(\infty)}$$

(1.40)

where:

$$f_l \sim \sqrt{\frac{2}{\pi}} \sin\left[kR - \frac{l\pi}{2} + \delta_l(b)\right]$$

(1.41)

and $g_l^+(kR)$ is irregular solution with the boundary condition at large R.

$$g_l^+ \sim \sqrt{\frac{2}{\pi}} \exp i\left[kR - \frac{l\pi}{2} + \delta_l(b)\right]$$

(1.42)

and $\delta_l(b)$ is a phase shift.

The total wave function (2.3) must be symmetric under the interchange of the H nuclei, so that $F_a(\mathbf{R}) = -F_a(-\mathbf{R})$ and $F_{k\alpha}(\mathbf{R}) = F_{k\alpha}(-\mathbf{R})$. Now we solve equations (2.4) and (2.5) in the distorted wave approximation. Then $F_a(\mathbf{R})$ is the solution of the (2.4) with the coupling term set to be zero and it can be expressed in the form:

$$F_a(\mathbf{R}) = \sum_{l=1}^{\infty} \cos(l\,\theta)(2l+1)i^l\sqrt{\pi} \times \exp[i\delta_l(a)]\frac{s_l(k_a\mathbf{R})}{k_a\mathbf{R}}$$

(1.43)

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The asymptotic form for (2.13) is:

$$F_a(\mathbf{R}) \sim \frac{1}{\sqrt{2}}\left[e^{ik_a z} - e^{-ik_a z} + [f(\theta,\phi) - f(\theta - \pi, \phi + \pi)]\frac{e^{ik_a R}}{R}\right] \qquad (1.44)$$

By inserting (2.13) and (2.9) into (2.8) we get the asymptotic form for the (2.8):

$$F_{k\alpha}(\mathbf{R}) \sim \frac{e^{ik_a R}}{R} f_{k\alpha}(\theta) \qquad (1.45)$$

where:

$$f_{k\alpha}(\theta) = sum_l \cos(l\,\theta)\left[\sum_{J=1}^{\infty} \frac{2\pi\mu}{k_a k_b}(2J+1)\left(\frac{\pi kc}{A}\right)^{1/2} e^{i\delta_j(b)}e^{i\delta_j(a)}i^{J+l-1}\right]\sqrt{2l+1)2\pi} \qquad (1.46)$$

In this summation, the j is restricted to the odd integers, and

$$M_{l,l'}(k_a, k_b) = \frac{1}{\sqrt{k_a, k_b}}\int_0^{\infty} dR s_l(k_a, R)D(R)f_{l')(k_b, R)} \qquad (1.47)$$

The cross section of the collision induced transition between the H atom and the H^+ ion is obtained by summing $|f_{k\alpha}(\theta)|^2$ over all final states that conserve energy with an inital state, and dividing the result with the flux of the incident channel.

The $H\left(2^1S\right) \to H\left(1^1 1S\right)$ is a linear combination of $A1\sigma_u^+$ and $X1\sigma_g^+$ states. Since the excited gerade state is not allowed to make a radiative transition to a gerade ground state, the flux in the incident channel is twice the flux in the $A1\sigma_u^+$ channel.

So for the cross section we get:

$$
\sigma = \int_0^{\omega_{max}} d\omega \frac{d\sigma}{d\omega} =
$$

$$
= \sum_\alpha \int \frac{d^2k}{(2\pi)^2} \frac{A}{2\mu k_a} \int d^2k_b \delta \left[\frac{k_b^2}{2\mu} - \frac{k_a^2}{2\mu} + \Delta E - \hbar\omega \right] |f_{k\alpha}(\theta)|
$$

(1.48)

where

$$
\frac{d\sigma}{d\omega} = \frac{8}{3} \left[\frac{\pi\mu}{k_a} \right]^2 \frac{1}{c^3} \omega^3 \sum_J \left[JM_{J,J-1}^2(k_a, k_b) + (J+1)M_{J,J+1}(k_a, k_b) \right]
$$

(1.49)

ΔE is the energy of the transition at $R = \infty$ and ω_{max} is the maximum frequency of the emitted photon. Expression (2.18) is an equivalent expression to the Fermi's Golden Rule. Equation (2.19) provides the spectrum of the emitted radiation, in addition to the scattering cross section.

Optical Potential Method

The approximation that does not require the integration over the total spectrum is the optical potential method. TODO: Insert optical potential method.

To derive it here we insert the equation (2.8) for the amplitude $F_{k\alpha}(\mathbf{R})$ into the equation (2.4) to obtain the equation for the amplitude $F_a(\mathbf{R})$

$$
\left[-\frac{1}{2\mu} \nabla_R^2 + V_a(R) - E \right] F_a(\mathbf{R}) = \sum_{k\alpha} d^2 R' G^+(\mathbf{R}, \mathbf{R}') U_{k\alpha}^\dagger(\mathbf{R}') U_{k\alpha}(\mathbf{R}) F_a(\mathbf{R}')
$$

(1.50)

The right hand of (2.20) contains a complex, non-local potential

$$V(\mathbf{R}, \mathbf{R}') = \sum_{k\alpha} G^{+}(\mathbf{R}, \mathbf{R}') U_{k\alpha}^{\dagger}(\mathbf{R}') U_{k\alpha}(\mathbf{R}) \tag{1.51}$$

that arises because of the interaction of the electron with the vacuum. Now the real part of this potential induces the shift in the eigenvalue $V_a(R)$. Since the coupling on an electron with the radiation is weak, we can ignore it and consider only the imaginary part.

The imaginary part of $V(\mathbf{R}, \mathbf{R}')$ is an absorptive potential, representing a process where electron in excited state emits a photon and decays to a ground state. This potential is non-local, as we take is for $R = \infty$. In the optical potential aprroxmation, we take replace potential by the local one, whose range is limited to the scattering area. This potential is essentialy classical.

Because the term $U_{k\alpha}^{\dagger}(\mathbf{R}') U_{k\alpha}(\mathbf{R})$ appearing in equation (2.21) is real, the optical potential is proportional to the imaginary part of the retarded Green's function, which is expressed as:

$$\text{Im} G^{+}(\mathbf{R}, \mathbf{R}) = \pi \sum_{l=0}^{\infty} \cos(l\,\theta) \cos(l\,\theta') \int_{0}^{\infty} dk\, \delta \left[\frac{k^2}{2\mu} - \frac{k_a}{2\mu} + \hbar\omega - DeltaE \right] \frac{f_l(kR) f_l(kR')}{R\,R'} \tag{1.52}$$

This result is obtained using the spectral representation of the retarted Green's function and the identity $1/(x + i\epsilon) \to P/x - i\pi\delta(x)$ as $\epsilon \to 0$. Using (2.22) one obtains for the non-local optical

potential:

$$V(\mathbf{R},\mathbf{R}') = \frac{i}{2\pi}\sum_{\alpha}\int d\Omega_k \int_0^{k_{max}} \sum_{l=0}^{\infty}\cos(l\,\theta)\cos(l\,\theta') \times \frac{\omega^3}{c^3}\frac{f_l(kR)f_l(kR')}{R\,R'}D(R)D(R')(\hat{\mathbf{R}}\cdot\epsilon_{k\alpha})(\hat{\mathbf{R}}'\cdot\epsilon_{k\alpha})$$

$$(1.53)$$

where $\omega(k) = k_{\alpha}/2\mu + \Delta E - k^2/mu$. Now for the optical-potential approximation we make the semi-classical approximation that the values of k that give the largest contribution are given by:

$$\frac{k^2}{2\mu} \simeq= \Delta E + \frac{k_{\alpha}^2}{2\mu} + V_b(r) - V_a(r) \qquad (1.54)$$

Now the frequency term $\omega^3 = |\Delta E(R)|^3$ can now be taken outside the integral.

