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INTRODUCTION TO
INTERMOLECULAR POTENTIALS
STUDY. A PRACTICAL CASE:
 $He - H_2^+$ INTERACTION

by

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DEDICATION

Este trabajo no sería posible de no ser por el apoyo proveniente de mis padres, mis abuelos y mis tías a que siguiese estudiando. Es por ello que dedico este último paso del camino para convertirme en Físico a ellos, que lo hicieron posible. También me gustaría agradecer el apoyo incondicional a todas esas personas que estuvieron ahí en los momentos más duros de esta etapa de mi vida: mi hermana, mis primas y primos, así como los amigos y amigas de toda la vida, y las personas que se incorporaron a ella en esta etapa universitaria. No sería quien soy ahora de no ser por ellos. Gracias de corazón.

Pilli, lo conseguí.

"Mejor que ayer, peor que mañana."

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"The Universe is under no obligation to make sense to you."- Neil deGrasse Tyson

SUMMARY

La física cuántica como rama científica ocupa el estudio de la materia y posibles interacciones entre partículas a una escala en la que la física clásica no puede interpretar los sucesos observados. Dentro de dicha rama, este trabajo se centrará en el campo de la física atómica y molecular para abordar el estudio de un sistema que, si bien pudiera parecer simple, esconde propiedades de interés a la par que complejas a la hora de su estudio en profundidad. Se estudia el átomo de Helio, sistema compuesto por un núcleo y dos electrones, y a su vez el catión Hidrógeno molecular H_2^+ compuesto por dos núcleos y un electrón. Asimismo, se estudiará la interacción átomo-molécula. El fin de dichos estudios será hallar las curvas de energía potencial (PEC) en función de la distancia internuclear para los sistemas en el estado fundamental.

Para el análisis de estos sistemas se aplicarán diversas aproximaciones las cuales simplifican considerablemente el estudio sin suponer errores cuyo orden influya gravemente en el resultado. Partiendo de la ecuación no relativista de Schrödinger independiente del tiempo, asumiendo núcleos infinitamente masivos y usando la aproximación de Born-Oppenheimer, se consiguen Hamiltonianos electrónicos a fin de estudiar dicha estructura electrónica. Dada la fijación de las posiciones de los núcleos, la función de onda resultante de la resolución de la ecuación de Schrödinger electrónica se verá simplificada, pues no dependerá de las posiciones nucleares como variables.

El cálculo de estos sistemas se realiza mediante la implementación de los métodos ab initio. Este conjunto de métodos variacionales plantean una manera de resolver teóricamente las ecuaciones de Schrödinger basándose en el uso de constantes universales, la posición de los núcleos y el número de electrones. Se parte del método de campo autoconsistente Hartree-Fock, el cual asume una función de onda antisimétrica basada en el producto de orbitales monoeléctricos en forma de

determinante de Slater para resolver la ecuación de Schrödinger electrónica. Una vez resuelta, se realizan iteraciones del mismo método con la función de onda refinada hasta obtener diferencias despreciables en la energía de estado fundamental. Debido a la suposición de la función de onda como producto de orbitales monoeléctricos, aunque sea antisimétrica y cumpla el Principio de Exclusión de Pauli, no contempla la interacción entre electrones a la hora de la consecuente deformación de estos orbitales. Esto desemboca en una diferencia entre la energía real del sistema y aquella hallada por el método Hartree-Fock, la cual se define como el término de correlación electrónica. Es por esto que se añade al estudio el método de clusters acoplados. Este introduce un operador que modifica la función de onda para que al resolver la ecuación de Schrödinger sí se tenga en cuenta este efecto.

De la misma forma que el método de clusters acoplados mejora los resultados obtenidos mediante Hartree-Fock, los cálculos pueden sufrir mejoras por medio de el uso de un *ansatz* de función de onda más ajustado a modelos reales. Para los sistemas a tratar en este trabajo, se utilizará una familia de bases para las funciones de onda que tiene en cuenta la correlación y efectos de polarización entre orbitales atómicos (bases de Dunning *aug-cc-pVNZ*). Un problema común a cualquier base usada para el cálculo de estos métodos es la necesidad de truncar el número de funciones de esa base, lo cual se intenta solventar mediante el ajuste a través de una función dada de la energía en función del número de bases utilizadas, para ver el valor que toma la energía con la regresión en el límite de base infinita. La teoría detrás de los métodos y las funciones de onda que se usan para implementarlos se explica en detalle en el Capítulo 2.

En cuanto a la resolución de la ecuación de Schrödinger por los métodos previamente explicados, dada la naturaleza iterativa y la complejidad de la computación, se utiliza el software de libre distribución NWCHEM mediante el cual a través de un fichero de comandos, éste calculará las distintas propiedades que se necesitan para el estudio llevado a cabo. Este software de química computacional es de gran utilidad

no solo para este trabajo sino para cualquier tipo de estudio teórico computacional de sistemas atómicos y moleculares, abarcando posibilidades de computación tanto clásicas como cuánticas desde sistemas monoatómicos hasta interacciones entre moléculas más grandes que la tratada en el presente proyecto.

El estudio se lleva a cabo en tres partes similares. Primero, se calcula la energía del estado fundamental del Helio mediante los diferentes métodos para observar la falta del término de correlación electrónica cuando se implementa Hartee-Fock en comparación a clusters acoplados. Posteriormente, se estudia el catión molecular, se usa el módulo de optimización de NWCHEM para hallar la geometría nuclear que otorga el mínimo de energía del estado fundamenal. Con estos valores de energía y distancia internuclear, se calcula la PEC en el entorno de dicho punto. El hecho de que se observe un mínimo implica que la configuración es estable. Finalmente, se juntan los dos subsistemas tratados en los apartados previos para realizar cálculos sobre la PEC resultante de la interacción átomo-molécula. Dada la simetría rotacional sobre el eje que une los átomos de Hidrógeno en la molécula, se estudian dos configuraciones de interacción: uno con el Helio se encuentra en el eje que pasa por el centro de masas del H_2^+ y el otro con el Helio localizado en la perpendicular a dicho eje. Ambas configuraciones presentan un mínimo, si bien es cierto que los pozos de energía son de distinta magnitud. Es por ello que se trata de estudiar el Hessiano de las configuraciones para verificar si se trata de mínimos de energía estables, o por contraparte, de puntos de silla que implicarían una inestabilidad del sistema a pesar de observarse un mínimo en la PEC.

Para finalizar, se comentan ciertos errores que se hallan podido cometer, como el desplazamiento de las PEC debido a la superposición de bases (solventable teniendo en cuenta el Basis Set Superposition Error en el NWCHEM) o las consecuencias de haber usado una base como la *aug-cc-pVdZ* la cual introduce error debido al corto número de funciones del que consta. A su vez, se proponen maneras de continuar el estudio de este sistema que presenta interesantes propiedades.

Chapter 1

INTRODUCTION

Amongst all the different branches of physics, one common practice nowadays would be the use of computation to help understanding and solving problems we couldn't before. Some physical problems such as the three-body problem are not analytically solvable. In comparison, other aspects of physics will forever remain impossible to know as there is a limit for what we can measure, for example Heisenberg's uncertainty principle. For those problems that are not analytically solved, numerical methods have been developed to treat them with computers in order to be able to understand their behaviours. The way quantum computers have revolutionized computing can be compared to how computers as we know them today were a revolution in their time. At the same time as computing helps with the simulation of massive many-body systems, it is also equally helpful for those systems that are not so substantial in size but require a big amount of calculations. Thus, from complex calculations such as astrophysics simulations to the understanding of the quantum systems, the ability of performing calculations without the need of pen and paper reduces the time implied on some problems, therefore improving the understanding of the universe.

