

Plutonium tricarbide isomers: A theoretical approach

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Introducirse en el mundo de la Química Teórica, más cuando eres un Licenciado en Químicas, es difícil, pero puedo garantizar que es la actividad académica más gratificante con la que me he encontrado.

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1. INTRODUCTION.

The study of new potential molecules has amazing applications in chemistry, physics, material science and a lot of related fields. The study and synthesis of this kind of molecules constitutes one of the fundamental pillars of the chemistry as a major science.

Traditionally, the research of new molecular species have been devoted to experimental procedures and therefore limited in a way by the reachable experimental conditions, which in the vast majority of the cases only allows the synthesis and study of a low portion of the potential molecules to be studied. In this way, and with the help of spectroscopic setups, the species involved in a reaction, including the low life ones such as the reactive intermediate can be studied. However, for special cases, experiments not always can solve all the questions for the systems. Furthermore, in most cases, experiments do not give scientists any predictive capability in order to generalize the obtained results (obviously, this is true only at some extent since there exists a whole variety of known chemistry thanks to experimental work)

In the cases where an experimental design is not viable enough to carry out a study of a certain molecule, first principle predictions show a great capability of surpass the problem. First principle predictions rely in quantum mechanics laws for molecular systems in order to study a certain system. Since these laws are well defined, the study can be carried out in a systematic way, ensuring the goodness of the results. For this reason modelization studies, are nowadays a routinely tool in most of the chemical research worldwide.

A brief summary, of the tools available for this kind of theoretical studies, which will be extended in the next chapters, can be made if we attend, for example to the inclusion of a time scale in our problem giving rise to dynamic methods (Molecular dynamics, Montecarlo simulations) or static ones (different methods for the resolution of the time independent Schrodinger equation). We can also focus on how we are going to treat our system, allowing to a full quantum mechanics description or to a classical mechanics one. We can make use of some experimental data in our calculations obtaining a semi empiric calculation or use only first principles, like in the ab initio methods and so on.

As can be seen, the variety of the problems that can be studied with this kind of tools is enormous and a generic name for the discipline which is devoted to the development and applications in this field is called theoretical chemistry.

Due to the huge amount of mathematical operations in a single calculation, it is wise to automatize the process by means of computer algorithms constituting the so called computational chemistry which is referred to the application of computer science in order to solve theoretical chemistry problems. It is usual though to use computational and theoretical chemistry as synonyms.

The present work makes use of computational chemistry to approach to the solution of the molecular structure of a non detected (yet) molecule, namely the plutonium

tricarbide PuC_3 . The group of Química Teórica y Computacional at the Universidad de Valladolid has been studying the structure and bonding properties of several carbides as one of its main research lines [1-5]

Recently, the study of these carbides has been centered to the study of how small chains of carbon atoms interact with actinide atoms covering one of the main topics in nuclear science research, this is, the chemical structure of the gas phase residues arising from nuclear reactions. Recent studies of the group in this field cover the study of uranium dicarbide and tricarbide [6-7].

The study of such systems is important since the high temperature obtained in nuclear reactors ensures that vaporization constitutes an important process in these reactors. Experimental approaches for the study of this bulk can be found in several studies [8-10]. Spectroscopic studies such as infrared spectroscopy or mass spectrometry have been carried out for the study of these systems but as can be imagined the bulk of the conditions of the nuclear reactor are not always achievable and therefore not all of the hypothetical compounds present in the reaction bulk can be studied by experimental ways.

A potential application for the study of this kind of systems is that can be potentially used as new generation nuclear fuels [11 and references therein], and recycled from nuclear common processes. In this way, the study of the electronic structure of the compounds as addition to its nuclear counterpart, will give valuable information about its energetic and spectroscopic characteristics helping to the determination and applications of these materials.

The main goal behind this work is to predict the molecular structure and infrared spectra of the possible isomers in order to characterize the most stable one, a previous job in the experimental recognition of the system. Furthermore, a systematic study of the bonding in these systems will give us some information about the chemical nature and possible formation paths of this kind of systems.

To the best of our knowledge no information regarding PuC_3 has been found and this study present the first results for this species.

This master thesis is composed of several chapters each one regarding to a fundamental piece of the research. Chapter one (this chapter) presents a very general insight of the philosophy behind the computational chemistry, approaches to a problem and the general practical motivation behind the study of this kind of systems. Chapter two presents a review of the theoretical basis and formal foundations of the methods used for the computational study of the system. Chapter three is devoted to the description of the methodology used in the project; including the general theoretical approach to the problem and the computational facilities used in the calculations. Chapter four present the main results of the calculations along with figures and explications of the obtained data. Chapter five summarizes the results presented in chapter four extracting the main

ideas and reaching to a conclusion to the main questions (most stable isomer, IR spectrum, bonding characteristics) regarding the system. Chapter six will present some of the bibliography that supports the present work.

2. THEORY

a) THE ELECTRONIC PROBLEM

Quantum chemistry is often related to the solution of the time independent Schrödinger equation (TISE) [12] for a given system of chemical interest. Such a famous equation reads:

$$H|\Psi\rangle = E|\Psi\rangle \quad (1.1)$$

Hamiltonian operator H for a molecular system is written as a function of the different distances involved in the molecule; this is, as a function of the distance between electrons and nucleus, electron with the other electrons and nuclei with other nuclei:

$$H = -\sum_{i=1}^N \frac{1}{2} \nabla_i^2 - \sum_{A=1}^M \frac{1}{2M_A} \nabla_A^2 - \sum_{i=1}^N \sum_{A=1}^M \frac{Z_A}{r_{iA}} + \sum_{i=1}^N \sum_{j>1}^N \frac{1}{r_{ij}} + \sum_{A=1}^M \sum_{B>A}^M \frac{Z_A Z_B}{R_{AB}} \quad (1.2)$$

In which the first term and second term corresponds to the kinetic energy of the electrons and of the nuclei respectively, the last three terms correspond to the different contributions that, in absence of an external field define the potential energy of the molecule, all of them having a coulombic profile, and are referred as the interaction between electron-nuclei, electron-electron and nuclei-nuclei, respectively.