Using the expansion: TODO: delta function expansion in 2 dimensions and verify below

$$\delta^2\left(\mathbf{R},\mathbf{R}'\right) = \sum_{l=0}^{\infty}\cos(l\,\theta)\cos(l\,\theta')\frac{\delta(R-R')}{R\,R'} \qquad (1.55)$$

we get:

$$V_{opt}(\mathbf{R},\mathbf{R}) \approx= \frac{i}{2}\delta^2\left(\mathbf{R},\mathbf{R}'\right)A(R),$$

$$A(R) = \frac{4}{3}D^2(R)\frac{|\Delta E(R)|^3}{c^3}$$

$$(1.56)$$

and equation (2.23) becomes:

$$\left[-\frac{1}{2\mu}\nabla_R^2 + V_a(R) - E\right] F_\alpha(\mathbf{R}) = \frac{i}{2}A(R)F_\alpha(\mathbf{R}) \tag{1.57}$$

The cross section for the radiative quenching is given by:

$$\sigma = \frac{\pi}{k_a^2} \sum_{J=0}^{\infty} (2J+1)\left(1 - e^{-4\eta_j}\right) \tag{1.58}$$

where eta_j is the imaginary component of the phase shift of the Jth partial wave of the solution (2.23). The sum on J is restricted to the odd integers. Also because the right hand of (2.23) is small, we can use the distorted wave approximation to obtain the expression for the phase shift eta_j

$$\eta_j = \frac{\pi\mu}{2k_a} \int_0^\infty dR \left|s_J\left(k_a R\right)\right|^2 A(R) \tag{1.59}$$

TODO: JWKB

Using the JWKB approximation to the (2.29), by replacing the sum with an integral, and recognizing that η_J is small, we obtain the semi-classical cross section:

$$\sigma = 2\pi\sqrt{\frac{2\pi}{E}} \int dp\, p \int_{R_c}^\infty dR \frac{A(R)}{\sqrt{1 - \frac{V_a(R)}{E} - fracp^2 R^2}} \tag{1.60}$$

where R_c is the classical turning point and E is the kinetic energy.

As expected, there does not exist the analytic solution to this differential equation . Ergo, I used the numerical method, namely Mathematica code to solve this equation. This equations behaves 'well'

so the solution is easy to find numerically.

1.1 CHARGE TRANSFER

TODO: Make this a new chapter.

TODO: Electronic translation factor (ETF)

As usual, we also employ the Born-Oppenheimer (BO) approximation. We expand the scattering wave function in the terms of BO wave functions, modifed by the electronic translation factor. If we set $\chi_i^a(\mathbf{R})$ to the be wave function of the nuclear motion in the electronic state i, we get for the wavefunction:

$$\Psi(\mathbf{r}, \mathbf{R}) = \sum_i exp\left[\frac{1}{\mu}\mathbf{S} \cdot \nabla_R\right] \phi(\mathbf{r}, \mathbf{R})\chi_i^a(\mathbf{R}) \qquad (1.61)$$

with μ being the reduce mass, and

$$S = \frac{1}{2}f_i(\mathbf{r}, \mathbf{R})\mathbf{r} \qquad (1.62)$$

where f_is are the switching functions that incorporte the molecular character of the ETF. The equations for the $\chi_i^a(\mathbf{R})$ can be obtain in a matrix form:

$$\left\{-\frac{1}{2\mu}\left[\underline{I}\nabla_R - i(\underline{\mathbf{P}} + \underline{\mathbf{rAP}})\right]^2 + \underline{V}\right\}\underline{\chi}^a(\mathbf{R}) = E\underline{\chi}^a(\mathbf{R}) \qquad (1.63)$$

with:

$$\mathbf{P}_{ij} = \langle \phi_i \,|\, -i\nabla_R \,|\, \phi_j \rangle$$

$$\mathbf{A}_{ij} = i(E_i - E_j)\,\langle \phi_i \,|\, \mathbf{S} \,|\, \phi_j \rangle \tag{1.64}$$

$$V_{ij}(R) = \delta_{ij} V_i(R)$$

where E is the energy of the nuclear motion in the center of mass frame, and $\underline{I}$ is the identity matrix. The matrix $\mathbf{P}_{ij}$ represents the non-adiabatic coupling, the $\mathbf{A}_{ij}$ is the ETF correction, and the $V_i(R)$ is the potential energy of the ith Born-Opennheimer state.

1.1.1   Radiative charge transfer and radiative association

The radiative charge transfer cross-section can be calculated using the formula (2.18) for σ with M calculated using formula (2.17), where the k_a and k_b are the wave numbers of the initial and final state.

The partial waves $f_j(kR)$ and $s_j(kR)$ are the regular solutions of the homogenou radial equations.

$$\left\{ \frac{d^2}{dR^2} - \frac{J(J+1)}{R^2} - 2\mu \left[V_a(R) - V_b(\infty)\right\} + k^2 \right\} s_j(kR) = 0 \tag{1.65}$$

and

$$\left\{ \frac{d^2}{dR^2} - \frac{J(J+1)}{R^2} - 2\mu \left[V_b(R) - V_a(\infty)\right\} + k^2 \right\} f_j(kR) = 0 \tag{1.66}$$

with $V_a(R)$ and $V_b(R)$ being the potential energy curves of the final ground state and the initial

excited state, respectively. The ks are the wave numbers, given by:

$$k_b = \sqrt{2\mu\left[E - \hbar\omega - V_b(\infty)\right]}$$
$$k_a = \sqrt{2\mu\left[E - V_a(\infty)\right]}$$

(1.67)

where ω is the angular frequency of the emitted photon, E is the total collision energy in the center of mass frame.

Again, we get calculate the total cross section given by the radiative decay as:

One has to be careful though, since it seems that most numerical methods are very sensitive to the choice of initial conditions. As a second order equation, the solution requires two initial conditions, either in the form of function value at the ends of the interval, or value of the function and its derivative at some point. Now, this partial wave represents an incoming particle (electron) and thus the function $f(kR)$ is defined on the infinite interval and it is oscillatory for large values of kR. Because of that, it is impossible to specify a boundary condition for value of $f(kR)$ at infinity. So the boundary conditions have to be in the form of the value of function at some point and the value of the derivative at the same point.

In my calculation, I assume that for $kR \to 0$, the function $f(kR)$ is finite and 'well behaving', so the appropriate boundary conditions seem to be:

$$\text{For } kR \to 0, \ f(kR) = 1; \ f'(kR) = 0$$

(1.68)

The Mathematica code for the $f(kR)$ is in appendix TODO: add code.

Following the approach in the [52] I apply a semi-classical approach to the system of two H_2^+ molecules.

In this approach, I assume that a photon is emitted with energy equal to the energy difference between two Born-Oppenheimer potential surfaces, at the distance where the transition occurs. This leads to the Local Optical Potential Method, and following the semi-classical approach, the total rate is estimated as a classical integral over all localized transitions.

The cross section of the spontaneous radiative association is given by [7] . This can also be derived using the Fermi's Golden Rule (which turns out to be published by Dirac's 20 years before Fermi):

$$\sigma_{CT} = \int_0^{\omega_{max}} d\omega \, \frac{d\sigma}{d\omega}$$

where : $\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad$ (1.69)

$$\sigma_{sp}(k) = \sum_J \sum_n \frac{64}{3} \frac{\pi^5 \nu^3}{c^3 k^2} \left[(J+1) M_{J+1,J}^2 + J \, M_{J-1,J}^2 \right]$$

The sum extends over the rho-vibrational quantum numbers n and angular momentum J of the H_2^+ ion. Due to the topological constraints the direction of J remains fixed, and only its magnitude changes. As expected, for the ground state we have $J = 0$.

The $M_{J,J'}$ is an overlap integral defined by:

$$M_{J,J'} = \int_0^\infty dR \, f_j(kR) D(R) \phi_{J'}^n(R)$$
$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad$ (1.70)

where $f_j(kR)$ is a partial wave defined above.

Vibrational Levels

The $\phi_{J',n}(R)$ represent the vibrational eigenfunction of the ground state $X^2\Sigma^+$ with the energy $\epsilon_n J$. TODO: Show picture. Given the nature of the problem 2D, the ground state has the $J = 0$. So the differential equation for the $\phi_{0,n}(R)$, in the potential well, is:

$$\phi''_{0,n}(R) + [E(R) + V(R)]\, \phi(R)_{0,n} = \epsilon_n \phi(R)_{0,n} \tag{1.71}$$

Of course the solution to this equation can only be calculated numerically (appendix TODO: shows the Mathematica code.). To solve the equation one must set the boundary conditions to $\phi(R)_{0,n} \Rightarrow 0, \phi(R)'_{0,n}$ for $R \Rightarrow 0$. For actual numerical evaluation, the important boundary condition is the value of $\phi(R \approx 0)_{0,n}$. With these boundary conditions set, the values of ϵ_n must satisfy the boundary condition on the other side of the potential well, namely that the $\phi(R)_{0,n}$ remains bounded, which translates into: $\phi(R)_{0,n} \Rightarrow 0$ for $R \Rightarrow \infty$.

So calculations show (TODO: Verify) that there are

Dipole Transition in 2 Dimension

The $D(R)$ is the transition dipole moment between $X^2\Sigma^+$ and $A^2\Sigma^+$,

$$D(R) = \langle \psi_1(R) \,|\, r_1 + r_2 \,|\, \psi_0(R) \rangle \quad \text{where in our case :}$$

$$r_1 + r_2 = \lambda R \tag{1.72}$$

Now the 2 dimension case comes into effect. I consider the case where the electrons are confined in 2 dimensions, but where the underlying space is still 3 dimensional, Euclidean. Thus while electrons'

movement is confined in 2D, they can radiate photons in any direction in 3D.