Regarding one of the biggest parts of modern physics, quantum mechanics shows how simple and big the world we see is, yet how tiny and complex the universe can get. The present bachelor's thesis (TFG) will try to approach one of the many aspects this branch of physics has to show, while using computation and theory as the roots to grow the understanding of specific problems like the one approached in this work.

As undergraduates, students are introduced to the quantum world with systems like particles in infinite wells, harmonic oscillators and the Hydrogen atom. Here,

additional complexity will be given, approaching the first molecule that is studied in molecular physics (H_2^+), whilst Helium is studied as a many-electron atom, to finally put the interaction between these two systems into sight.

The Hydrogen Molecular Ion can be treated with different algebraic methods. Despite that, its eigenvalue equations cannot be solved analytically and neither does the molecule-atom interaction. Thus, computation comes into the picture to give the possibility of analyzing this problem theoretically. Using a free distribution chemistry package called NWCHEM, it is possible to analyze the quantum behaviour of the different particles as well as the whole system. Making use of the Born-Oppenheimer approximation and different ab initio methods, this work aims to study the ground state energy for those nuclei and electrons involved to find properties such as the energies of the system and its possible stable configurations.

Throughout the development of this study some aspects are found interesting but rather too complex to discuss in this TFG. They are left as open ideas in Chapter 5 as to where the study on this $He - H_2^+$ interaction could continue to develop.

Chapter 2

THEORETICAL BACKGROUND

El sistema cuántico a tratar en este TFG consta de un átomo y una molécula. Para su estudio, deberá hacerse uso tanto de la aproximación de Born-Oppenheimer para simplificar la resolución como de métodos ab initio para resolver numéricamente la ecuación de Schrödinger y hallar la energía del estado fundamental. Los métodos variacionales ab initio proponen una energía para el estado fundamental basándose en constantes universales y la geometría del sistema. En este capítulo, se abordan los métodos Hartree-Fock y Coupled Cluster, los cuales se usan para analizar el sistema con el que se trabaja. Por otra parte, se explican los conjuntos de bases usados para implementar estos cálculos, así como el límite de base completa, técnica usada a fin de mejorar los errores provenientes del truncamiento de lo que debería ser una base infinita. Para la escritura de este capítulo se ha usado el conjunto de las siguientes referencias: [1, 2, 3, 4, 5, 6, 7, 8, 9]

Any quantum system one could try to describe needs to be approached by solving the Schrödinger equation. In this work, we will restrict the study of the system by approaching the non-relativistic time-independent Schrödinger equation, because in terms of the system to treat in this work that implies almost no measurable error.

Initially, the molecular problems in quantum mechanics are usually complex due to the big amount of particles involved. One way of overcome these complexities is using the Born-Oppenheimer approximation [1]. Essentially, from the Hamiltonian for a system written in atomic units ($m_e = \hbar = c = 4\pi\epsilon_0 = 1$):

$$H = -\frac{1}{2} \sum_{\alpha} \frac{1}{m_{\alpha}} \nabla_{\alpha}^2 - \frac{1}{2} \sum_i \nabla_i^2 + \sum_{\alpha} \sum_{\beta > \alpha} \frac{Z_{\alpha} Z_{\beta}}{r_{\alpha\beta}} - \sum_{\alpha} \sum_i \frac{Z_{\alpha}}{r_{i\alpha}} + \sum_i \sum_{i > j} \frac{1}{r_{ij}}, \quad (2.1)$$

where the first and second terms are the kinetic energy of both the nuclei with

mass m_α and the electrons respectively, and the last ones consider the potential energy that comes from nucleus-nucleus, nucleus-electron and electron-electron interactions. The Born-Oppenheimer approximation is now used to simplify the study of such a system. It assumes that the nuclei of the atoms in the system have fixed positions at the same time their masses are considered infinite since compared to the electrons' masses they are significantly bigger. The system then can be tackled by studying the Schrödinger equation for the electrons:

$$(\hat{H}_{el} + V_{NN})\psi(\mathbf{r};\mathbf{R}) = E_{el}\psi(\mathbf{r};\mathbf{R}). \quad (2.2)$$

The wavefunction in the equation is a function of both the set of electron positions $\mathbf{r} = \{r_i\}$ and the set of nuclear positions $\mathbf{R} = \{r_\alpha\}$

The electronic Hamiltonian to study would be written as follows:

$$\hat{H}_{el} = -\frac{1}{2} \sum_i \nabla_i^2 - \sum_\alpha \sum_i \frac{Z_\alpha}{r_{i\alpha}} + \sum_i \sum_{i>j} \frac{1}{r_{ij}}, \quad (2.3)$$

$$V_{NN} = \sum_\alpha \sum_{\beta>\alpha} \frac{Z_\alpha Z_\beta}{r_{\alpha\beta}}. \quad (2.4)$$

Since the Born-Oppenheimer approximation fixes the positions of the nuclei, \mathbf{R} distances will be constant from now on.

Once the Hamiltonian has been simplified to work with it, it is time for using the different known ab initio calculations. These methods are based on solving the time-independent Schrödinger equation (2.2) with the only input of known universal constants, and both the location of the nuclei and number of electrons. With those, these methods aim to get an approximate value of the ground state energy of the system.

2.1 Ab initio calculations

These methods, based on the given parameters, aim to get results that could approximate to exact values on the energy and give useful information about the system

with no experimental needs. This section is devoted to understand how the different ab initio methods used in this project work.

2.1.1 Hartree-Fock and Self Consistent Field

In order to solve the electronic Schrödinger equation (2.2), the Hartree-Fock (HF), as a variational method, needs an ansatz to find a value for the ground state energy. At first this method implies the assumption of mono-electronic wavefunctions that are affected by the nuclei attractive interaction and the repulsive interaction with the other electrons. Once a first spin-orbital and its energy is achieved, self consistency is used on an iterative method for the convergence of the energy value.

Firstly, starting with the Eq.(2.2) (one should note that the eigenvalue of the energy is also a function of the nuclei coordinate, i.e. $E_{el} = E_{el}(\mathbf{R})$), it is seen that the term V_{NN} is the interaction potential between nuclei, and therefore fixing the position of these particles would make this term be a constant, so that it can be studied separately, and focus the study only on the electronic Hamiltonian (2.3). One should denote all of its components separately, as this Hamiltonian can be separated into mono-electron and bi-electron operators:

$$\hat{H}_{el} = \sum_i \hat{h}_i + \sum_i \sum_{j>i} \hat{g}_{ij}, \quad (2.5)$$

where \hat{h}_i represents mono-electronic hydrogenic hamiltonians:

$$\hat{h}_i = -\frac{1}{2} \nabla_i^2 - \sum_{\alpha} \frac{Z_{\alpha}}{r_{i\alpha}}, \quad (2.6)$$

and \hat{g}_{ij} is the electron-electron interactions:

$$\hat{g}_{ij} = \frac{1}{r_{ij}}. \quad (2.7)$$

With the given Hamiltonian (2.3), impossible to be solved analytically, it is necessary to find a way of getting the ground state energy, as this is the purpose of the work. Variational methods are the fundamentals of ab initio calculations, and

in the present project the Rayleigh-Ritz method is used. The ground state energy is demonstrated to satisfy the inequality:

$$E_g \leq E[\Psi] = \frac{\langle \Psi | \hat{H}_{el} | \Psi \rangle}{\langle \Psi | \Psi \rangle}, \quad (2.8)$$

where the wavefunction Ψ used in the right term is a first ansatz, a trial function that aims to describe the system as a first approximation. The HF method implies the use of the product of monoelectronic orthonormal wavefunctions:

$$\Psi(x_1, x_2, \dots, x_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_i(x_1) & \phi_j(x_1) & \dots & \phi_N(x_1) \\ \phi_i(x_2) & \phi_j(x_2) & \dots & \phi_N(x_2) \\ \vdots & & \ddots & \\ \phi_i(x_N) & \phi_j(x_N) & \dots & \phi_N(x_N) \end{vmatrix}. \quad (2.9)$$