Since nuclei are much heavier than electrons, their movement is much slower, or in the opposite way, electrons move much faster than nuclei. This fact allows us to formulate the Born-Oppenheimer [13] approximation that plays a fundamental role in quantum chemistry. Given the equation (1.2) and removing every term that is not explicitly related to the electron coordinates we have the so called electronic Hamiltonian:

$$H_{elec} = -\sum_{i=1}^N \frac{1}{2} \nabla_i^2 - \sum_{i=1}^N \sum_{A=1}^M \frac{Z_A}{r_{iA}} + \sum_{i=1}^N \sum_{j>1}^N \frac{1}{r_{ij}} \quad (1.3)$$

Introduction of the electronic Hamiltonian in the TISE:

$$H_{elec} \Phi_{elec} = \varepsilon_{elec} \Phi_{elec} \quad (1.4)$$

In which Φ_{elec} denotes the electronic wavefunction. The electronic wavefunction therefore has an explicit dependence on the electron coordinate and a parametric one on the nuclei coordinate:

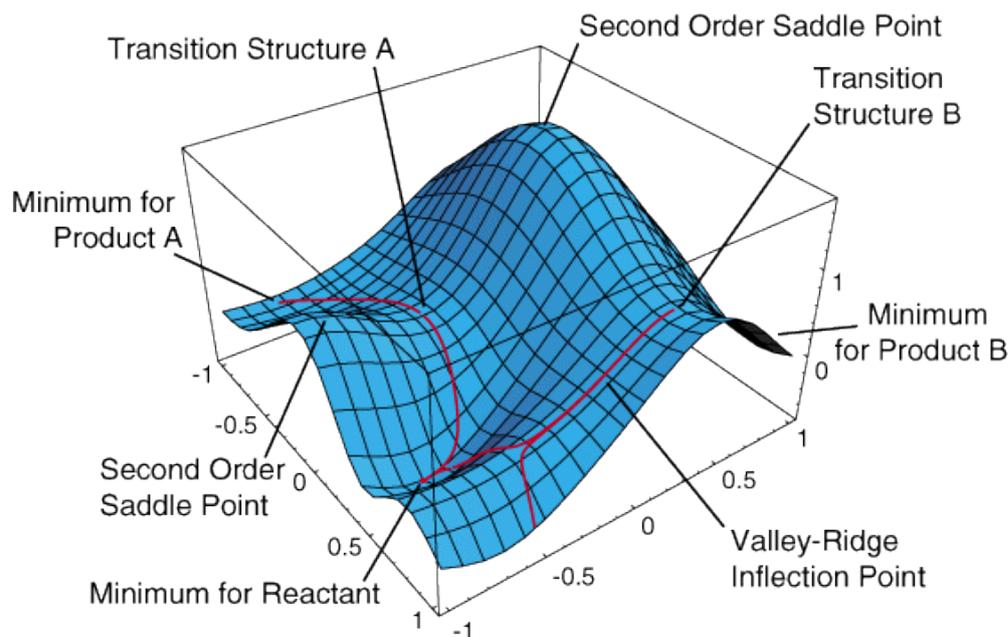
$$\Phi_{elec} = \Phi_{elec}(\{r_i\}; \{R_A\}) \quad (1.5)$$

This means that a full set of nuclei coordinates for a given system gives rise to one Φ_{elec} and other different set of nuclear coordinates gives rise to a different Φ_{elec} .

In this way, we can say that the electronic energy depends parametrically on the nuclear coordinates, and that a term of correction is needed in order to evaluate the total energy of the molecule in a fixed nuclei framework:

$$E_{tot} = \varepsilon_{elec} + \sum_{A=1}^M \sum_{B>A}^M \frac{Z_A Z_B}{R_{AB}} \quad (1.6)$$

This total energy representation as a function of one (or several) nuclear coordinate corresponds to a key concept in quantum chemistry, the potential energy surface (PES)



In the upper figure a PES as a function of two different coordinates is represented along with singular points in its structure. Such singular points contain chemical relevant information and will be discussed further on.

It is important to remark that the nuclear wavefunction ϕ_{nuc} contains important information regarding to the dynamics (translational, rotational and vibrational) of the molecule, which in fact will be used in this study, but for the purposes of the explanation of the theoretical background such component will be omitted and all the work will be referred to the electronic one.

So far we have determined that for the study of the properties of a molecule we need to know the electronic wavefunction of the molecule whose energy is determined by the application of the electronic Hamiltonian operator, but we have not said anything about how this electronic wavefunction is constructed.

b) CONSTRUCTION OF THE ELECTRONIC WAVEFUNCTION. BASIS SETS

In the previous section we have determined the energy of an electron as a function of its spatial coordinates, but a complete set of commuting observables for an electron however includes a fourth coordinate regarding its spin. From a non relativistic point of view the inclusion of the spin must be done ad hoc. Therefore each electron has a $\frac{1}{2}$ quantum number whose sign depends on its alignment in the presence of a magnetic field. The spin eigenfunctions of the spin operator are denoted as $|\alpha\rangle$ and $|\beta\rangle$ and follow the orthonormality conditions:

$$\langle\alpha|\alpha\rangle=\langle\beta|\beta\rangle=1 \quad (1.6)$$

$$\langle\alpha|\beta\rangle=\langle\beta|\alpha\rangle=0 \quad (1.7)$$

The spin coordinate (denoted as s) and the spatial coordinates (denoted as r) can be grouped in a single coordinate x, such as:

$$x=\{r,s\} \quad (1.8)$$

Therefore, the electronic wavefunction of a N-electron system is a function of the coordinates of each electron:

$$\Phi=\Phi(x_1,x_2,x_3,\dots,x_N) \quad (1.9)$$

Since electrons are fermionic particles the wavefunction associated to them must be antisymmetric [14] . Slater [15] stated that a possible expression that fulfilled all this conditions was a determinantal one such as:

$$\Phi_{SD}=\frac{1}{\sqrt{N!}}\begin{vmatrix} \phi_1(1) & \phi_2(1) & \dots & \phi_N(1) \\ \phi_1(2) & \phi_2(2) & \dots & \phi_N(2) \\ \dots & \dots & \dots & \dots \\ \phi_1(N) & \phi_2(N) & \dots & \phi_N(N) \end{vmatrix} \quad (1.10)$$

In which we introduce for the first time the concept of orbital, which are single electron wavefunctions that can represent either an electron in an atom (atomic orbital, AO), an electron in a molecule (molecular orbital, MO), an electron in a crystal etc. These orbital are represented along the columns of the determinant. Along the rows we vary the electronic coordinates. Later on we will discuss how to obtain the energy of a system using this representation either with a monodeterminantal or with a multideterminantal description.

For the time being, let's discuss how the orbitals are constructed. As all the systems involved in the present work are molecular ones so it is clear that our Slater determinant should be constructed with MO. Although there exist methods that solve the different

equations regarding the energy of a system mapping the orbitals along a grid of points (numerical Hartree-Fock) essentially almost all calculations expand the unknown functions in terms of a set of functions. Mathematically we have that:

$$\phi_i = \sum_{\alpha}^K c_{\alpha i} \chi_{\alpha} \quad (1.10)$$

In which χ_{α} denotes functions representing the AO (atomic orbitals). The concept of atomic orbital should be treated with caution in this context since the mathematical functions that will be used as orbitals are not in general solutions of an atomic Schrödinger equation.