TODO: Add appendix for the radiation in 1D and 2D.

Now with the separation of variable, the solution is a product of two function. So the integral above come to:

$$D(R) = \int_{-1}^{1} \int_{1}^{\infty} d\mu \, d\lambda \, M_u(\mu) L_u(\lambda) \lambda R M_g(\mu) L_g(\lambda) \tag{1.73}$$

where $M_u L_u$ and $M_g L_g$ are the odd/even solutions to the original Schrodinger equation (2.1).

Since the functions $M(\mu)L(\lambda)$ and do not exist in the closed form, the dipole integral (2.43) is numerically calculated using Wolfram Mathematica. First the two Mathematica modules (functions) are created, which solve the equations $L(\lambda)$ and $M(\mu)$, as function of the internuclear distance R and corresponding variables. Then the second module calculates the integral above, as the function of R.

The Mathematica code for the dipole is in appendix TODO: add code and indicate that I wrote it. :)

From the table TODO: add reference one could calculate the spectrum of these transitions. For the electron to transition from $A^2\Sigma^+$ to $X^2\Sigma^+$ level, it needs to emit photon $\Delta E \approx -3.2\,au = 0.1176 eV$, so the corresponding wavelength is $\lambda \approx 380\,nm$ TODO: Verify the numbers. TODO: verify the depth of the potential well compared to the paper [31]

TODO: Possible spectrum of such transitions

Distorted Wave Approximation

TODO: Scattering in 2 D

The distorted wave Born approximation (DWBA) is an extension to the (first) Born approximation in scattering processes. Starting from the Schrodinger equation for the scattering problem, we solve it by method of Green's function

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r}) \right] \psi_k(\mathbf{r}) = E\psi_k(\mathbf{r})$$

(1.74)

$$\text{with } V(\mathbf{r}) = 0 \quad \text{except in the target region} \implies$$

The energy E is the energy of the incident plane wave, $E = \hbar^2 k^2/2m$. Applying the Green's function

$$\left[\frac{\hbar^2}{2m}\nabla^2 + E \right] G_0(\mathbf{r}, \mathbf{r}'|E) = V(\mathbf{r})\psi_k(\mathbf{r})$$

(1.75)

we get the integral form of the Schwinger-Lippmann equation:

$$\psi_k'(\mathbf{r}) = \psi_k(\mathbf{r}) + \int d^3r' \, G_0(\mathbf{r}, \mathbf{r}'|E)V(\mathbf{r}')\psi_k'(\mathbf{r})$$

(1.76)

The scattering amplitude is given by [10]

$$f_k(\mathbf{r}) = -\frac{2m}{\hbar^2}\frac{1}{4\pi}\int d^3r' \, e^{-i\mathbf{k}\mathbf{r}'} V(\mathbf{r}')\psi_k'(\mathbf{r}') \tag{1.77}$$

Since the Schwinger-Lippmann equation (2.46) is unsolvable, the first Born approximation assumes that the scattered field is small when compared to the incident field. Therefore it treats the scattered way as a perturbation. As the $0-th$ order the scattered wave is an unperturbed incident plane wave:

$$\psi_0'(\mathbf{r}) = e^{i\mathbf{k}\mathbf{r}} \tag{1.78}$$

and then the equation (2.46) is solved iteratively:

$$\psi_{n+1}'(\mathbf{r}) = e^{i\mathbf{k}\mathbf{r}} + \int d^3r' \, G_0(\mathbf{r}, \mathbf{r}'|E)V(\mathbf{r}')\psi_k'(\mathbf{r}) \tag{1.79}$$

So if we expand the wave function in the powers of the interaction potential V we get:

$$\psi_k' = \psi_{\mathbf{k}}'^{(0)} + \psi_{\mathbf{k}}'^{(1)} + \psi_{\mathbf{k}}'^{(2)} + \dots$$

$$= \psi_{\mathbf{k}}'^{(0)} + G_0 V \psi_{\mathbf{k}}'^{(0)} + G_0 V G_0 V \psi_{\mathbf{k}}'^{(0)} + \dots \tag{1.80}$$

$$= (1 + G_0 T)\psi_{\mathbf{k}}'^{(0)} \quad \text{with } T = V + G_0 V + \dots = \frac{1}{1 - VG_0}$$

The equation (2.50) represents a scattering process where incident particle undergoes multiple scat-

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tering events from the potential. Since this makes the calculations very complicated, only the first iteration of the series is takes into account and the matrix T is approximated by the potential V. This first order term in which the exact wave function $\psi_{\mathbf{k}}'(\mathbf{r})$ is replaced by the plane wave $e^{i\mathbf{k}\mathbf{r}}$ is the First Born Approximation. It is very useful, however it is not always valid and one way to extend its validity is the DWBA.

In the DWBA, we do not assume any more that the scattered field is small compared to the incident field. So in this case, it is possible to generalize the Born approximation. The free space zero potential $V_0(\mathbf{r}) = 0$ is replaced by the non-trivial reference potential $V_1(\mathbf{r}) = 0$. It is assumed that the scattered wave function $\psi_{\mathbf{k}}'^{1}$ due to this potential is known, either analytically or numerically as a solution to the following Schwinger-Lippmann equation:

$$\psi_{n+1}'(\mathbf{r}) = e^{i\mathbf{k}\mathbf{r}} + \int d^3r' \, G_0(\mathbf{r}, \mathbf{r}'|E) V_1(\mathbf{r}') \psi_k'^{1}(\mathbf{r}) \tag{1.81}$$

Then the interaction potential is treated as a perturbation to the reference potential V_1, i.e:

$$V(\mathbf{r}) = V_1(\mathbf{r}) + \delta V(\mathbf{R} \quad \text{with} \quad |\delta V| << |V_1| \tag{1.82}$$

So in the DWBA the scattering field is determined by applying the Born approximation:

$$\psi'(\mathbf{r}) = \psi'^{1}(\mathbf{r}) + \int d^3r' \, G_0(\mathbf{r}, \mathbf{r}'|E) V_1(\mathbf{r}') \psi_k'^{1}(\mathbf{r}) \tag{1.83}$$

to the scattered wave $\psi'(\mathbf{r})$. This distorted wave is the solution of the outgoing-wave Schrodinger

equation:

$$\left[\frac{\hbar^2}{2m} \nabla^2 - V_1(\mathbf{r}) + E \right] \psi'^1(\mathbf{r}) = 0 \tag{1.84}$$

where we can use the Green's function method.

To satisfy the boundary conditions, the asymptotic form of the $\psi'^1(\mathbf{r})$ for $r \to \infty$ is:

$$\psi'^1(\mathbf{r}) \to e^{i\mathbf{kr}} + \frac{1}{r} e^{ikr} f_k^1(\theta) \tag{1.85}$$

where the scattering amplitude is:

$$f_k^1(\theta) = -\frac{2m}{\hbar^2} \frac{1}{4\pi} \int d^3r' \, e^{-i\mathbf{kr}'} V_1(\mathbf{r}') \psi_k'^1(\mathbf{r}') \tag{1.86}$$

This would be the scattering amplitude if the potential V_1 were the only potential present. The total scattering amplitude is the sum:

$$f_k(\theta) = f_k^1(\theta) + \delta f_k(\theta) \tag{1.87}$$

and $\delta f_k(\theta)$ is calculated in the Born approximation:

$$\delta f_k(\theta) \simeq -\frac{2m}{\hbar^2} \frac{1}{4\pi} \int d^3r' \, \psi_{k'}'^{1(-)*}(\mathbf{r}') V_1(\mathbf{r}') \psi_k'^1(\mathbf{r}') \tag{1.88}$$

The $\psi_{k'}'^{1(-)*}$ is the known incoming wave, corresponding to the reference potential V_1 (i.e. solution of the Schrodinger equation).

The condition for the (2.58) to be a good approximation is for the $\delta V(\mathbf{r})$ to be sufficiently small.

What that means is that possible additional scattering does not modify significantly the wave function.