To fulfill the fact that the electrons are fermions, the antisymmetric operator is applied to the product of monoelectronic orbitals, and when normalized the result of this antisymmetrization is the Slater's determinant expressed above. These spinorbital are orthonormal ($\langle \phi_i | \phi_j \rangle = \delta_{ij}$). Each spinorbital $\phi_i(x_1)$ contains the spin and space coordinates of the electrons¹. Notice that the fact that the wavefunction is normalized reduces the calculation of the bound energy to the mean value of the electronic Hamiltonian. Moreover, this wavefunction also obeys the Pauli Exclusion Principle, necessary for fermion systems.

When following the calculations of this mean value that gives a first bound to the ground state energy in the variational approach, we get the following expression:

$$E[\Psi] = \sum_i \langle \phi_i | \hat{h}_i | \phi_i \rangle + \frac{1}{2} \sum_{i,j} (\langle \phi_i \phi_j | \hat{g}_{ij} | \phi_i \phi_j \rangle - \langle \phi_i \phi_j | \hat{g}_{ij} | \phi_j \phi_i \rangle), \quad (2.10)$$

where we have, from left to right, the effects of the monoelectronic hamiltonians, and the two-body interaction average values. From this point, Hartree-Fock equations can be taking into account, having the form:

¹The labels i, j, \dots, N denotes the monoelectronic quantum numbers and x_1, x_2, \dots, x_N the spatial and spin coordinates of the electrons

$$F(x_i)|\phi_i(x_i)\rangle = \epsilon_i|\phi_i(x_i)\rangle \quad \forall i, \quad (2.11)$$

where the Fock operator $F(x_i)$ is defined as it follows:

$$F(x_i) = \hat{h}_i(x_i) + \sum_{j \neq i} (J_j(x_i) + K_j(x_i)). \quad (2.12)$$

It is seen that the Fock operator for an electron depends on the mono-electronic Hamiltonian of that electron \hat{h}_i , whereas the Coulomb operator J and exchange operator K depend on all the electrons. These two operators, J and K , are defined as:

$$J_j|\phi_i\rangle = \left[\int \phi_j^*(x_j) \frac{1}{r_{ij}} \phi_j(x_j) dx_j \right] |\phi_i\rangle, \quad (2.13)$$

$$K_j|\phi_i\rangle = \left[\int \phi_j^*(x_j) \frac{1}{r_{ij}} \phi_i(x_j) dx_j \right] |\phi_i\rangle. \quad (2.14)$$

The Coulomb operator takes into account the potential that the electron feels due to the rest of the electrons, while the exchange operator comes from the fact that the wavefunction must be antisymmetric. From here, the Hartree-Fock equation for the energy can be written:

$$E_{HF}[\Psi] = \sum_i \hat{h}_i + \frac{1}{2} \sum_{ij, i \neq j} (J_{ij} - K_{ij}), \quad (2.15)$$

where

$$J_{ij} = \int \phi_i^* \phi_j^* \frac{1}{r_{ij}} \phi_i \phi_j dx_i dx_j = \langle \phi_i \phi_j | \hat{g}_{ij} | \phi_i \phi_j \rangle, \quad (2.16)$$

$$K_{ij} = \int \phi_i^* \phi_j^* \frac{1}{r_{ij}} \phi_j \phi_i dx_i dx_j = \langle \phi_i \phi_j | \hat{g}_{ij} | \phi_j \phi_i \rangle. \quad (2.17)$$

At this point it is reasonable to start the calculations. With a trial function such as the wavefunction described previously in (2.9), the components of the Hartree-Fock equation can be obtained in order to get an initial guess on the bound energy on the variational method. Once obtained the Fock matrix and solved the Hartree-Fock

equations, a new and more precise set of spinorbitals arise. Iterating in such a way that the process is repeated with a starting trial wavefunction based on the new set of spinorbitals obtained, so on and so forth, the process converges to a solution, where the difference between iterations are negligible, and the desired precision is obtained into the calculations. This iterative method is known as the Self-Consistent Field method (SCF) and even though the starting point of the solution might be far from getting close results to accurate values, the iteration provides a better approach to the ground state energy with a variational method. However, it is important to notice that this method gives the energy of a system of independent particles, and it does not take into consideration the electron correlation, since the wavefunction is built by the product of monoelectronic spinorbitals, which actually is not a true assumption. Moreover, the fact that each electron feels a mean potential energy based on the other electrons is a mere approximation of the actual behaviour of the system. Indeed, this correlation energy is defined as the difference between the real non-relativistic energy of the system and the Hartree-Fock energy calculated with the method:

$$\Delta E = E_g - E_{HF}. \quad (2.18)$$

Despite that, this method is useful for the Hydrogen Molecular Ion since it has no electronic correlation, therefore being able to get very accurate results.

At this point in the Hartree-Fock method, it is reasonable to think that at least for atoms the trial wavefunction can be good enough to get information about the system due to their spherical symmetry, but for molecules this approach might need to be properly improved. As mentioned in [2], C.C.J. Roothan and G.G. Hall proposed a different set of known wavefunctions so that they could be used for expanding the spatial part of the spinorbitals, transforming the Hartree-Fock equations in a matrix problem, solvable by matrix manipulations. Roughly, this method states that using a set of M basis function, each monoelectronic wavefunction could be described as

a linear combination of atomic orbitals (LCAO):

$$\phi_i = \sum_j^M c_{ji} \theta_j, \quad (2.19)$$

with unknown coefficients c_{ji} . Even though it could seem more complicated, this transforms the wavefunction calculation into a computing problem of getting the unknown coefficients. More detailed information regarding basis sets and their importance will be described in section 2.2

To improve HF results and take the correlation energy into account, as it is essential in most molecular problems, many other methods have been developed. Møller-Plesset's method gets this improvement by means of the Rayleigh-Schrödinger's perturbation theory, using perturbation to second order (MP2) up to fourth order (MP4). The following section will focus on explaining the Coupled-Cluster method, as the post-HF ab initio method used in this project to get the accuracy needed on the ground state energy.

2.1.2 Coupled Cluster calculations

The following post-Hartree-Fock method is a well known ab initio method which provides really precise and accurate results coming from approximations for atomic and molecular physics. Coupled Cluster calculations (CC) are widely used because of its affinity involving the correlation energy as well as its property of being size-extensive, meaning that correlation energies scale depending on the amount of electrons involved in the system. The theory explained here is based on References [3], [4].