For the election of the functions representing χ_{α} we must take into account two main factors:

Physical – Since we are dealing with molecular systems we must use functions that are adequate for the physics of the problem. This can be seen if the problem converges to a solution with the increase of basis functions. The requirement for these kind of problems is that the functions tend to zero with the increase of the distance between electron and nucleus.

Computational – Since problems in quantum chemistry are usually solved with the usage of a certain computer code, the functions used in the expansion should be easy to handle by a program; this is the same as to say that these basis functions should be computationally affordable in terms of economy of time.

So, following these requirements several approaches have been made. Slater [16] proposed that AO should have a mathematical form similar to:

$$\chi_{\zeta,n,l,m}(r, \theta, \varphi) = N Y_{l,m}(\theta, \varphi) r^{n-1} e^{-\zeta r} \quad (1.11)$$

In which, N is a normalization constant, $Y_{l,m}$ are the spherical harmonics functions, and ζ is a constant related with the effective nuclear charge of the nucleus under consideration, n,l,m reads for the quantum numbers associated to that orbital.

An analysis of the structure of this expression reveals that it does not include any radial nodes, so the introduction of radial nodes is made by linear combinations of these functions, called STO (Slater type orbitals). The main problem with the usage of this kind of structures is that all the three and four centre integrals have to be calculated numerically which leads to a computational problem when the size of the system is large enough, this is more than a pair of light atoms.

As it can be inferred from the last sentence, this type of structures are not commonly used for the problems in quantum chemistry. An alternative to this was presented by Boys [17]. This alternative was to use gaussian functions instead of exponential ones in

the expression of the orbitals. GTO (gaussian type orbitals) therefore present a mathematical structure:

$$\chi_{\zeta,n,l,m}(r, \theta, \varphi) = NY_{l,m}(\theta, \varphi) r^{(2n-2+l)} e^{-\zeta r^2} \quad (1.12)$$

And, in cartesian coordinates:

$$\chi_{\zeta,l_x,l_y,l_z}(x, y, z) = N x^{l_x} y^{l_y} z^{l_z} e^{-\zeta r^2}$$

GTO are, in a physical context worse than STO since the r^2 dependence in the exponential leads to a zero slope behavior in the nucleus limit whereas the STO reproduces well the typical "nuclear cusp". Other problem of the GTO is related to the speed of decay of the function, which gives a poor description of the "tail" of the function.

Since both STO and GTO functions are parts of a linear expansion it is obvious that, in order to obtain a comparable accuracy when using GTO we need to include more functions than the number of functions if STO were used. For visual purposes it is common to say that three GTO approximates to a STO.

Being said that, for the sake of accuracy, one will be tempted to say that it is better to use STO but, the increase in the number of GTO needed to achieve a certain level of accuracy is greatly compensated by the computational ease-of-use of this kind of functions, due to certain properties such as the product of two GTO is another GTO.

Finally, a brief comment of where to place the center of these functions. Normally they will be centered coinciding with the nucleus, but they can be centered anywhere depending in the applications, for example they can be centered in the center of a bond.

Once explained the mathematical form of the basis function to be used, and the location for these functions (commonly the nucleus) it is time to define how the basis sets used in real calculations are constructed.

A basis set containing all the essential number of functions is called minimal basis set, this approach implies only to use the number of functions needed for the evaluation of the ground state of each atom. For the elements in the first row of the periodic table this means two s-functions and one set of p-functions for example. John Pople's group proposed the family of most common minimal basis set [18]. This family of basis sets named STO-NG where N corresponds to a natural number, are made by one STO for each electron, with the STO constructed as a fit of a set of N GTO.

$$\chi_{STO-NG} = \sum_i c_i \chi_{i,GTO} \quad (1.13)$$

The linear expansion does not have an imposition in the number of functions, but it is commonly truncated to three (STO-3G), four (STO-4G) or six (STO-6G) terms being

three the most popular. χ_{STO-NG} are called contracted functions and $\chi_{i,GTO}$ primitive functions

The description for the properties of the system performing calculations with this kind of basis sets is very poor, and the results are commonly rough approximations for the real values.

As mentioned above, this basis sets are not adequate for the resolution of real systems so, they have to be improved. One way to improve these basis sets consist in adequate the number of functions to the known problems in chemistry. In this way, split valence basis sets are constructed. The number of functions needed to reproduce the valence electrons which intuitively are the ones more involved in a chemical bond is more than one. This split is usually done leaving two differentiated groups, one tight and compact and another one, more diffuse. The explanation for this lies in that in chemical problems the contribution of the orbitals to a bond, for example is not always the same depending on the bond and therefore we must be able to adjust the molecular environment to the needings of the system, it is not similar to describe a σ bond than a π one in terms of size of the orbitals, and a proper basis set has to be able to adjust to that particular environment

Depending on the number of types of functions used for the valence, we can have DZ (double zeta), TZ (triple zeta), QZ (quadruple zeta) and so on basis sets. In this context zeta refers to the exponent of the GTO basis functions.

In the present work split-valence Pople basis sets [19] will be used. The construction of this basis sets is explained by its notation. Taking, for example a generic DZ basis set of this type, X-YZG, X is referred to the number of primitive gaussian functions used in each of the core electrons, whereas Y and Z stands for the number of primitive functions used for each one of the valence functions. The hyphen is used for marking that the basis set is split valence, finally G stands for Gaussian in order to point that gaussian primitive functions are always used.

Being said that, not always splitting a valence is the solution for the flexibility problems of the basis set of a system. In many cases additional functions must be added in order to ensure that our basis is adequate for the problem we are dealing with, polarization functions and diffuse functions help in this description.

Polarization functions are functions that describe an orbital of higher angular momentum. Polarization functions are used to improve the description and the geometries of a bond since the addition of higher angular momentum functions increase the description of the anisotropy of a bond in the directions of the space. This can be seen considering a bond in which a hydrogen atom is involved, if only one s function is included the spherical distribution of the orbital will not take into account the different molecular environments that are possible for that atom. The inclusion of p functions will help to this problem. In the Pople basis sets, the notation for the inclusion of this type of functions vary, it can be noted adding an asterisk after the G of Gaussian. A

second asterisk implies that hydrogens are also treated in this way. For simplicity and ease to read it is convenient to note these functions with a parenthesis in which the angular momentum of the polarization functions is indicated, in this way X-YZG(d,p) means that all heavy atoms have an additional d function and hydrogens an additional p function.