Laplacian Eigenfunctions and Green's function in 2D

Starting from the Laplace operator and switching to polar coordinates:

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} = \frac{\partial}{\partial r^2} + \frac{1}{r}\frac{\partial}{\partial r} + \frac{\partial^2}{\partial \theta^2}$$

(1.89)

$$\nabla^2 u(r, \theta) = 0$$

If the assume that the solution admits separation of variables:

$$u(r, \theta) = R(r)\Theta(\theta) \implies$$

(1.90)

the Laplacian transforms into

$$\frac{R''}{R} + \frac{R'}{rR} + \frac{\Theta''}{r^2\Theta} = -\lambda$$

(1.91)

Set $\frac{\Theta''}{\Theta} = -\gamma$ and we obtain 2 ODEs:

$$\Theta'' + \gamma^2\Theta = 0$$

(1.92)

$$R'' + \frac{1}{r}R' + \left(\lambda - \frac{\gamma}{r^2}\right)R = 0$$

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From this we can see that the solution for the Θ equation is:

$$\Theta(\theta) = A \cos \sqrt{\gamma} + B \sin \sqrt{\gamma} \tag{1.93}$$

and using the substitution $\rho = \sqrt{\lambda} r$ we get the Bessel equation for R.

$$R_\rho'' + \frac{1}{\rho} R_\rho' + \left(1 - \frac{n^2}{\rho^2}\right) R = 0 \tag{1.94}$$

CHAPTER 2

The Radiative Association in Ion Atom Collisions in 2D Space

Radiative Association is a reactive process in which two particles (atoms, or ionized molecules) collide to form a large(r) molecule while emitting a photon. The simplest such case is the formation of the hydrogen molecular ion, in the process $H^+ + H \rightarrow H_2^+ + \hbar\omega$.

For the radiative association process to be efficient, it is necessary that the molecules form a stable state, and that it is able to shed the excess energy by emitting a photon [53], [7] . Therefore this can be modeled as a scattering problem, and moreover a scattering at a low energy and non-relativistic. I am not aware of any experiments regarding charge transfer in 2D, so at this point the results below would benefit from the experimental confirmation.

In 3D, the radiative association of (cold) atoms and ions ccurs in astrophysics, TOOD: References and they are considered to be responsible for the molecular synthesis in the interstellar clouds. In addition to strictly Hydrogen reactions, the process that leads to the formation of HeH molecule have been well analyzed in the past [7]. This has lead to the analysis of the polyatomic, complex systems, most recently the interaction of ultra cold Yb^+ ion with the Ca atoms. However, in the case of H_2 molecule, the 2 dimensional case has not been considered yet.

2.0.1 THEORY

In this thesis we will calculate the cross section and the emission spectra of the reaction $H^+ + H \rightarrow$ $H_2^+ + \hbar\omega$.

The restriction is that atoms are confined in 2 dimensions, while the radiation is not. Therefore the photon can be emmited in any direction and the potential felt by the incoming ion is the standard Coulomb potential.

Now, this is a scattering problem, with a twist of a Born-Oppenheimer approximation. The Hamiltonian in this case will contain another term, namely the interaction of the radiation field with the electron. Following [12] [53], in the center of the mass of the nuclei, the Hamiltonian for the system is given by:

$$H = -\frac{1}{2\mu}\nabla_{\mathbf{R}}^2 + H_{el}(\mathbf{R}, \mathbf{r}) + H_{rad} + H_{int} \tag{2.1}$$

where μ is the reduced mass, $nabla_{\mathbf{R}}$ is the gradient operator for the relative nuclear motion. $H_{el}(\mathbf{R}, \mathbf{r})$ is the fixed nuclei Hamiltonian for the electron, whose coordinate are labeled by $\mathbf{r}$. H_{rad} is the Hamiltonian of the radiation field, and H_{int} is the radiation-matter coupling. Since we are dealing with the interaction of an atom with the EM radiation, it is common to use the length gauge.

The length gauge is a gauge transformation that replaces the vector potential for the field by the scalar potential for the quasi-static electric field [35]. In this gauge we take the Hamiltonian as: $H = \mathbf{p}^2/2m + V(\mathbf{r}) + e\mathbf{E}\mathbf{r}$. The length gauge is convenient since both the Coulomb and the external fields are represented by the scalar potentials, which are additive. In the presence of the radiation

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field, the length gauge is obtained by the gauge transformation of the vector potential $\mathbf{A}$, such that $\mathbf{A} \rightarrow \mathbf{A} + \nabla\chi$ where $\chi = -\mathbf{r} \cdot \mathbf{A}$.

In the length gauge, the interaction Hamiltonian is:

$$H_{int} = -\sum_j \mathbf{r} \cdot \mathbf{E}$$

$$\mathbf{E} = i \sum_{k\alpha} \left(\frac{2\pi ck}{V} \right)^{1/2} \hat{\epsilon}_{k\alpha} \left(a_{k\alpha} - a_{k\alpha}^\dagger \right)$$

(2.2)

where $a_{k\alpha}$ and $a_{k\alpha}^\dagger$ are destruction and creation operators for the photon of momentum $\hbar k$ and polarization α respectively.

TODO: Verify charge transfer vs resonant charge transfer So if we regard this process as a transition induced by the radiation field from the $A^1\Sigma_u^+$ state to of the H_2^+ molecule formed by the approaching atom and an H ion, to the $X^1\Sigma_g^+$ state in which the atom and the ion separate.

Now we write the system wave function:

$$|\Psi\rangle = F_a(\mathbf{R})\chi_a(\mathbf{R}, \mathbf{r}) |0\rangle + \sum_{k\alpha} F_{k\alpha}(\mathbf{R})\chi_b(\mathbf{R}, \mathbf{r}) |k\alpha\rangle$$

(2.3)

where $\chi_a(\mathbf{R}, \mathbf{r})$ and $\chi_b(\mathbf{R}, \mathbf{r})$ are the eigenstates of the fixed position nuclei Hamiltonian H_{el} corresponding to the $A^1\Sigma_u^+$ and $X^1\Sigma_g^+$ state in body fixed frame respectively. The $F_a(\mathbf{R})$ and $F_{k\alpha}(\mathbf{R})$ are the amplitudes for the relative nuclear motion and $|0\rangle$ and $|k\alpha\rangle$ are the kets for the photon vacuum and single photon states. The ansatz (2.3) is valid at low speed collisions, where the other channels are unaccessible. In the adiabatic approximation (i.e. ignoring the non-adiabatic ef-

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fects) the amplitudes $F_a(\mathbf{R})$ and $F_{k\alpha}(\mathbf{R})$ obey the set of coupled equations:

$$\left[-\frac{1}{2\mu}\nabla_R^2 + V_a(R) - E \right] F_a(\mathbf{R}) = \sum_{k\alpha} F_{k\alpha}(\mathbf{R})U_{k\alpha}(\mathbf{R}) \qquad (2.4)$$

$$\left[-\frac{1}{2\mu}\nabla_R^2 + V_b(R) + \hbar\omega - E \right] F_{k\alpha}(\mathbf{R}) = F_a(\mathbf{R})U_{k\alpha}^\dagger(\mathbf{R}) \qquad (2.5)$$

where

$$U_{k\alpha}(\mathbf{R}) = -i \left[\frac{2\pi ck}{V} \right]^{1/2} D(R)\hat{\mathbf{R}} \cdot \hat{\epsilon}_{k\alpha} \qquad (2.6)$$

and $V_a(R), V_b(R)$ are the potential energy curves for the $A^1\Sigma_u^+$ and $X^1\Sigma_g^+$ states respectively. $D(R)$ is the radial transitional dipole moment between them. E is the initial energy of the relative motions and ω is the angular frequency of the emitted photon.

Now to solve this. We find the Green function for the equation (2.5) which satisfies the retarted boundary conditions so that $F_{k\alpha}$ contains only outgoing waves in the limit $R \to \infty$:

$$\left[-\frac{1}{2\mu}\nabla_R^2 + V_b(R) + \hbar\omega - E \right] G^+(\mathbf{R}, \mathbf{R}') = \delta^3(\mathbf{R}, \mathbf{R}') \qquad (2.7)$$

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and from the equation (2.7) we get:

$$F_{k\alpha}(\mathbf{R}) = \int d^3 R' G^+(\mathbf{R}, \mathbf{R}') F_a(\mathbf{R}') U_{k\alpha}^\dagger(\mathbf{R}') \tag{2.8}$$

We can express this function in the partial waves bases. Since V_b contains no bound states we get for $\mathbf{R} = \mathbf{R}(R, \theta)$:

$$G^+(\mathbf{R}, \mathbf{R}') = \frac{\pi\mu}{k_b} \sum_{l=0}^{\infty} \sqrt{\frac{1}{2\pi}} \cos(l\,\theta) \cos(l\,\theta') \times \frac{f_l(k_b R_<) g_l^+(k_b R_>)}{RR'} \tag{2.9}$$

where $P_l(\cos\theta)$ are Legendre polynomials, also $m = 0$ part of the spherical harmonics: $P_l(\cos\theta) = Y_{l0}\theta, \phi$.