The CC method takes the HF electronic wavefunction as a starting point to build a new wavefunction:

$$|\Phi_{CC}\rangle = e^T |\Psi\rangle, \quad (2.20)$$

where Ψ is taken in the form of eq.(2.9). The operator e^T takes the form of its

Taylor expansion, and T is the so called cluster operator. This cluster operator is defined as:

$$\left\{ \begin{array}{l} T = T_1 + T_2 + T_3 + \dots \\ T_1 = \sum_{i,a} t_i^a X_a^\dagger X_i \\ T_2 = \frac{1}{4} \sum_{i,a,j,b} t_{ij}^{ab} X_a^\dagger X_i X_b^\dagger X_j \\ \vdots \end{array} \right. , \quad (2.21)$$

T_3 and higher cluster operators are defined similarly growing as its subindex. The notation refers to i, j, \dots as already-occupied spinorbitals in the HF wavefunction, and a, b, \dots are the subscripts for virtual spinorbitals². Coefficients t_{ij}^{ab} are unknown at first, and the operators X_i and X_a^\dagger are annihilation and creation of spinorbitals operators, respectively.

The procedure to implement this method can vary. Nevertheless, the most common approach is to start implementing $|\Phi_{CC}\rangle$ in the Schrödinger equation:

$$\hat{H}_{el} e^T |\Psi\rangle = E e^T |\Psi\rangle, \quad (2.22)$$

so then defining the correlation energy as in eq. (2.18), subtracting the HF energy and left multiply by e^{-T} , we can get the following equation:

$$e^{-T} H' e^T |\Psi\rangle = \Delta E |\Psi\rangle, \quad (2.23)$$

where $H' = \hat{H}_{el} - \langle \Psi | \hat{H}_{el} | \Psi \rangle$. After that, if the equation is projected over the HF trial function:

$$\langle \Psi | e^{-T} H' e^T |\Psi\rangle = \Delta E, \quad (2.24)$$

and the correlation energy finally can be achieved. The coefficients on the cluster operators are calculated by solving the non-linear coupled equations that arise from

²these virtual spinorbitals refer to the ones given when solving the eigenvalue equations for the reference wavefunction

projecting the equation (2.24) onto the excited determinants³, so that the projections are equal to zero.

$$\langle ij^{ab} | e^{-T} H' e^T | \Psi \rangle = 0, \quad (2.25)$$

where the $\langle ij^{ab} |$ stands for the different excited states⁴ possibly given by the equations used.

The CC method ideally could consist on the infinite series of cluster operators T_i , however this ideal situation is impossible to achieve computationally. Indeed, the method is really consuming in terms of computational power and time, therefore its common to use finite models, for example CCSD fixes T as $T_1 + T_2$, whereas the CCSDT model uses $T = T_1 + T_2 + T_3$.

2.2 Basis sets

As aforementioned, the ab initio methods explained rely on a wavefunction that is assumed to be the one that describes the system, at least as a starting point. However, in order to achieve theoretical results, a complete and infinite basis set of wavefunctions needs to be used, but it is not possible to compute an infinite amount of them. Despite the fact that they need to be truncated, one must find a basis that can fit the problem as efficiently as possible. Nowadays, there are lots of different basis that have already been researched and studied for different atoms and molecules. Nevertheless, it is necessary to point where the basis used come from, and how to apply them.

At first, different basis sets can be found in [9]. In the present TFG, the trial functions used for the computation of the system are the Gaussian-type functions (GTFs), which take the following expression:

$$g_{\nu\lambda\gamma}(\mathbf{r}) = N_{\nu\lambda\gamma} x^\nu y^\lambda z^\gamma e^{-\beta^2}, \quad (2.26)$$

³Those excited states are given when annihilation and creation operators act on $|\Psi\rangle$.

⁴ $\langle i^a |$ would be states given by T_1 , $\langle ij^{ab} |$ by T_2 and so on.

where ν, λ and γ are non-negative integers, β is a real positive exponent, and $N_{\nu, \lambda, \gamma}$ is the normalization constant. Some rules are applied to the exponents ν, λ, γ so that the resulting functions are grouped based on their forms. For example, s-type orbital is the one where $\nu + \lambda + \gamma = 0$, when $\nu + \lambda + \gamma = 1$ the GTFs are p-type orbitals (3 possible p-types having one integer to be 1 and the rest 0) where the direction whose exponent is equal to 1 is called the privileged spatial direction. Moreover, d-type orbitals are those with $\nu + \lambda + \gamma = 2$ (6 different possibilities) and so on. The sum of this non-negative integer is, indeed, the total orbital momentum of the atom described by the GTF ($\nu + \lambda + \gamma = l$).

Another family of commonly used functions are the Slater-type orbitals (STOs). Their value comes from the fact that using a linear combination of STOs centered in the nuclei of the atoms is more accurate than using GTFs. However, when lots of atoms are involved, the calculation of the integrals that arise from using STOs is computationally hard, therefore the evaluation of the integrals could be improved time-wise by using GTFs since they take the form of Gaussians.

When it comes to computing, it is necessary to talk about the concept of minimal basis set. This term refers to the smallest amount of STOs required to describe the system (that means each atom's inner shell and valence shell atomic orbitals are described by STOs). Despite their complexity, a flaw of the more optimal GTFs is that their functions don't have one to one relations between the atomic orbitals and the functions. Since the idea of the minimal basis set is to strike a balance between accuracy and computational efficiency, neither of those are the best approach for the efficiency, and that's why, to reduce the number of basis functions on the GTFs, the contracted Gaussian-type functions (CGTFs) are used. These take the following form:

$$\omega_r = \sum_u d_{ur} g_u, \quad (2.27)$$

where d_{ur} are known constants (contraction coefficients) from previous opti-

mizations, and g_u are normalized Cartesian Gaussians centered in the same atom and with same indexes $\nu\lambda\gamma$, but different orbital exponent β . Using these contracted forms reduce the number of basis functions of GTFs to the same number of functions as STOs, while being simpler than these last mentioned ones, which implies a reduction of the computational costs with few losses in accuracy. In the present TFG, only CGTFs are used and it will be explained the way of using those down below.

As it should be mentioned, an atomic orbital usually requires more than one CGTF to be described accurately, so it can be said that the more functions you use to describe an atomic orbital, the better the description of it will be. In the present TFG we narrow the calculations to the usage of Dunning basis sets [5]. Using double the basis function is referred to as Double-Zeta (DZ), Triple-Zeta would be using triple the basis functions and so on⁵. In addition, the interaction between atoms should be noted in each atomic orbital due to polarization effects, therefore, additional polarization terms must be introduced (calling these newly formed basis the polarized (P) basis sets). Taking into account electron correlation, we can see that the different CGTF basis sets are called *cc-pVNZ* (with $N = 2,3,4,5,\dots$), where *cc* stands for "correlation consistent". Finally, the basis sets used in these TFG are the augmented Dunning basis sets *aug-cc-pVNZ*, where the augmentation takes into account the diffuse primitive non-polarized and the polarization functions for the *cc-pVNZ* basis sets. Molecules with Hydrogen bonding are specially well described by these kind of basis sets.