Diffuse functions are additional functions needed when the system has distances between orbitals and nuclei that are higher than expected, such in ionic atoms, weakly bounded systems or bond breaking situations. Normally they are included with an s function and a set of p functions for each atom. In Pople basis sets are denoted with a + sign if they are added only to heavy atoms and with a ++ if they are also added to hydrogens (X-YZ++G)

In the present work, the basis set used are triple zeta ones with the inclusion of diffuse and polarization functions, for example, for the carbon atoms in each isomer the Pople Basis Set 6-311+G(3df) is used. This basis set is composed of 6 basis functions for each electron in the core and the valence electrons are splitted in three, each one described by three functions, one formed by linear combination of three primitives and the other two by only one primitive. Furthermore, diffuse functions will be added and polarization functions including three d functions and one f function for each atom will also be included

There exist a plethora of different basis sets including correlation consistent ones, Dunning-Huzinaga ones, ANO basis sets, etc, but for the purpose of this work only Pople basis sets and Stuttgart-Dresden (which will be discussed in a further section) are relevant.

c) PSEUDOPOTENTIALS

When the system under consideration have elements belonging to the third row or higher in the periodic table there is a large number of core electrons, that are essentially unimportant from a chemical point of view and represent a large computational cost. However, these electrons have to be treated since electron-electron interactions of the valence electrons with them do matters in a chemical sense. Furthermore, for really heavy atoms relativistic effects in these electrons are not negligible at all and the Schrodinger equation can't deal with such effects.

The solution for the problem of the computational cost and the inclusion of relativistic effect lies in the use of pseudopotentials. The philosophy behind this technique is that a certain function that is fitted from high level calculations including scalar relativistic effects (mass-velocity effect and Darwin correction) or not, is used in the modelization of the core electrons, leaving the explicit treatment of only the valence ones. In this way, computational cost can be reduced significantly and for example, electron-electron interactions remain considered.

Pseudo potentials (or ECP, effective core potentials) are commonly fitted to a gaussian function:

$$U_{ECP}(r) = \sum_i a_i r^{n_i} e^{-\alpha_i r^2} \quad (1.14)$$

the parameters a_i, n_i, α_i depend on the angular momentum of the electrons are fitted by least squares.

In the present work, Plutonium core electrons have been modeled with an Stuttgart-Dresden ECP. Concretely, the ECP used in the work is the ECP60MWB[20]. this means that is a potential that includes 60 electrons and that has been done choosing as a reference a neutral atom with a quasirelativistic Wood-Boring [21] treatment. In conjunction with this potential a complementary [8s7p6d4f] double zeta basis set of the same lab, named as ECP60SEG[22] is used for the rest of the plutonium electrons.

d) HARTREE-FOCK EVALUATION OF THE ENERGY

So far we have been talking about how to represent the electronic wavefunction as a construction of single electron wavefunctions but nothing has been discussed about the evaluation of the energy and therefore of all properties related to it. The first approach to that purpose is the self-consistent field theory. In this way only one Slater determinant is used in the evaluation of the energy. This election implies some considerations related to the electron-electron repulsion energy and this effect is only treated in an average way by means of the interaction of one electron with all electrons in the average field formed by them.

When a single Slater determinant is minimized according to the variational principle we can derive the Hartree-Fock equations.

The first step for deriving these equations is to represent (1.10) as a sum of permutations over the product of the diagonal elements of the determinant:

$$\Phi = A[\phi_1(1)\phi_2(2)\dots\phi_N(N)] = A\Pi \quad (1.15)$$

Being A:

$$A = \frac{1}{\sqrt{N!}} \sum_{p=0}^{N-1} (-1)^p P = \frac{1}{\sqrt{N!}} \left[1 - \sum_{ij} P_{ij} + \sum_{ijk} P_{ijk} - \dots \right] \quad (1.16)$$

A is named the antisymmetrizing operator, with 1 the identity operator, P_{ij} generates all possible permutations of 2 electron coordinates, P_{ijk} of three and so on. Some of the properties of the presented operator are that:

- Is nearly idempotent since : $AA = \sqrt{N!}A \quad (1.17)$

- It commutes with the Hamiltonian operator : $HA = AH \quad (1.18)$

Now we may rewrite the Hamiltonian operator for a molecule written in (1.3) adding a term for the internuclear repulsion which do not depend on the electron coordinates and it is a constant for a fixed configuration of nuclei.

$$H = -\sum_{i=1}^N \frac{1}{2} \nabla_i^2 - \sum_{i=1}^N \sum_A^M \frac{Z_A}{|R_A - r_i|} + \sum_{i=1}^N \sum_{j>1}^N \frac{1}{|r_i - r_j|} + \sum_{A=1}^M \sum_{B>A}^M \frac{Z_A Z_B}{|R_A - R_B|} \quad (1.19)$$

The operators can be grouped regarding the number of electrons involved and in this way we can define monoelectronic operators, a bielectronic operator and a constant:

$$h_i = -\frac{1}{2} \nabla_i^2 - \sum_a \frac{Z_a}{|R_a - r_i|} \quad (1.20)$$

$$g_{ij} = \frac{1}{|r_i - r_j|} \quad (1.21)$$

$$V_m = \sum_{A=1}^M \sum_{B>A}^M \frac{Z_A Z_B}{|R_A - R_B|} \quad (1.22)$$

Therefore the hamiltonian operator:

$$H = \sum_{i=1}^N h_i + \sum_{i=1}^N \sum_{j>1}^N g_{ij} + V_m \quad (1.23)$$

The energy therefore assuming Φ is normalized:

$$E = \langle \Phi | H | \Phi \rangle = \langle A\Pi | H | A\Pi \rangle \quad (1.24)$$

Applying the (1.17) property:

$$E = \sqrt{N!} \langle \Pi | H | A\Pi \rangle \quad (1.25)$$

And, developing the permutation operator shown in (1.16):

$$E = \sqrt{N!} \sum_{p=0}^{N-1} (-1)^p \langle \Pi | H | P\Pi \rangle \quad (1.26).$$

According to this the next step is to decompose (1.26) in each of the terms that we have define in (1.23) for the energy. The first one is the energy of the system associated to the nucleus-nucleus interaction which is trivial:

$$\langle \Phi | V_m | \Phi \rangle = V_m \langle \Phi | \Phi \rangle = V_m \quad (1.27)$$

Next one is the one electron operator, for the first coordinate:

$$\langle \Pi | h_1 | \Pi \rangle = \langle \phi_1(1)\phi_2(2)\dots\phi_N(N) | h_1 | \phi_1(1)\phi_2(2)\dots\phi_N(N) \rangle = \langle \phi_1(1) | h_1 | \phi_1(1) \rangle \langle \phi_2(2) | \phi_2(2) \rangle \dots \langle \phi_N(N) | \phi_N(N) \rangle \quad (1.28)$$