The $f_l(kR)$ is a regular solution of the homogenous Schrodinger radial equation for the 2D case: [51]:

$$\left\{ \frac{d^2}{dR^2} - \frac{l(l+1)}{R^2} - 2\mu \left[V_b(R) - V_b(\infty) \right] + k^2 \right\} f_l(kR) = 0 \tag{2.10}$$

$$k \equiv \sqrt{2\mu[E - \hbar\omega - V_b(\infty)}$$

where:

$$f_l \sim \sqrt{\frac{2}{\pi}} \sin\left[kR - \frac{l\pi}{2} + \delta_l(b) \right] \tag{2.11}$$

and $g_l^+(kR)$ is irregular solution with the boundary condition at large R.

$$g_l^+ \sim \sqrt{\frac{2}{\pi}} \exp i \left[kR - \frac{l\pi}{2} + \delta_l(b) \right] \qquad (2.12)$$

and $\delta_l(b)$ is a phase shift.

The total wave function (2.3) must be symmetric under the interchange of the H nuclei, so that $F_a(\mathbf{R}) = -F_a(-\mathbf{R})$ and $F_{k\alpha}(\mathbf{R}) = F_{k\alpha}(-\mathbf{R})$. Now we solve equations (2.4) and (2.5) in the distorted wave approximation. Then $F_a(\mathbf{R})$ is the solution of the (2.4) with the coupling term set to be zero and it can be expressed in the form:

$$F_a(\mathbf{R}) = \sum_{l=1}^{\infty} \cos(l\,\theta)(2l+1)i^l \sqrt{\pi} \times \exp[i\delta_l(a)] \frac{s_l(k_a\mathbf{R})}{k_a\mathbf{R}} \qquad (2.13)$$

The asymptotic form for (2.13) is:

$$F_a(\mathbf{R}) \sim \frac{1}{\sqrt{2}} \left[e^{ik_a z} - e^{-ik_a z} + [f(\theta, \phi) - f(\theta - \pi, \phi + \pi)] \frac{e^{ik_a R}}{R} \right] \qquad (2.14)$$

By inserting (2.13) and (2.9) into (2.8) we get the asymptotic form for the (2.8):

$$F_{k\alpha}(\mathbf{R}) \sim \frac{e^{ik_a R}}{R} f_{k\alpha}(\theta) \qquad (2.15)$$

where:

$$f_{k\alpha}(\theta) = sum_l \cos(l\,\theta) \left[\sum_{J=1}^{\infty} \frac{2\pi\mu}{k_a k_b}(2J+1) \left(\frac{\pi kc}{A} \right)^{1/2} e^{i\delta_j(b)} e^{i\delta_j(a)} i^{J+l-1} \right] \sqrt{2l+1)2\pi} \qquad (2.16)$$

In this summation, the j is restricted to the odd integers, and

$$M_{l,l'}(k_a, k_b) = \frac{1}{\sqrt{k_a, k_b}} \int_0^\infty dR s_l(k_a, R) D(R) f_{l')(k_b, R)} \tag{2.17}$$

The cross section of the collision induced transition between the H atom and the H^+ ion is obtained by summing $|f_{k\alpha}(\theta)|^2$ over all final states that conserve energy with an inital state, and dividing the result with the flux of the incident channel.

The $H\left(2^1 S\right) \rightarrow H\left(1^1 1 S\right)$ is a linear combination of $A1\sigma_u^+$ and $X1\sigma_g^+$ states. Since the excited gerade state is not allowed to make a radiative transition to a gerade ground state, the flux in the incident channel is twice the flux in the $A1\sigma_u^+$ channel.

So for the cross section we get:

$$\sigma = \int_0^{\omega_{max}} d\omega \frac{d\sigma}{d\omega} =$$
$$= \sum_\alpha \int \frac{d^2 k}{(2\pi)^2} \frac{A}{2\mu k_a} \int d^2 k_b \delta \left[\frac{k_b^2}{2\mu} - \frac{k_a^2}{2\mu} + \Delta E - \hbar\omega \right] |f_{k\alpha}(\theta)| \tag{2.18}$$

where

$$\frac{d\sigma}{d\omega} = \frac{8}{3} \left[\frac{\pi\mu}{k_a} \right]^2 \frac{1}{c^3} \omega^3 \sum_J \left[J M_{J,J-1}^2(k_a, k_b) + (J+1) M_{J,J+1}(k_a, k_b) \right] \tag{2.19}$$

ΔE is the energy of the transition at $R = \infty$ and ω_{max} is the maximum frequency of the emitted photon. Expression (2.18) is an equivalent expression to the Fermi's Golden Rule. Equation (2.19) provides the spectrum of the emitted radiation, in addition to the scattering cross section.

Optical Potential Method

The approximation that does not require the integration over the total spectrum is the optical potential method. TODO: Insert optical potential method.

To derive it here we insert the equation (2.8) for the amplitude $F_{k\alpha}(\mathbf{R})$ into the equation (2.4) to obtain the equation for the amplitude $F_a(\mathbf{R})$

$$\left[-\frac{1}{2\mu}\nabla_R^2 + V_a(R) - E\right]F_a(\mathbf{R}) = \sum_{k\alpha} d^2R' G^+(\mathbf{R}, \mathbf{R}')U_{k\alpha}^\dagger(\mathbf{R}')U_{k\alpha}(\mathbf{R})F_a(\mathbf{R}') \quad (2.20)$$

The right hand of (2.20) contains a complex, non-local potential

$$V(\mathbf{R}, \mathbf{R}') = \sum_{k\alpha} G^+(\mathbf{R}, \mathbf{R}')U_{k\alpha}^\dagger(\mathbf{R}')U_{k\alpha}(\mathbf{R}) \quad (2.21)$$

that arises because of the interaction of the electron with the vacuum. Now the real part of this potential induces the shift in the eigenvalue $V_a(R)$. Since the coupling on an electron with the radiation is weak, we can ignore it and consider only the imaginary part.

The imaginary part of $V(\mathbf{R}, \mathbf{R}')$ is an absortive potential, representing a process where electron in excited state emits a photon and decays to a ground state. This potential is non-local, as we take is for $R = \infty$. In the optical potential aprroxmation, we take replace potential by the local one, whose range is limited to the scattering area. This potential is essentialy classical.

Because the term $U_{k\alpha}^\dagger(\mathbf{R}')U_{k\alpha}(\mathbf{R})$ appearing in equation (2.21) is real, the optical potential is pro-

portional to the imaginary part of the retarded Green's function, which is expressed as:

$$\text{Im}G^+(\mathbf{R}, \mathbf{R}) = \pi \sum_{l=0}^{\infty} \cos(l\,\theta) \cos(l\,\theta') \int_0^{\infty} dk\, \delta \left[\frac{k^2}{2\mu} - \frac{k_a}{2\mu} + \hbar\omega - DeltaE \right] \frac{f_l(kR)f_l(kR')}{R\,R'}$$

$$(2.22)$$

This result is obtained using the spectral representation of the retarted Green's function and the identity $1/(x + i\epsilon) \to P/x - i\pi\delta(x)$ as $\epsilon \to 0$. Using (2.22) one obtains for the non-local optical potential:

$$V(\mathbf{R}, \mathbf{R}') = \frac{i}{2\pi} \sum_{\alpha} \int d\Omega_k \int_0^{k_{max}} \sum_{l=0}^{\infty} \cos(l\,\theta) \cos(l\,\theta') \times \frac{\omega^3}{c^3} \frac{f_l(kR)f_l(kR')}{R\,R'} D(R)D(R')(\hat{\mathbf{R}} \cdot \epsilon_{k\alpha})(\hat{\mathbf{R}}' \cdot \epsilon_{k\alpha})$$

$$(2.23)$$

where $\omega(k) = k_\alpha/2\mu + \Delta E - k^2/mu$. Now for the optical-potential approximation we make the semi-classical approximation that the values of k that give the largest contribution are given by:

$$\frac{k^2}{2\mu} \simeq= \Delta E + \frac{k_\alpha^2}{2\mu} + V_b(r) - V_a(r) \qquad (2.24)$$

Now the frequency term $\omega^3 = |\Delta E(R)|^3$ can now be taken outside the integral.