In the present TFG, where the study was restricted to Helium and the Hydrogen Molecular Ion, the previously discussed basis set is considered efficient since the molecule to study has only one electron, and the Helium atom has been proven to be well represented by that basis set. The system was tackled by using the same basis set (*aug-cc-pVNZ*), and increasing N from 2 to 4 to see a growth in accuracy. Table

⁵In these thesis the basis set function used go from Double-Zeta to Quadruple-Zeta

2.2 shows the different characteristics of the basis sets depending on N :

Basis Name	Shells	Functions	Orbitals
aug-cc-pVDZ	5	9	3s2p
aug-cc-pVTZ	9	25	4s3p2d
aug-cc-pVQZ	14	55	5s4p3d2f

Table 2.1: Different Basis sets used in this work and their specifications

The columns on the table are easily readable. The number of shells is the same as the amount of orbitals (for example, aug-cc-pVDZ has 5 shells which means 3 s orbitals + 2 p orbitals), and the number of functions comes from how much functions each different type of orbital can be described with (s-type orbitals require $\nu + \lambda + \gamma = 0$ so one function, p-type ones $\nu + \lambda + \gamma = 1$, so three functions, and $\nu + \lambda + \gamma = 2$, so 6 functions).

2.2.1 CBS limit

As previously said, the theoretical infinite basis set must be used in order to get the most accurate value possible. Despite that, to be able to compute the problem, the infinite basis needs to be truncated. Nevertheless, it is essential to see that the more functions used to describe the system, the more accurate the results will be. Indeed, taking advantage of this behaviour, the energy results achieved with same basis but more number of functions are seen to follow a non linear function. That is, using the energy values from different basis assuming those values fall in the domain of a certain function. In terms of the work performed in this project, according to reference [6] for the aug-cc-pVNZ family of basis sets in the systems studied, the energies follow the empirical expression:

$$E(n) = a + \frac{b}{n^c}. \quad (2.28)$$

A regression can be made to approach the asymptotic limit of the function as n tends to infinity. In (2.28), $E(n)$ is the energy, n depends on the basis used (in this

project $n=2,3,4$), and a, b, c are unknown constants that are found with least squares non-linear regression. The idea of finding these asymptotic limits for different energies as function of the basis sets is called the Complete Basis Set (CBS) limit, and gives a closer approach to the theoretical energy that could be found using an infinite basis set without taking an infinite amount of time to compute.

Chapter 3

NWCHEM: OPEN SOURCE HIGH-PERFORMANCE COMPUTATIONAL CHEMISTRY PACKAGE

Dada la complejidad del cálculo computacional del sistema referente a este Trabajo de Fin de Grado, se usa el programa de libre distribución NWCHEM, instalado en un Cluster de ordenadores del Departamento de Física de la Universidad de La Laguna. En este capítulo se explicará cómo se llevan a cabo los cálculos numéricos así como la estructura del archivo creado para ejecutar el programa.

The ab initio calculations that need to be done in this bachelor's thesis are done using the free distribution chemistry package NWCHEM, developed by the Experimental Molecular Science Laboratory (EMSL) at the Pacific Northwest National Laboratory (PNNL) [10]. The program allows solving quantum mechanical systems, from biomolecules and nanostructures to partly classical as well as both relativistic and non-relativistic systems. Therefore, it is useful for atoms and molecules as the ones studied in this project. NWCHEM gives the user free will to choose the desired method (from HF and post-HF to Density Functional Theory and more advanced ones) to perform the calculations as long as the system fulfills the requirements of the method to be calculated. Calculations made to solve this quantum system were run in cluster Molec3, node 38 in the Physics' Department of the University of La Laguna. This section is devoted to show the process of describing the system by an input file that the program will get the information from to solve it.

3.1 Input File

NWCHEM requires a specific input file structure to perform properly the calculations. To give some perspective, the essential structure of the file must describe: the computational specifications for running the calculations, the description of the system (how particles are placed in the space and how they are represented) and the method to use as well as the values one wants to get. The different directives used to write the input file are the following:

- **START + "name"**: initiates and gives name to the files that will be created to perform the calculations.
- **TITLE + "name"**: specifies the name of the output.
- **ECHO**: will include the input file text in the output. Useful for identifying the calculations in the output.
- **CHARGE**: gives information about the electrons in the system. If not used the program assumes the atoms in the system are neutral.
- **GEOMETRY**: this directive is used for describing where the atoms of the system are initially placed, and within these section of the input one must choose the coordinates as well as the length units. If not specified defaults are cartesian coordinates in angstroms.
- **BASIS**: allows to indicate which basis sets are used for which atoms of the system. The program itself already comes with libraries full of different basis sets, therefore one should only specify the name (e.g. *aug-cc-pVDZ*).
- **CONSTRAINTS**: If the program is going to make changes in the information given to do the ab initio calculations, some of this information can be fixed so that the algorithm does not modify the desired parameters.

- SCF/TCE: directives related to the chosen methods for computing the calculations. SCF is the already known Self Consistent Field, and TCE stands for Tensor Contraction Engine, a module of NWCHEM that is said to converge at the exact solution of the Schrödinger's equation. Within this directive, subdirectives are used to determine the ab initio method as well as the parameters of computing:
 - UHF/CCSDT: Unrestricted HF and Coupled-Cluster SDT, the methods themselves. The first one is the most commonly used for open shell molecules, where the number of electrons with different spin is not equal, and CCSDT takes into account the correlation energy previously discussed in chapter 2.
 - MAXITER + *int*: Restriction to the number of iterations for the methods
 - SINGLET/DOUBLET: gives information about the spin multiplicity of the system to calculate.
 - NOPEN + *int*: number of open-shells in the system.
 - THRESH: used for setting the precision of the calculation.
- DRIVER: module for performing optimizations in the calculation based on the GEOMETRY given.
 - EPREC: determines the precision of the energy in the optimization
- TASK + *method* + *energy/optimize/frequencies*: directive to input explicitly the desired calculation to be done by the program. *Optimize* will search the minimum in energy for different positions of the atoms, whereas *energy* will compute the ground energy of the system based on the given information in CHARGE, GEOMETRY and BASIS. *Frequencies*, on the other hand, evaluates certain parameters that are not computed if not specified, such as the Hessian given for the system on that point.

As every directive is completed, before starting to write new directives it is mandatory to explicitly write *end* in order to separate the directives in different blocks of code. An example of an input file can be found in the Appendix.

One should note that NWCHEM allows for more complex systems than those studied in this TFG, so that the directives explained in this chapter are the ones used in the present work, being this directives the top of the iceberg regarding the power and complexity of the program itself.

Chapter 4

RESULTS AND DISCUSSIONS

Este capítulo presenta los cálculos realizados tanto para el Helio como para el catión de la molécula de Hidrógeno, así como para el sistema que resulta de sus interacciones. Se mostrarán los valores calculados para la energía del estado fundamental del Helio, así como las curvas de energía potencial para el H_2^+ como para la interacción $He - H_2^+$ en dos distintas geometrías posibles. A su vez, se compararán los resultados obtenidos con valores de la literatura, discutiendo posibles discrepancias entre los valores calculados y los de referencia.

The study of the $He - H_2^+$ interaction is carried out by firstly getting solutions on the behaviour of the different components of the particle system. Studying the Helium atom and the Hydrogen Molecular Ion separately serves as the starting point for analyzing the whole system. Both parts will be studied for their ground states, aiming to find the most accurate lowest energy possible given by the methods explained in Chapter 2 with the NWCHEM program.