So:

$$h_1 = \langle \phi_1(1) | h_1 | \phi_1(1) \rangle \quad (1.29)$$

This is the evaluation of the diagonal elements of the Slater determinant and it is done when the antisymmetrizing operator corresponds to the identity operator, and, as it is going to be shown right away is the only contributive term since, for example a permutation of a single electron:

$$\langle \Pi | h_1 | P_{12} \Pi \rangle = \langle \phi_1(1)\phi_2(2)\dots\phi_N(N) | h_1 | \phi_2(1)\phi_1(2)\dots\phi_N(N) \rangle = \langle \phi_1(1) | h_1 | \phi_2(1) \rangle \langle \phi_2(2) | \phi_1(2) \rangle \dots \langle \phi_N(N) | \phi_N(N) \rangle \quad (1.30)$$

And

$$\langle \phi_2(2) | \phi_1(2) \rangle = 0 \quad (1.31)$$

Because the MO are orthonormal.

The two electron operator is evaluated in the same way, first for the diagonal elements:

$$\langle \Pi | g_{12} | \Pi \rangle = \langle \phi_1(1) \phi_2(2) \dots \phi_N(N) | g_{12} | \phi_1(1) \phi_2(2) \dots \phi_N(N) \rangle = \langle \phi_1(1) \phi_2(2) | g_{12} | \phi_1(1) \phi_2(2) \rangle \dots \langle \phi_N(N) | \phi_N(N) \rangle \quad (1.32)$$

$$\langle \Pi | g_{12} | \Pi \rangle = \langle \phi_1(1) \phi_2(2) | g_{12} | \phi_1(1) \phi_2(2) \rangle = J_{12} \quad (1.33)$$

J_{12} is called Coulomb integral because it represent the classic electronic repulsion between two charge distributions denoted by the square of the MO. This time when we apply the permutation operator between only two coordinates P_{ij} :

$$\langle \Pi | g_{12} | P_{12} \Pi \rangle = \langle \phi_1(1) \phi_2(2) \dots \phi_N(N) | g_{12} | \phi_2(1) \phi_1(2) \dots \phi_N(N) \rangle = \langle \phi_1(1) \phi_2(2) | g_{12} | \phi_2(1) \phi_1(2) \rangle \dots \langle \phi_N(N) | \phi_N(N) \rangle \quad (1.34)$$

$$\langle \Pi | g_{12} | P_{12} \Pi \rangle = \langle \phi_1(1) \phi_2(2) | g_{12} | \phi_2(1) \phi_1(2) \rangle \dots \langle \phi_N(N) | \phi_N(N) \rangle = K_{12} \quad (1.35)$$

K_{12} is called exchange integral. Finally is remarkable that all the permutations of high order (exchange of three coordinates for example) give rise to null contributions.

With all the terms defined we must rewrite our expression for the energy as:

$$E = \sum_{i=1}^N h_i + \frac{1}{2} \sum_{i=1}^N \sum_{j=1}^N (J_{ij} - K_{ij}) + V_m \quad (1.36)$$

In which the 1/2 factor is used for no sum twice the self-interaction term in exchange and coulomb term J_{ii}, K_{ii} which is exactly the same term. The minus sign in the exchange integral arises from the antisymmetrizing operator.

The next step is the minimization of the energy. This minimization will be done using the Lagrange multipliers method, imposing the orthonormality condition within MO as a restriction. Firstly it is convenient to rewrite the Coulomb and Exchange integrals in an easier way to handle, this is to express the energy in terms of Coulomb and Exchange operators:

$$E = \sum_{i=1}^N \langle \phi_i | h_i | \phi_i \rangle + \frac{1}{2} \sum_{i=1}^N \sum_{j=1}^N (\langle \phi_j | J_i | \phi_j \rangle - \langle \phi_j | K_i | \phi_j \rangle) + V_m \quad (1.37)$$

Both operators are applied in the following way:

$$J_i |\phi_j(2)\rangle = \langle \phi_i(1) | g_{12} | \phi_i(1) \rangle |\phi_j(2)\rangle; K_i |\phi_j(2)\rangle = \langle \phi_i(1) | g_{12} | \phi_j(1) \rangle |\phi_i(2)\rangle \quad (1.38)$$

The definition of our Lagrange function is:

$$L = E - \sum_{ij}^N \lambda_{ij} (\langle \phi_i | \phi_j \rangle - \delta_{ij}) \quad (1.39)$$

Minimization of the Lagrange function can be written as:

$$\delta L = \delta E - \sum_{ij}^N \lambda_{ij} (\langle \delta \phi_i | \phi_j \rangle + \langle \phi_i | \delta \phi_j \rangle) \quad (1.40)$$

The variation for the energy reads, after some manipulations:

$$\delta E = \sum_{i=1}^N \langle \delta \phi_i | h_i | \phi_i \rangle + \langle \phi_i | h_i | \delta \phi_i \rangle + \sum_{ij}^N (\langle \delta \phi_i | J_j - K_j | \phi_i \rangle + \langle \phi_i | J_j - K_j | \delta \phi_i \rangle) \quad (1.41)$$

Now, we can define a new mono-electronic operator which collects both kinetic energy of the electrons and the attraction-repulsion of one electron with all their surroundings. This operator is called the Fock operator and is denoted with F_i :

$$F_i = h_i + \sum_j^N (J_j - K_j) \quad (1.42)$$

Writing the variation of the energy with respect to this new operator:

$$\delta E = \sum_{i=1}^N \langle \delta \phi_i | F_i | \phi_i \rangle + \langle \phi_i | F_i | \delta \phi_i \rangle \quad (1.43)$$

Therefore, the Lagrange function becomes:

$$\delta L = \sum_{i=1}^N \langle \delta \phi_i | F_i | \phi_i \rangle + \langle \phi_i | F_i | \delta \phi_i \rangle - \sum_{ij}^N \lambda_{ij} (\langle \delta \phi_i | \phi_j \rangle + \langle \phi_i | \delta \phi_j \rangle) \quad (1.44)$$

$$\delta L = \sum_{i=1}^N \langle \delta \phi_i | F_i | \phi_i \rangle - \sum_{ij}^N \lambda_{ij} (\langle \delta \phi_i | \phi_j \rangle) + \sum_{i=1}^N \langle \delta \phi_i | F_i | \phi_i \rangle^* - \sum_{ij}^N \lambda_{ij} (\langle \delta \phi_i | \phi_j \rangle^*) \quad (1.45)$$

The minimization applies when $\delta L = 0$ and this means that either $\langle \delta \phi |$ or $\langle \delta \phi |^*$ should make the Lagrangian function equal zero, this implies that either the first two terms of 1.45 are 0 or the last two terms are. Taking the complex conjugate of the last two terms and subtracting them from the first two terms gives:

$$\sum_{ij}^N (\lambda_{ij} - \lambda_{ji}^*) \langle \delta \phi_i | \phi_j \rangle = 0 \quad (1.46)$$

It can be extracted that the Lagrange parameter are elements of a Hermitian matrix . This concludes the development of the Hartree-Fock equations:

$$F_i \phi_i = \sum_j^N \lambda_{ij} \phi_j \quad (1.47)$$

Now we can make an unitary transformation to the set of MO that gives rise to a pseudoeigenvalue equation in which the eigenvalues correspond to the MO energies:

$$F_i \phi_i' = \varepsilon_i \phi_i' \quad (1.48)$$

the MO of this equations are called canonical orbitals.