Using the expansion: TODO: delta function expansion in 2 dimensions and verify below

$$\delta^2 \left(\mathbf{R}, \mathbf{R}' \right) = \sum_{l=0}^{\infty} \cos(l\,\theta) \cos(l\,\theta') \frac{\delta(R - R')}{R\,R'} \qquad (2.25)$$

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we get:

$$V_{opt}(\mathbf{R}, \mathbf{R}) \approx= \frac{i}{2}\delta^2\left(\mathbf{R}, \mathbf{R}'\right) A(R),$$

$$A(R) = \frac{4}{3}D^2(R)\frac{|\Delta E(R)|^3}{c^3}$$

(2.26)

and equation (2.23) becomes:

$$\left[-\frac{1}{2\mu}\nabla_R^2 + V_a(R) - E\right] F_\alpha(\mathbf{R}) = \frac{i}{2}A(R)F_\alpha(\mathbf{R})$$

(2.27)

The cross section for the radiative quenching is given by:

$$\sigma = \frac{\pi}{k_a^2}\sum_{J=0}^{\infty}(2J+1)\left(1 - e^{-4\eta_j}\right)$$

(2.28)

where eta_j is the imaginary component of the phase shift of the Jth partial wave of the solution (2.23). The sum on J is restricted to the odd integers. Also because the right hand of (2.23) is small, we can use the distorted wave approximation to obtain the expression for the phase shift eta_j

$$\eta_j = \frac{\pi\mu}{2k_a}\int_0^{\infty} dR\, |s_J(k_aR)|^2 A(R)$$

(2.29)

TODO: JWKB

Using the JWKB approximation to the (2.29), by replacing the sum with an integral, and recognizing

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that η_J is small, we obtain the semi-classical cross section:

$$\sigma = 2\pi\sqrt{\frac{2\pi}{E}} \int dp\, p \int_{R_c}^{\infty} dR \frac{A(R)}{\sqrt{1 - \frac{V_a(R)}{E} - fracp^2R^2}} \tag{2.30}$$

where R_c is the classical turning point and E is the kinetic energy.

As expected, there does not exist the analytic solution to this differential equation . Ergo, I used the numerical method, namely Mathematica code to solve this equation. This equations behaves 'well' so the solution is easy to find numerically.

2.1 Charge Transfer

TODO: Make this a new chapter.

TODO: Electronic translation factor (ETF)

As usual, we also employ the Born-Oppenheimer (BO) approximation. We expand the scattering wave function in the terms of BO wave functions, modifed by the electronic translation factor. If we set $\chi_i^a(\mathbf{R})$ to the be wave function of the nuclear motion in the electronic state i, we get for the wavefunction:

$$\Psi(\mathbf{r}, \mathbf{R}) = \sum_i exp\left[\frac{1}{\mu}\mathbf{S} \cdot \nabla_R\right] \phi(\mathbf{r}, \mathbf{R})\chi_i^a(\mathbf{R}) \tag{2.31}$$

with μ being the reduce mass, and

$$S = \frac{1}{2}f_i(\mathbf{r}, \mathbf{R})\mathbf{r} \tag{2.32}$$

where f_is are the switching functions that incorporte the molecular character of the ETF. The equations for the $\chi_i^a(\mathbf{R})$ can be obtaind in a matrix form:

$$\left\{-\frac{1}{2\mu}\left[\underline{I}\nabla_R - i(\underline{\mathbf{P}} + \underline{\mathbf{rAP}})\right]^2 + \underline{V}\right\}\underline{\chi}^a(\mathbf{R}) = E\underline{\chi}^a(\mathbf{R}) \qquad (2.33)$$

with:

$$\begin{aligned}
\mathbf{P}_{ij} &= \langle \phi_i \,|\, -i\nabla_R \,|\, \phi_j \rangle \\
\mathbf{A}_{ij} &= i(E_i - E_j)\,\langle \phi_i \,|\, \mathbf{S} \,|\, \phi_j \rangle \qquad (2.34) \\
V_{ij}(R) &= \delta_{ij}V_i(R)
\end{aligned}$$

where E is the energy of the nuclear motion in the center of mass frame, and $\underline{I}$ is the identity matrix. The matrix $\mathbf{P}_{ij}$ represents the non-adiabatic coupling, the $\mathbf{A}_{ij}$ is the ETF correction, and the $V_i(R)$ is the potential energy of the ith Born-Opennheimer state.

2.1.1 Radiative charge transfer and radiative association

The radiative charge transfer cross-section can be calculated using the formula (2.18) for σ with M calculated using formula (2.17), where the k_a and k_b are the wave numbers of the initial and final state.

The partial waves $f_j(kR)$ and $s_j(kR)$ are the regular solutions of the homogenou radial equations.

$$\left\{\frac{d^2}{dR^2} - \frac{J(J+1)}{R^2} - 2\mu\left[V_a(R) - V_b(\infty)\right\} + k^2\right\}s_j(kR) = 0 \qquad (2.35)$$

and

$$\left\{ \frac{d^2}{dR^2} - \frac{J(J+1)}{R^2} - 2\mu \left[V_b(R) - V_a(\infty) \right\} + k^2 \right\} f_j(kR) = 0 \qquad (2.36)$$

with $V_a(R)$ and $V_b(R)$ being the potential energy curves of the final ground state and the initial excited state, respectively. The ks are the wave numbers, given by:

$$
\begin{aligned}
k_b &= \sqrt{2\mu \left[E - \hbar\omega - V_b(\infty) \right]} \\
k_a &= \sqrt{2\mu \left[E - V_a(\infty) \right]}
\end{aligned}
\qquad (2.37)
$$

where ω is the angular frequency of the emitted photon, E is the total collision energy in the center of mass frame.

Again, we get calculate the total cross section given by the radiative decay as:

One has to be careful though, since it seems that most numerical methods are very sensitive to the choice of initial conditions. As a second order equation, the solution requires two initial conditions, either in the form of function value at the ends of the interval, or value of the function and its derivative at some point. Now, this partial wave represents an incoming particle (electron) and thus the function $f(kR)$ is defined on the infinite interval and it is oscillatory for large values of kR. Because of that, it is impossible to specify a boundary condition for value of $f(kR)$ at infinity. So the boundary conditions have to be in the form of the value of function at some point and the value of the derivative at the same point.

In my calculation, I assume that for $kR \to 0$, the function $f(kR)$ is finite and 'well behaving', so

the appropriate boundary conditions seem to be:

$$\text{For } kR \to 0, \ f(kR) = 1 \, ; \ f'(kR) = 0 \qquad\qquad (2.38)$$

The Mathematica code for the $f(kR)$ is in appendix TODO: add code.

Following the approach in the [52] I apply a semi-classical approach to the system of two H_2^+ molecules. In this approach, I assume that a photon is emitted with energy equal to the energy difference between two Born-Oppenheimer potential surfaces, at the distance where the transition occurs. This leads to the Local Optical Potential Method, and following the semi-classical approach, the total rate is estimated as a classical integral over all localized transitions.

The cross section of the spontaneous radiative association is given by [7] . This can also be derived using the Fermi's Golden Rule (which turns out to be published by Dirac's 20 years before Fermi):

$$\sigma_{CT} = \int_0^{\omega_{max}} d\omega \, \frac{d\sigma}{d\omega}$$

where : $\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad (2.39)$

$$\sigma_{sp}(k) = \sum_J \sum_n \frac{64}{3} \frac{\pi^5 \nu^3}{c^3 k^2} \left[(J+1)M_{J+1,J}^2 + J \, M_{J-1,J}^2 \right]$$

The sum extends over the rho-vibrational quantum numbers n and angular momentum J of the H_2^+ ion. Due to the topological constraints the direction of J remains fixed, and only its magnitude changes. As expected, for the ground state we have $J = 0$.

The $M_{J,J'}$ is an overlap integral defined by:

$$M_{J,J'} = \int_0^\infty dR\, f_j(kR)D(R)\phi_{J'}^n(R) \qquad (2.40)$$

where $f_j(kR)$ is a partial wave defined above.

Vibrational Levels

The $\phi_{J',n}(R)$ represent the vibrational eigenfunction of the ground state $X^2\Sigma^+$ with the energy $\epsilon_n J$. TODO: Show picture. Given the nature of the problem 2D, the ground state has the $J = 0$. So the differential equation for the $\phi_{0,n}(R)$, in the potential well, is:

$$\phi_{0,n}^{''}(R) + [E(R) + V(R)]\,\phi(R)_{0,n} = \epsilon_n \phi(R)_{0,n} \qquad (2.41)$$

Of course the solution to this equation can only be calculated numerically (appendix TODO: shows the Mathematica code.). To solve the equation one must set the boundary conditions to $\phi(R)_{0,n} \Rightarrow 0, \phi(R)_{0,n}^{'}$ for $R \Rightarrow 0$. For actual numerical evaluation, the important boundary condition is the value of $\phi(R \approx 0)_{0,n}$. With these boundary conditions set, the values of ϵ_n must satisfy the boundary condition on the other side of the potential well, namely that the $\phi(R)_{0,n}$ remains bounded, which translates into: $\phi(R)_{0,n} \Rightarrow 0$ for $R \Rightarrow \infty$.