4.1 Helium Atom

Considering the atom itself, neutral Helium ($Z=2$) has one nucleus and two electrons. Correlation energy takes an important place in the study of the simplest many-electron atoms. The generic electronic Hamiltonian described in eq.(2.3) for Helium is written as follows:

$$\hat{H}_{el} = -\frac{1}{2} \sum_{i=1}^2 \nabla_i^2 - \sum_{i=1}^2 \frac{2}{r_i} + \frac{1}{r_{12}}. \quad (4.1)$$

Since there is only one nucleus, r_i refers to the the distance between the nucleus itself and the electrons, and r_{12} is the electron-electron distance. For the HF method to be carried out, it would be easier to visualize it as:

$$\hat{H}_{el} = \hat{h}_1 + \hat{h}_2 + \hat{g}_{12}. \quad (4.2)$$

From this Hamiltonian, both HF and then CC methods shall be used for achieving the ground state energy. In terms of complexity, results given by the program used to perform the calculation were the fastest on this atom since there is no need for optimization to minimize the energy based on the nucleus position. Nevertheless, it is important to mention that since HF method does not take into account the electronic correlation, the useful values for this calculation will be the ones achieved with the CCSDT method, as it does consider this energy term. The following table shows the different obtained values for the ground state energy and the figure represents the non-linear regression made with expression (2.28) to achieve the CBS limit on the energy:

Basis Name	RHF (a.u.)	CCSDT (a.u.)	Corr. Energy (a.u.)
aug-cc-pVdZ	-2.85570467	-2.88954849	-0.03384382
aug-cc-pVtZ	-2.86122253	-2.90083640	-0.03961387
aug-cc-pVqZ	-2.86153946	-2.90272034	-0.04118088
CBS limit	-2.86159106	-2.90358432	-0.04199326

Table 4.1: NWCHEM ground state energies for Helium

From the data achieved with NWCHEM, one can reasonably say that electronic correlations is essential to get an accurate value. Moreover, having the value of reference $E_{He}^{ref} = -2.9036816a.u.$ given in [11] shows that the value gets closer to the reference value once CBS limit is made, reducing the error by one order of magnitude. The calculations agree with the values achieved by [12], however the ones calculated in this TFG might be more precise since the driver precision was fixed to be on the order of 10^{-8} .

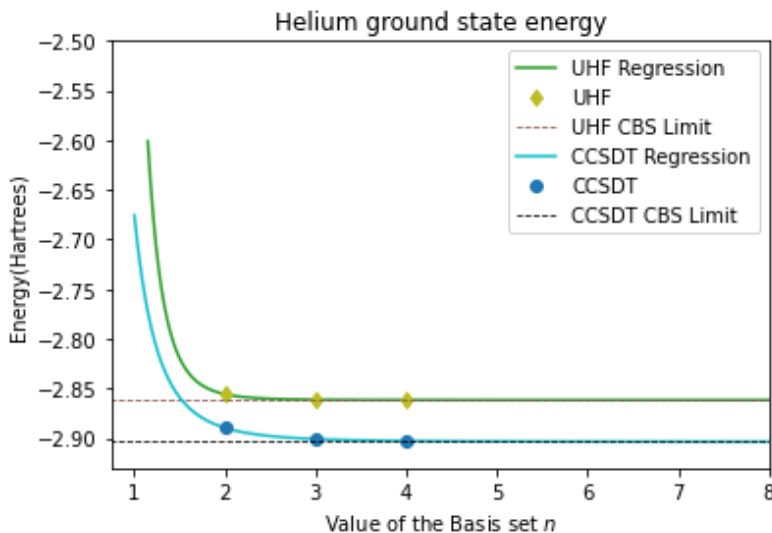


Figure 4.1: CBS Calculations for the Helium Ground State Energy

As it can be seen in the Fig 4.1, Coupled Cluster calculations are essential to describe properly this atom since the energy gap between methods is big enough to not to be neglected. It is notable that, and it will be seen further in the results, the *aug-cc-pVDZ* basis set on its own is not acceptable to get accurate results. Furthermore, there is a strong possibility that the fact of it being not that precise leads to inaccuracies when performing the CBS limit. However, in terms of consistency throughout this work, it is needed to use it since using the *aug-cc-pV5Z* basis set in the following system required more computational power than the one being used, and in order to perform a non linear regression with 3 parameters, one must provide at least 3 data values, making the usage of the value given by the *aug-cc-pVDZ* basis set unavoidable.

4.2 Hydrogen Molecular Ion (HMI)

Contrary to the Helium atom, the H_2^+ cation has two nuclei, and one electron shared by them. The reduction of complexity from Helium having just one electron, removing the electronic correlation, is counteracted by the addition of two atom nuclei that need to be set in an stable configuration. To start with, the electronic

Hamiltonian (2.3) for the molecular cation is given by the following expression in atomic units:

$$\hat{H}_{el} = -\frac{1}{2}\nabla_1^2 - \frac{1}{r_{\alpha 1}} - \frac{1}{r_{\beta 1}}. \quad (4.3)$$

Following a similar approach to the one for the Helium atom, the Hamiltonian could be rewritten in a more appropriate way, similar to eq.(4.2). It is a matter of interest to mention that, as it is seen in many different books on the subject [3] [1], as the Schrödinger's equation for the system is written with the Hamiltonian (4.3), the problem could be studied by changing the electronic coordinates used, from cartesian to confocal elliptic coordinates, in order to separate the Schrödingers' equation into a couple of Partial differential equations (PDEs) that depend on each of the coordinates separately [13].

To find the distance that minimizes the ground state energy, NWCHEM's *task optimize* function is required, as it looks for the distribution whose ground state energy is minimum. Once this distance is found, different calculations are done to find the Potential Energy Curves (PEC) for the HMI, that is, doing the calculation for different fixed internuclear distances and proceeding calculating the CBS limit on each distance given so that we can plot the energy as a function of the distance R between the protons. In the following table we can see the different values achieved for the ground state energy with the equilibrium internuclear distance $R = -1.997296$ bohr¹:

Basis Name	UHF (a.u.)
aug-cc-pVdZ	-0.60124654
aug-cc-pVtZ	-0.60234356
aug-cc-pVqZ	-0.60256395
CBS Limit	-0.602689571

Table 4.2: NWCHEM values for the minimum for the H_2^+

¹The distance used for the minimum of the ground state energy was found when using the *optimize* input in NWCHEM while using the aug-cc-pVqZ basis set

Figure 4.2 shows the data obtained for the HMI, once CBS limits are done with the expression 2.28 using the values for each point and the different basis sets:

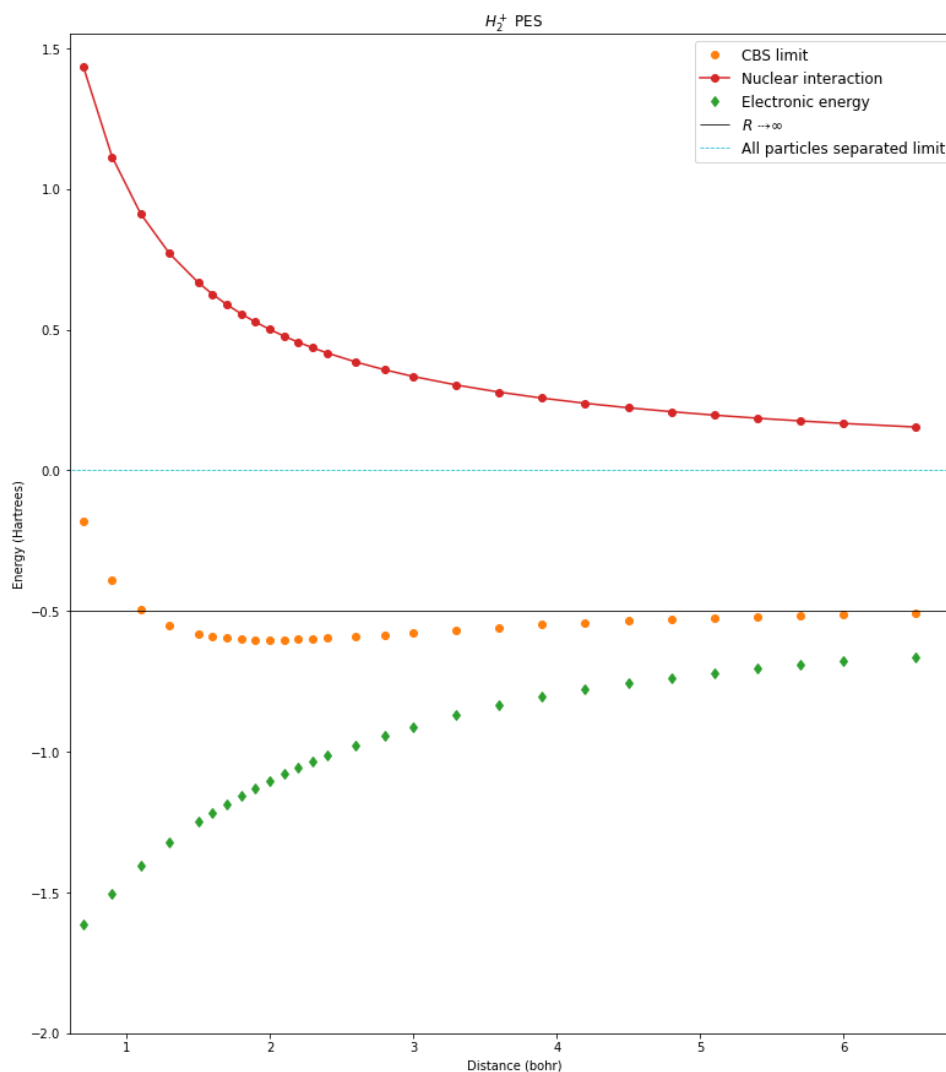


Figure 4.2: PEC values and different energy contributions achieved with NWChem for H_2^+

It is seen that the nuclear contribution decreases proportionally with the inverse of the internuclear distance. Indeed, as this distance R tends to zero, the electronic energy approaches -2 Hartrees, which would be the value for a Helium cation, a particle with two protons on its nucleus and only one electron. Fig. 4.3 shows a closer look into the PEC itself:

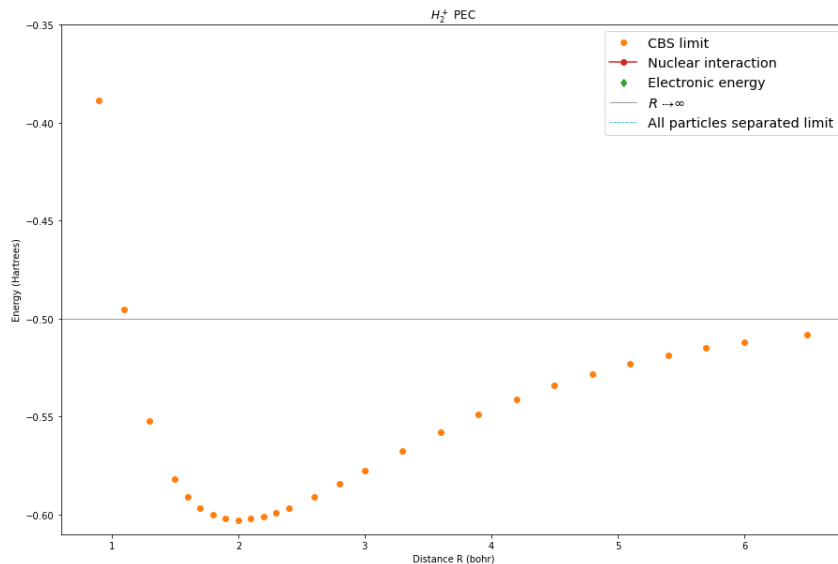


Figure 4.3: Potential Energy Curve for H_2^+

This clearly shows a minimum, which means the molecule has a stable configuration for which it will maintain its geometry if unperturbed. In addition, it is seen that if the nuclei were to be separated an infinitely distance (i.e. $R \rightarrow \infty$), the HMI would have a ground state energy equal to the one of a Hydrogen atom, since there would be a proton infinitely far away, therefore not interacting with it. Furthermore, from the data achieved it can be concluded that the equilibrium dissociation energy is found to be $D_E = -0.10265093$ Hartrees, nothing but 17.03% of the total energy of the molecule ion in its stable state.

From a reference perspective, the minimum ground state energy value is consistent with the one given by the Reference [14], where they found the energy value to be $E_{el}(R = R_{min}) = -0.6026$ Hartrees. It is reasonable to state that the performed calculations conclude with precise results for the energy of the ionic molecule.

From this point, once the Helium atom and the Hydrogen Molecular Ion have been studied, the system where they are interacting is the next step to understand the interaction.

4.3 Helium-Hydrogen Molecule Ion Interaction

The complete problem that comes when Helium and H_2^+ interact may be tackled from different perspectives. Now, the whole system consists of 3 nuclei and 3 electrons, overall charge being $+1 q_e$. Back in the HMI, one should optimize in order to get a minimum in the ground state energy for the H-H interaction. Here, there are different ways one can tackle the problem: either optimizing to see how the three nuclei arrange themselves, or restrict the interaction fixing the positions of some nuclei. The procedure followed to study the system in this project was to fix the Hydrogen nuclei, so that they are at a distance which gives them the lowest ground state energy (i.e. their equilibrium configuration), and then move the Helium around to see how the PEC changes depending on its position relative to the ion molecule. Helium atom is then placed in two different configurations:

- **Linear Configuration:** Placing the Helium along the H_2^+ internuclear axis, varying its distance respect to the HMI midpoint. ($\varphi = 0^\circ$)
- **Perpendicular Configuration:** Helium falls in the perpendicular line that cross the HMI internuclear distance in the midpoint. Frequently known as T-shape configuration ($\varphi = 90^\circ$)

Because of the structure of the system, it could be said that the symmetry of the problem makes it so that it is only necessary to study the system when $0^\circ \leq \varphi \leq 90^\circ$. Therefore, this two configurations will give the bound PES for how the system could behave when fixing H_2^+ internuclear distance.

Figure 4.4 shows the different calculated points for both the linear and perpendicular configurations of the system. Since these atoms have weak bonds when interacting (acting as Van der Waals molecules), it is necessary to change the units to Angstroms (\AA) in distance and milielectron-volts (meV) for energy, at the same

time the energies are represented compared to the sum of the He and H_2^+ energies as separated systems for a better visualization of the PEC.