Fock equations only can be solved by iterative methods since the knowledge of a certain MO is determined by the rest of the molecular orbitals. In this way the set of orbitals that iteratively leads to a stationary (or at least as stationary as possible) energy is called SCF orbitals and are considered solutions of the Hartree-Fock equations. The total energy is then calculated adding to orbital energies ε_i both two-electron and nucleus-nucleus interaction terms:

$$E = \sum_i^N \varepsilon_i - \frac{1}{2} \sum_{ij}^N (J_{ij} - K_{ij}) + V_{nn} \quad (1.49)$$

For the time being it has been explained how the energy in terms of the MO are calculated, but as we have seen in (1.10), these MO are constructed as an expansion of a certain basis, if we introduce (1.10) into (1.48):

$$F_i \sum_{\alpha}^K c_{\alpha i} \chi_{\alpha} = \varepsilon_i \sum_{\alpha}^K c_{\alpha i} \chi_{\alpha} \quad (1.50)$$

Multiplying by the left for a certain basis function and integrating gives us the Roothan-Hall equations [23,24], which in matrix notation:

$$FC = SC\varepsilon \quad (1.51)$$

With the matrix S containing all the overlap elements and the matrix F containing all the Fock matrix elements.

Fock operator can be developed to be formed by the product of two new matrices, one accounting the two electron integrals and another called density matrix (D) which contains the product of the coefficients of the electrons involved in the two electron integrals.

$$F_{\alpha\beta} = h_{\alpha\beta} + \sum_{\gamma\delta} G_{\alpha\beta\gamma\delta} D_{\gamma\delta} \quad (1.52)$$

$$D_{\gamma\delta} = \sum_j^{occ.MO} c_{\gamma j} c_{\delta j} \quad (1.53)$$

Finally, the expression for the energy can be written as (in term of the integrals):

$$E = \sum_{\alpha\beta}^M D_{\alpha\beta} h_{\alpha\beta} + \frac{1}{2} \sum_{\alpha\beta\gamma\delta}^M (D_{\alpha\beta} D_{\gamma\delta} - D_{\alpha\delta} D_{\beta\gamma}) (\langle \chi_\alpha \chi_\gamma | g | \chi_\beta \chi_\delta \rangle) + V_{nn} \quad (1.54)$$

in which some parts of the demonstration have been omitted for the ease of read.

Both one and two electron integrals written in explicit integral notation in the atomic basis are:

$$\langle \chi_\alpha | h | \chi_\beta \rangle = \int \chi_\alpha(1) \left(-\frac{1}{2} \nabla^2 \right) \chi_\beta(1) dr_1 + \sum_a \int \chi_\alpha(1) \frac{Z_a}{|R_a - r_1|} \chi_\beta(1) dr \quad (1.55)$$

$$\langle \chi_\alpha \chi_\gamma | g | \chi_\beta \chi_\delta \rangle = \int \chi_\alpha(1) \chi_\gamma(2) \frac{1}{|r_1 - r_2|} \chi_\beta(1) \chi_\delta(2) dr_1 dr_2 \quad (1.56)$$

A general notation for two electron integrals can be used omitting the g operator:

$$\langle \chi_\alpha \chi_\gamma | g | \chi_\beta \chi_\delta \rangle = \langle \chi_\alpha \chi_\gamma | \chi_\beta \chi_\delta \rangle \quad (1.57)$$

These Roothan-Hall equations are the ones that are commonly used in the resolution of problems in quantum chemistry in the framework of HF theory. Moreover all the correlated methods that will be discussed later with the exception of the DFT theory (to some extent), begins with a SCF calculation so it is important to describe the theory behind it.

Finally, it is convenient to mention how the SCF scheme is performed since its implementation is commonly made with this scheme. Since the Fock matrix is only known if all the MO are known and we intend to determine the MO coefficients of the basic functions which in fact are calculated by a Fock matrix diagonalization we are truly in a problem. The solution to the problem lies in the selection of a guessed set of orbitals than can be taken from semiempirical methods, form the Fock matrix, diagonalize it, form a density matrix from the guessed orbitals and recalculate the Fock matrix with the use of the calculated Density matrix. The repetition of this scheme iteratively finally leads to the full solution of the problem.

A final comment regarding the orbitals obtained. They are a set of M orbitals (number of basis functions) with N occupied ones and M-N unoccupied ones named virtual MO. The utilization of these orbitals as a source of information must be done with caution since they dont have direct physical interpretation.

Hartree-Fock theory in a Roothan-Hall sense has two different sources of error; one arising from the nature of the theory, it cannot take into account the effects of electron

correlation and the lack of these contributions will be partially solved with correlated methods. The second error arises from the utilization of a basis set to expand the molecular orbitals because the expansion is truncated and therefore not complete, this is why an increase in the size of the basis set leads to an improvement in the energy, a basis set composed of infinite basis functions leads to the Hartree-Fock limit.

e) UNRESTRICTED HARTREE FOCK

In the context of this project all the molecular environments considered are open-shell ones since all the isomers have been proven to have unpaired electrons in its valence shell. However Hartree-Fock theory does not include any restriction or consideration in the spin of the orbitals. For the resolution of this problem Pople [25] proposed that both spin-up and spin-down parts of the system should be calculated separately.

Both parts are named depending on the spinfunction associated to them (α, β). It is obvious that the interactions between the electrons within the α part and the β are not the same and therefore spatial orbitals for both parts will not be essentially the same. However this fact can be avoided imposing a restriction to the spatial orbitals leading to a ROHF (restricted open shell Hartree Fock), but this theory will not be used in this project. UHF (unrestricted Hartree-Fock) however will be the choice for all the SCF calculations previous to the correlated calculations, and in this theory the different interactions between α and β spin is taken into account. The main problem for the theory is that the wavefunction is not normally an eigenfunction of the S^2 (only it is when a UHF is used in a RHF context). Therefore an UHF wavefunction can interact and have contributions from higher multiplicity states and S^2 value have to be carefully examined to avoid incorrect results

f) AN ALTERNATIVE METHOD IN THE EVALUATION OF THE ENERGY.
DENSITY FUNCTIONAL THEORY.