So calculations show (TODO: Verify) that there are

Dipole Transition in 2 Dimension

The $D(R)$ is the transition dipole moment between $X^2\Sigma^+$ and $A^2\Sigma^+$,

$$D(R) = \langle \psi_1(R) \,|\, r_1 + r_2 \,|\, \psi_0(R) \rangle \quad \text{where in our case :}$$

$$r_1 + r_2 = \lambda R$$

(2.42)

Now the 2 dimension case comes into effect. I consider the case where the electrons are confined in 2 dimensions, but where the underlying space is still 3 dimensional, Euclidean. Thus while electrons' movement is confined in 2D, they can radiate photons in any direction in 3D.

TODO: Add appendix for the radiation in 1D and 2D.

Now with the separation of variable, the solution is a product of two function. So the integral above come to:

$$D(R) = \int_{-1}^{1} \int_{1}^{\infty} d\mu \, d\lambda \, M_u(\mu) L_u(\lambda) \lambda R M_g(\mu) L_g(\lambda)$$

(2.43)

where $M_u L_u$ and $M_g L_g$ are the odd/even solutions to the original Schrodinger equation (2.1).

Since the functions $M(\mu)L(\lambda)$ and do not exist in the closed form, the dipole integral (2.43) is numerically calculated using Wolfram Mathematica. First the two Mathematica modules (functions) are created, which solve the equations $L(\lambda)$ and $M(\mu)$, as function of the internuclear distance R and corresponding variables. Then the second module calculates the integral above, as the function of R.

The Mathematica code for the dipole is in appendix TODO: add code and indicate that I wrote it.

:)

From the table TODO: add reference one could calculate the spectrum of these transitions. For the electron to transition from $A^2\Sigma^+$ to $X^2\Sigma^+$ level, it needs to emit photon $\Delta E \approx -3.2\,au = 0.1176eV$, so the corresponding wavelength is $\lambda \approx 380\,nm$ TODO: Verify the numbers. TODO: verify the depth of the potential well compared to the paper [31]

TODO: Possible spectrum of such transitions

DISTORTED WAVE APPROXIMATION

TODO: Scattering in 2 D

The distorted wave Born approximation (DWBA) is an extension to the (first) Born approximation in scattering processes. Starting from the Schrodinger equation for the scattering problem, we solve it by method of Green's function

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r})\right]\psi_k(\mathbf{r}) = E\psi_k(\mathbf{r})$$

(2.44)

with $V(\mathbf{r}) = 0$ except in the target region $\implies$

The energy E is the energy of the incident plane wave, $E = \hbar^2 k^2/2m$. Applying the Green's function

$$\left[\frac{\hbar^2}{2m}\nabla^2 + E\right]G_0(\mathbf{r}, \mathbf{r}'|E) = V(\mathbf{r})\psi_k(\mathbf{r})$$

(2.45)

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we get the integral form of the Schwinger-Lippmann equation:

$$\psi_k'(\mathbf{r}) = \psi_k(\mathbf{r}) + \int d^3r' \, G_0(\mathbf{r}, \mathbf{r}'|E)V(\mathbf{r}')\psi_k'(\mathbf{r}) \tag{2.46}$$

The scattering amplitude is given by [10]

$$f_k(\mathbf{r}) = -\frac{2m}{\hbar^2}\frac{1}{4\pi}\int d^3r' \, e^{-i\mathbf{k}\mathbf{r}'} V(\mathbf{r}')\psi_k'(\mathbf{r}') \tag{2.47}$$

Since the Schwinger-Lippmann equation (2.46) is unsolvable, the first Born approximation assumes that the scattered field is small when compared to the incident field. Therefore it treats the scattered way as a perturbation. As the $0 - th$ order the scattered wave is an unperturbed incident plane wave:

$$\psi_0'(\mathbf{r}) = e^{i\mathbf{k}\mathbf{r}} \tag{2.48}$$

and then the equation (2.46) is solved iteratively:

$$\psi_{n+1}'(\mathbf{r}) = e^{i\mathbf{k}\mathbf{r}} + \int d^3r' \, G_0(\mathbf{r}, \mathbf{r}'|E)V(\mathbf{r}')\psi_k'(\mathbf{r}) \tag{2.49}$$

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So if we expand the wave function in the powers of the interaction potential V we get:

$$\psi_k^{'} = \psi_\mathbf{k}^{'(0)} + \psi_\mathbf{k}^{'(1)} + \psi_\mathbf{k}^{'(2)} + ...$$

$$= \psi_\mathbf{k}^{'(0)} + G_0 V \psi_\mathbf{k}^{'(0)} + G_0 V G_0 V \psi_\mathbf{k}^{'(0)} + ... \tag{2.50}$$

$$= (1 + G_0 T) \psi_\mathbf{k}^{'(0)} \quad \text{with } T = V + G_0 V + ... = \frac{1}{1 - V G_0}$$

The equation (2.50) represents a scattering process where incident particle undergoes multiple scattering events from the potential. Since this makes the calculations very complicated, only the first iteration of the series is takes into account and the matrix T is approximated by the potential V. This first order term in which the exact wave function $\psi_\mathbf{k}^{'}(\mathbf{r})$ is replaced by the plane wave $e^{i\mathbf{k}\mathbf{r}}$ is the First Born Approximation. It is very useful, however it is not always valid and one way to extend its validity is the DWBA.

In the DWBA, we do not assume any more that the scattered field is small compared to the incident field. So in this case, it is possible to generalize the Born approximation. The free space zero potential $V_0(\mathbf{r}) = 0$ is replaced by the non-trivial reference potential $V_1(\mathbf{r}) = 0$. It is assumed that the scattered wave function $\psi_\mathbf{k}^{'1}$ due to this potential is known, either analytically or numerically as a solution to the following Schwinger-Lippmann equation:

$$\psi_{n+1}^{'}(\mathbf{r}) = e^{i\mathbf{k}\mathbf{r}} + \int d^3 r^{'} \, G_0(\mathbf{r}, \mathbf{r}^{'}|E) V_1(\mathbf{r}^{'}) \psi_k^{'1}(\mathbf{r}) \tag{2.51}$$

Then the interaction potential is treated as a perturbation to the reference potential V_1, i.e:

$$V(\mathbf{r}) = V_1(\mathbf{r}) + \delta V(\mathbf{R} \quad \text{with} \quad |\delta V| << |V_1| \tag{2.52}$$

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So in the DWBA the scattering field is determined by applying the Born approximation:

$$\psi^{'}(\mathbf{r}) = \psi^{'1}(\mathbf{r}) + \int d^3r^{'} \, G_0(\mathbf{r}, \mathbf{r}^{'}|E) V_1(\mathbf{r}^{'}) \psi_k^{'1}(\mathbf{r}) \tag{2.53}$$

to the scattered wave $\psi^{'}(\mathbf{r})$. This distorted wave is the solution of the outgoing-wave Schrodinger equation:

$$\left[\frac{\hbar^2}{2m} \nabla^2 - V_1(\mathbf{r}) + E \right] \psi^{'1}(\mathbf{r}) = 0 \tag{2.54}$$

where we can use the Green's function method.

To satisfy the boundary conditions, the asymptotic form of the $\psi^{'1}(\mathbf{r})$ for $r \to \infty$ is:

$$\psi^{'1}(\mathbf{r}) \to e^{i\mathbf{k}\mathbf{r}} + \frac{1}{r} e^{ikr} f_k^1(\theta) \tag{2.55}$$

where the scattering amplitude is:

$$f_k^1(\theta) = -\frac{2m}{\hbar^2} \frac{1}{4\pi} \int d^3r^{'} \, e^{-i\mathbf{k}\mathbf{r}^{'}} V_1(\mathbf{r}^{'}) \psi_k^{'1}(\mathbf{r}^{'}) \tag{2.56}$$

This would be the scattering amplitude if the potential V_1 were the only potential present. The total scattering amplitude is the sum:

$$f_k(\theta) = f_k^1(\theta) + \delta f_k(\theta) \tag{2.57}$$

and $\delta f_k(\theta)$ is calculated in the Born approximation:

$$\delta f_k(\theta) \simeq -\frac{2m}{\hbar^2}\frac{1}{4\pi}\int d^3r' \, \psi_{k'}'^{1(-)*}(\mathbf{r}')V_1(\mathbf{r}')\psi_k'^1(\mathbf{r}') \qquad (2.58)$$

The $\psi_{k'}'^{1(-)*}$ is the known incoming wave, corresponding to the reference potential V_1 (i.e. solution of the Schrodinger equation) .