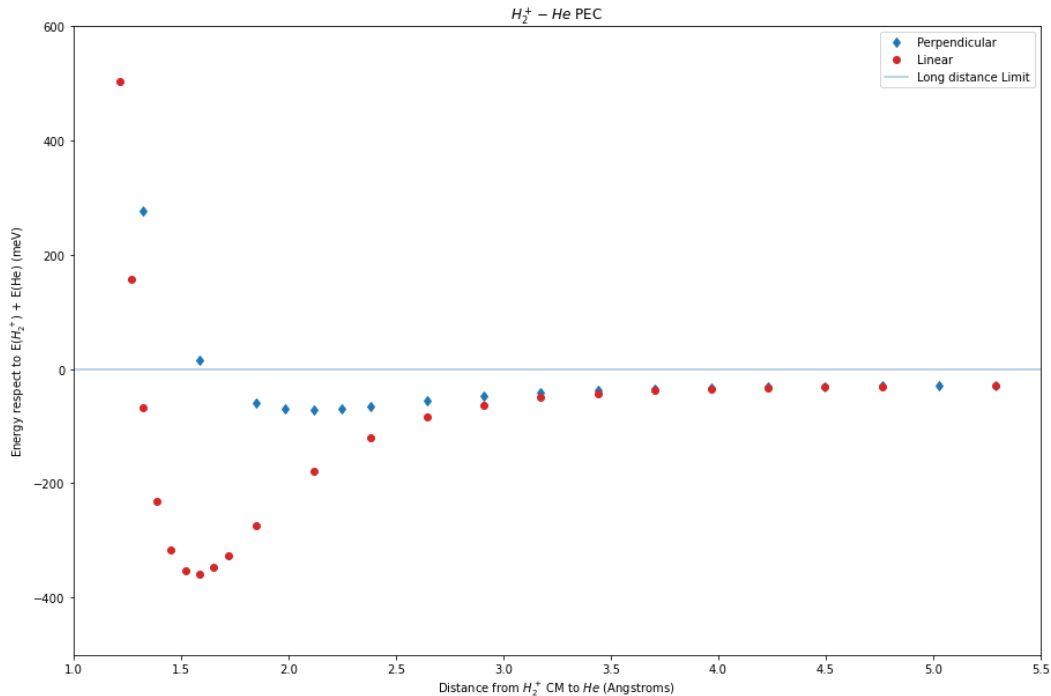


Figure 4.4: Different Configurations' PEC for the He- H_2^+ interaction

The linear configuration shows a minimum with $D_B^{lin} = -358.59558 \text{ meV}$ when the Helium is at a distance of 1.58753 \AA from the center of masses of the molecular ion, which means it is a stable configuration. A slight minimum can be seen in the perpendicular configuration with $D_B^{per} = -71.99899 \text{ meV}$ at a distance of 2.11671 \AA , which makes the configuration eligible to be stable, while if it was a saddle point it wouldn't be stable even though there was a seemingly minimum in this PEC. To get information regarding this property of the system in that position, one must study the Hessian that comes from the system fixing the positions. For the linear configuration this Hessian when diagonalized shows only positive frequencies, which means that the point considered a minimum is, indeed, a minimum for the system. This means it is an equilibrium position for the system to stay at a ground state energy. On the other hand, the Hessian in the perpendicular configuration when the calculations are

done with the *aug-cc-pVTZ* basis set determines the point to be a minimum as well, but if the *aug-cc-pVQZ* basis is used one of the frequencies is negative, showing the existence of a saddle point. This result is consistent with the reference [15], concluding that this point is most likely a transition state, from where it eventually will fall to a real equilibrium position.

Chapter 5

CONCLUSIONS

Se listan diversas fuentes de errores en los cálculos efectuados a lo largo del estudio del sistema $He - H_2^+$. El uso imperativo de la base de Dunning *aug-cc-pVDZ* puede haber sido una fuente de error a la hora de realizar cálculos de límite CBS comparado con los posibles errores que hubiese supuesto el uso de la base *aug-cc-pV5Z*. Por otra parte, el hecho de no haber tenido en cuenta el Error de Superposición de Bases conlleva a un desplazamiento en energía en los cálculos realizados por el NWCHEM. Se propone a su vez ideas de estudios posibles a surgir en base al trabajo realizado en este TFG

Once results are shown, it can be concluded that calculations on the systems with the free distribution chemistry package NWCHEM are not only simple but also effective. However, notable improvements could be done in order to perform more precise results. Taking into account only accuracy on the results, if computational time was not to be taken into consideration, the study of the systems should have been studied with the *aug-cc-pV5Z* or even *aug-cc-pV6Z* basis sets, to be able to perform more consistent CBS limit extrapolations. In terms of this project, due to the sources for computation and the system to study, $He - H_2^+$ interaction when using *aug-cc-pV5Z* was happening to take more than a day in computation time for calculating the energy of the system at an specified geometry with CCSDT method, therefore it was discarded since this project required making those calculations for over 50 points in total. Moreover, the fact that it wasn't reasonable to use that basis set introduce the imperative necessity of using the results given by *aug-cc-pVDZ* basis set to perform the CBS limit calculations, which might be one of the primary sources of error on the results achieved.

From another perspective, some other sources of error have not been considered as they could have been if had enough time. That might be the case of the Basis Set Superposition Error (BSSE), a error that comes from the fact of assuming the basis used for each atom of the system to be separate, leading to a shift in energies calculated when not taken into account. Reference [15] shows that this project's calculations are shifted from higher accuracy calculations done there. Despite this shift, it is certain that these calculations are consistent with the behaviour one could expect from this system, as similar systems are studied and results are in consonance with those given in this project.

When it comes to the means of this project, it is certain that, as an undergraduate's project with the purpose of getting to know the world of atomic and molecular physics as well as the quantum chemistry field, this project serves its function more than completely. Nevertheless, the study on this system might not be said to be concluded. As it could have been the case if this project had a lifespan of more than one year, the work done on it could be the starting point for different studies on the $H_2^+ - He$ interaction. As a first improvement, the usage of bigger basis sets in the family of the *aug-cc-pVNZ* basis sets should be implemented, as well as the BSSE energy correction. Once these problems were fixed, many options on studying this system may arise. On one hand, the proposal of an analytic function to describe the PEC of the interaction could be treated as it is done in [15]. On the other hand, the study and understanding of this system could lead to the study of clusters of Helium atoms with H_2^+ , to see stabilities on the different possible systems given by that addition of atoms.

Appendix A

NWCHEM INPUT FILE

The following image shows a sample for an input file structure used to run the calculations on NWCHEM.

```
start H2_He_interaction
title "H2+He_lineal"
echo "H2+He_lineal"
memory total 10000 mb
charge +1
geometry units au
symmetry C1
H    0.0    0.0    0.0
H    0.0    0.0    1.9975627
He   0.0    0.0    3.9659304
end
basis
  * library aug-cc-pVqZ
end
constraints
  fix atom 1 2
end
driver
  eprec 1.e-8
  maxiter 1000
end
scf
  uhf
  doublet
  maxiter 5000
  nopen 1
end
tce
  scf
  ccSDT
  thresh 1.e-8
  maxiter 2000
end
task tce optimize
```

Figure A.1: NWCHEM Sample input file

When this file is run, the program takes the information of the system (geometry,

charge, constraints, basis set, etc.) and starting from the geometry given, it uses the TCE directive to minimize the energy using the CCSDT method with a maximum of 2000 iterations, considering the fixed positions for the Hydrogen nuclei.

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