Density functional theory is devoted to the determination of the electronic energy using a different object than traditional wavefunction methods. In DFT, in order to calculate the energy and energy related properties of a many electron system, electron density will be used. Hohenberg and Kohn stated [26] that the ground state electronic energy of a system is completely defined by its electron density.

The implications of this “change of object” can be seen in the number of spatial variables used in each development. Whereas wavefunction theory methods make use of a set of $3N$ coordinates (three for each electron, four if its spin is included), electron density only depends on three coordinates, independently of the number of electrons.

The main goal of DFT is to develop an exact functional (function of a function) that univocally connects the electron density with the energy of the system. Nowadays that problem remains unresolved or, better said the kinetic part of that functional remains unresolved considering non interacting particles, or the kinetic and exchange-correlation part for systems of interacting particles, and research in DFT is devoted to construct accurate approximate functionals.

i. USEFUL DEFINITIONS IN THE DFT CONTEXT

In the first place it is convenient to define some concepts that will be useful during all the discussion of the DFT theory. It is well known that the probability of finding electron 1 disregarding the position of all the other electrons in an N electron wavefunction is given by:

$$dx_1 \int \Psi(\vec{x}_1, \vec{x}_2, \dots, \vec{x}_N) \Psi^*(\vec{x}_1, \vec{x}_2, \dots, \vec{x}_N) d\vec{x}_2 \dots d\vec{x}_n \quad (1.58)$$

And, since the electrons are indistinguishable, the number of electrons times the probability will give us the density function:

$$\rho(\vec{x}_1) dx_1 = N dx_1 \int \Psi(\vec{x}_1, \vec{x}_2, \dots, \vec{x}_N) \Psi^*(\vec{x}_1, \vec{x}_2, \dots, \vec{x}_N) d\vec{x}_2 \dots d\vec{x}_n \quad (1.59)$$

The relationship between the density function and the electron density, which is our workhorse for this theory is an integration over the spin coordinate of the electron upon consideration:

$$\rho(\vec{r}_1) = N \int \Psi(\vec{x}_1, \vec{x}_2, \dots, \vec{x}_N) \Psi^*(\vec{x}_1, \vec{x}_2, \dots, \vec{x}_N) ds_1 d\vec{x}_2 \dots d\vec{x}_n \quad (1.60)$$

Just as the same that in Hartree-Fock, in which electrons can be divided regarding the spin eigenfunction associated to it, electron density can be only calculated to the α part of the density or for the β part. In this way the "excess" of electron density for a certain electrons can be referred as:

$$\rho^S(r) = \rho^\alpha(r) - \rho^\beta(r) \quad (1.61)$$

The above expression receives the name of spin density and can be used in certain applications, like open-shell systems.

When we need to know the probability of finding two electrons independently of where the others are located we use the expression:

$$d\vec{x}_1 d\vec{x}_2 \int \Psi(\vec{x}_1, \vec{x}_2, \dots, \vec{x}_N) \Psi^*(\vec{x}_1, \vec{x}_2, \dots, \vec{x}_N) d\vec{x}_3 \dots d\vec{x}_n \quad (1.62)$$

In the same way that in (1.59) We can define the second order density as:

$$\gamma_2(\vec{x}_1, \vec{x}_2) = N(N-1) \int \Psi(\vec{x}_1, \vec{x}_2, \dots, \vec{x}_N) \Psi^*(\vec{x}_1, \vec{x}_2, \dots, \vec{x}_N) d\vec{x}_3 \dots d\vec{x}_n \quad (1.63)$$

Now, the two-electron density reads:

$$\gamma_2(\vec{r}_1, \vec{r}_2) = \int \gamma_2(\vec{x}_1, \vec{x}_2) ds_1 ds_2 \quad (1.64)$$

As can be imagined, decomposition regarding spin parts of the electron density can be done, giving rise to four contributions

Later on, the Hamiltonian operator for a molecular system will be applied, and for certain applications of that operator it is convenient to have the First order reduced density matrix defined. For that, lets construct the Fock-Dirac density matrix and integrate it over the spin coordinates:

$$\rho_1(\vec{x}_1, \vec{x}'_1) = N \int \Psi(\vec{x}_1, \vec{x}_2, \dots, \vec{x}_N) \Psi^*(\vec{x}'_1, \vec{x}_2, \dots, \vec{x}_N) d\vec{x}_2 \dots d\vec{x}_n \quad (1.65)$$

$$\rho_1(\vec{r}_1, \vec{r}'_1) = \int \rho_1(\vec{x}_1, \vec{x}'_1) d\vec{s}_1 d\vec{s}'_1 \quad (1.66)$$

(1.64) contains information on the correlated motions of two electrons, since it gives the probability of finding simultaneously two electrons. This density can be decomposed in this way:

$$\gamma_2(\vec{r}_1, \vec{r}_2) = \rho(\vec{r}_1)\rho(\vec{r}_2) + \Gamma_{XC}(\vec{r}_1, \vec{r}_2) \quad (1.67)$$

$\Gamma_{XC}(\vec{r}_1, \vec{r}_2)$ is called exchange-correlation density, and it can be seen as the correlated density of a pair of electrons. The product $\rho(\vec{r}_1)\rho(\vec{r}_2)$ gives us the independent probability of finding an electron in \vec{r}_1 and other in \vec{r}_2 .

If we divide $\gamma_2(\vec{r}_1, \vec{r}_2)$ by $\rho(\vec{r}_1)$ we get:

$$P(\vec{r}_1, \vec{r}_2) = \frac{\gamma_2(\vec{r}_1, \vec{r}_2)}{\rho(\vec{r}_1)} \quad (1.68)$$

That gives the probability of finding an electron in a certain coordinate when we know that other electron is in another coordinate.

Dividing (1.67) by $\rho(\vec{r}_1)$ we obtain:

$$P(\vec{r}_1, \vec{r}_2) = \rho(\vec{r}_2) + \rho_{XC}(\vec{r}_1, \vec{r}_2) \quad (1.69)$$

Finally we have arrived to a very important definition in DFT that is:

$$\rho_{XC}(\vec{r}_1, \vec{r}_2) = \frac{\Gamma_{XC}(\vec{r}_1, \vec{r}_2)}{\rho(\vec{r}_1)} \quad (1.70)$$

Which defines the Fermi-Coulomb hole and has a similar meaning exchange and correlation context of HF theory.