The condition for the (2.58) to be a good approximation is for the $\delta V(\mathbf{r})$ to be sufficiently small. What that means is that possible additional scattering does not modify significantly the wave function.

LAPLACIAN EIGENFUNCTIONS AND GREEN'S FUNCTION IN 2D

Starting from the Laplace operator and switching to polar coordinates:

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} = \frac{\partial}{\partial r^2} + \frac{1}{r}\frac{\partial}{\partial r} + \frac{\partial^2}{\partial \theta^2}$$

$$\nabla^2 u(r,\theta) = 0 \qquad (2.59)$$

If the assume that the solution admits separation of variables:

$$u(r,\theta) = R(r)\Theta(\theta) \implies \qquad (2.60)$$

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the Laplacian transforms into

$$\frac{R''}{R} + \frac{R'}{rR} + \frac{\Theta''}{r^2\Theta} = -\lambda \tag{2.61}$$

Set $\frac{\Theta''}{\Theta} = -\gamma$ and we obtain 2 ODEs:

$$\Theta'' + \gamma^2\Theta = 0$$

$$R'' + \frac{1}{r}R' + \left(\lambda - \frac{\gamma}{r^2}\right)R = 0 \tag{2.62}$$

From this we can see that the solution for the Θ equation is:

$$\Theta(\theta) = A\cos\sqrt{\gamma} + B\sin\sqrt{\gamma} \tag{2.63}$$

and using the substitution $\rho = \sqrt{\lambda}r$ we get the Bessel equation for R.

$$R''_\rho + \frac{1}{\rho}R'_\rho + \left(1 - \frac{n^2}{\rho^2}\right)R = 0 \tag{2.64}$$

CHAPTER 3

Radiative Charge Transfer

TODO: Reference the Mathematica/Fortran code also.

3.1 Non-Adiabatic Charge Transfer

Similarly to the Radiative Association, this is another scattering process. In this case, we do not have the formation of a molecule as a results. Instead, we have an electron transition from the $A^2\Sigma^+$ to $X^2\Sigma^+$ level, accompanying by the emission of the photon. Since no stable state is formed, we have two partial waves, one incoming and one leaving the scattering area.

3.1.1 Description

The cross section of the spontaneous radiative association is again given by [7]

$$\sigma_{CT} = \int_0^{\omega_{max}} d\omega \, \frac{d\sigma}{d\omega}$$

$$\sigma_{sp}(k) = \sum_J \sum_n \frac{64}{3} \frac{\pi^5 \nu^3}{c^3 k^2} \left[(J+1) M_{J+1,J}^2 + J \, M_{J-1,J}^2 \right] \qquad (3.1)$$

where

$$\frac{d\sigma}{d\omega} = \sum_J \frac{8}{3} \frac{\pi^2 \omega^3}{c^3 k^2} \left[J \, M_{J,J-1}^2(k,k') + (J+1) M_{J,J+1}^2(k,k') \right] \qquad (3.2)$$

and

$$M_{J,J'}(k,k') = \qquad (3.3)$$

3.1.2 Calculation

CHAPTER 4

Conclusion

Center of Mass as a Plane Wave

Take the isolated system of 2 interacting spinless particles. The particles are of masses m_1 and m_2 and are located at positions $\mathbf{r}_1$ and $\mathbf{r}_2$. The potential energy of the particles depends only on their relative position $\mathbf{r}_1 - \mathbf{r}_2$. The Langrangian of this system can be written as:

$$L = T - V = \frac{1}{2}m_1 \cdot r_1^2 + \frac{1}{2}m_2 \cdot r_2^2 + V(\mathbf{r}_1 - \mathbf{r}_2 = \frac{1}{2}M \cdot R^2 + \frac{1}{2}\mu \cdot r^2 + V(\mathbf{r}) \qquad \text{(A.1)}$$

where

$M = m_1 + m_2$ is a total mass of the system

$\mu = \dfrac{m_1 m_2}{m_1 + m_2}$ is a reduced mass of the system

(A.2)

$\mathbf{R} = \dfrac{m_1\mathbf{r}_1 + m_2\mathbf{r}_2}{m_1 + m_2}$ are the coordinates of the center of the mass of the system, and

$\mathbf{r} = \mathbf{r}_1 - \mathbf{2}$ are the relative coordinates.

with:

$$p_i = \frac{\partial L}{\partial q_i} \text{ we define}$$

$$\mathbf{P} = M{\cdot}\mathbf{R} \quad \text{and } \mathbf{p} = \mu \cdot \mathbf{r} \text{ and we obtain} \tag{A.3}$$

$$\cdot\mathbf{P} = 0 \quad \cdot\mathbf{p} = -\nabla V \mathbf{r}$$

Now using the variables $\mathbf{P}, \mathbf{R}, \mathbf{p}, \mathbf{r}$ we get for the Hamiltonian:

$$H = \frac{P^2}{2M} + \frac{p^2}{2\mu} + V(\mathbf{R}) = H_{CM} + H_r \tag{A.4}$$

The first term represents the motion of the center of the mass, which is a uniform inertial motion, since $\cdot\mathbf{P} = 0$. The other terms represent the energy associated with the motion relative to the center of the mass. Now if we choose the inertial frame in which the center of the mass is at rest, we get the Hamiltonian to reduce to H_r, representing the motion of a single, fictitious particle in an external potential.

Now transitioning to a quantum case. The variables $H, \mathbf{P}, \mathbf{R}, \mathbf{p}, \mathbf{r}$ become operators, with the usual commutation relations:

$$[R_i, P_j] = [r_i, p_j] = i\delta_{ij} \text{ and } [R_i, p_j] = [r_i, P_j] = 0 \implies$$

$$\tag{A.5}$$

$$[H_{cm}, H_r] = 0, \; [H_r, H] = 0 \, [H_{CM}, H] = 0$$

Since all the Hamiltonians commute, there exists a common eigenbasis in some state space E of H, H_{CM}, H_r. We can express the space E as a tensor product of spaces E_R and E_{cm} with $E = E_{CM} \otimes E_r$. The operators $\mathbf{P}, \mathbf{R}$ operate in space E_{CM} and operators $\mathbf{p}, \mathbf{r}$ operate in E_r space.

From the Lagrangian and the Hamiltonian above we observe that the motion of the center of mass and the relative motion are completely independent of each other.

$$H_{CM} \left| \chi \right\rangle = E_{CM} Ket\chi \quad H_r \left| \omega \right\rangle = E_r Ket\omega$$

$$H \left| \phi \right\rangle = (H_{CM} + H_r)(\left| \chi \right\rangle \otimes Ket\omega) = H_{CM}(\left| \chi \right\rangle \otimes Ket\omega) + H_r(\left| \chi \right\rangle \otimes Ket\omega) = (E_{CM} + E_r)(\left| \chi \right\rangle \otimes Ket\omega)$$

$$(A.6)$$

Expressing the expressions above in coordinate representation, we have:

$$\phi(\mathbf{R}, \mathbf{r}) = \chi(\mathbf{R})\omega(\mathbf{r})$$

$$H_{CM}\chi(\mathbf{R}) = E_{CM}\chi(\mathbf{R}) \quad H_r\omega(\mathbf{r}) = E_r\omega(\mathbf{r}) \qquad (A.7)$$

$$-\frac{\hbar_R^2}{2M}\nabla^2\omega(\mathbf{R}) = E_{CM}\omega(\mathbf{R}) \quad -\frac{\hbar^2}{2M}\nabla_r^2\omega(\mathbf{r}) = E_r\omega(\mathbf{r})$$

So we can solve for $\chi(\mathbf{R})$ to obtain:

$$\chi(\mathbf{R}) = \frac{1}{(2\pi\hbar)^{3/2}}e^{\frac{i}{\hbar}} \qquad (A.8)$$

APPENDIX B

MATHEMATICA CODE FOR CALCULATING THE EIGENVALUES FOR THE H2

IO IN 3D

APPENDIX C

Radiation by Charges Oscillating in Lower Dimensions

Assume that the charge is confined to move in 1D but it can emit photon is any direction in 3D.

From [18]:

hapterWolfram Mathematica Code

To run the numerical calculations I used Wolfram Mathematica Student Edition, version 10.0.02 and gfortan 5.2.0, running on 2.2 GHz, Intel Code 7, Macbook Pro 15" Laptop (mid 2014), El Capitan 10.11. The numerial library used was Lapack, version 3.6.0, compiled on the same machine using the gfortran above.

C.0.1 Vibrational Modes

C.0.2 Dipole Transitions

C.0.3 Radial Wavefunction

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