To conclude lets decompose the Fermi-Coulomb hole into two various contributions to study them.

If we study the second-order density for an arrangement in which both spin eigenfunctions of the electrons are the same we have:

$$\gamma_2^{\alpha\alpha}(\vec{r}_1, \vec{r}_2) = \rho^\alpha(\vec{r}_1)\rho^\alpha(\vec{r}_2) + \Gamma_{XC}^{\alpha\alpha}(\vec{r}_1, \vec{r}_2) \quad (1.71)$$

And with the same procedure that (1.69):

$$P^{\alpha\alpha}(\vec{r}_1, \vec{r}_2) = \rho^\alpha(\vec{r}_2) + \rho_{XC}^{\alpha\alpha}(\vec{r}_1, \vec{r}_2) \quad (1.72)$$

$\rho_{XC}^{\alpha\alpha}(\vec{r}_1, \vec{r}_2)$ is called Fermi Hole and shows that the region of space in which an electron described with \vec{r}_1 has a reduced probability to contain another electron of the same spin described by \vec{r}_2 . Now, following the same argument for two electrons of different spin we have:

$$P^{\alpha\beta}(\vec{r}_1, \vec{r}_2) = \rho^\beta(\vec{r}_2) + \rho_{XC}^{\alpha\beta}(\vec{r}_1, \vec{r}_2) \quad (1.73)$$

$\rho_{XC}^{\alpha\beta}(\vec{r}_1, \vec{r}_2)$ is called Coulomb Hole and shows the region of the space on which the presence of an electron is disturbed by the presence of other electron of different spin.

ii) EVALUATION OF OPERATORS USING ELECTRON DENSITY RELATED VARIABLES.

The goal upon the utilization of DFT in quantum chemistry is to evaluate the energy and other properties of a system. Taking an arbitrary state vector of a pure state, the evaluation of an operator \hat{O} is given by:

$$\langle \hat{O} \rangle = \int \Psi^*(\vec{x}) \hat{O} \Psi(\vec{x}) d\vec{x} \quad (1.74)$$

For operators only containing products or divisions we can write:

$$\langle \hat{O} \rangle = \int \hat{O} \rho(\vec{x}) d\vec{x} \quad (1.75)$$

And, for operators containing derivatives as, for example, the kinetic energy operator:

$$\langle \hat{O} \rangle = \int_{\vec{x}=\vec{x}} \hat{O} \rho_1(\vec{x}, \vec{x}') d\vec{x} \quad (1.76)$$

The evaluation of a many electron system operator composed by the sum of mono-electronic operators:

$$\hat{\mathcal{G}}_1 = \sum_i \hat{h}(i) \quad (1.77)$$

can be evaluated as a function of the first order density matrix:

$$\langle \Psi | \hat{\mathcal{G}}_1 | \Psi \rangle = \int_{\vec{r}_1=\vec{r}_1} \hat{h}(\vec{r}_1) \rho_1(\vec{r}_1, \vec{r}_1') d\vec{r}_1 \quad (1.78)$$

And, in the same way for a generic two electron operator, represented as:

$$\hat{\mathcal{G}}_2 = \sum_i \sum_{j>i} \hat{g}(i, j) \quad (1.79)$$

We can take its value as:

$$\langle \Psi | \hat{\mathcal{G}}_2 | \Psi \rangle = \frac{1}{2} \iint \hat{g}'(1, 2) \gamma_2(\vec{r}_1, \vec{r}_2) d\vec{r}_1 d\vec{r}_2 \quad (1.80)$$

Now we are in disposition, recalling (1.3), of writing the expectation value of a normalized wavefunction as a function of variables derived from the electron density, but not entirely from the electron density itself:

$$E_{el} = \langle \Psi | \hat{H}_{el} | \Psi \rangle = \int_{\vec{r}_1=\vec{r}_1} \left(-\frac{1}{2} \nabla^2(1) + \hat{v}(1) \right) \rho_1(\vec{r}_1, \vec{r}_1') d\vec{r}_1 + \frac{1}{2} \iint \frac{\gamma(\vec{r}_1, \vec{r}_2)}{|\vec{r}_1 - \vec{r}_2|} d\vec{r}_1 d\vec{r}_2 \quad (1.81)$$

Or, alternatively:

$$E_{el} = \langle \Psi | \hat{H}_{el} | \Psi \rangle = \int_{\vec{r}_1 = \vec{r}_1} \left(-\frac{1}{2} \nabla^2(1) \right) \rho_1(\vec{r}_1, \vec{r}_1) d\vec{r}_1 + \int \hat{v}(1) \rho(\vec{r}_1) d\vec{r}_1 + \dots$$

$$\dots + \frac{1}{2} \iint \frac{\rho(\vec{r}_1) \rho(\vec{r}_2)}{|\vec{r}_1 - \vec{r}_2|} d\vec{r}_1 d\vec{r}_2 + \frac{1}{2} \iint \frac{\rho(\vec{r}_1) \rho_{xc}(\vec{r}_1, \vec{r}_2)}{|\vec{r}_1 - \vec{r}_2|} d\vec{r}_1 d\vec{r}_2 \quad (1.82)$$

The different terms correspond to, kinetic energy of the electrons, electron-nucleus attraction, Coulomb electron repulsion and the exchange-correlation term. Equation 1.81 shows that the energy of an atomic/molecular system can be expressed in terms of the first and second density function and matrices and therefore can be expressed as a functional of the density.

iii) HOHENBERG-KOHN THEOREMS. FUNDAMENTAL EQUATION OF DFT

So far we have seen that the energy can be determined as a functional of the energy. This conclusion is generalized by means of the first Hohenberg-Kohn theorem, that states:

"Any observable of a stationary, non-degenerate ground state can be calculated, exactly in theory, from the electron density of the ground state. Any observable can be written as a functional of the electron density of the ground state"

This statement puts electron density at the same level as ψ in the amount of information that it contains regarding ground states (DFT can be extrapolated to excited states but is out of the concern of this work). Proof for this statement is quite simple.

Having the exact density of a certain ground, non degenerate state. Let us consider that such a state is defined by two different external-potentials (the external potential in this context is referred to the electron-nucleus interaction) $v_1(r)$ and $v_2(r)$ giving rise obviously to two different electronic hamiltonians \hat{H}_1 and \hat{H}_2 .

It is also obvious that these hamiltonians produce two different wavefunctions for the same ground state ψ_1 and ψ_2 . This is the same as to say that the evaluation of their energies gives rise to a different energy:

$$E_1 = \langle \psi_1 | \hat{H}_1 | \psi_1 \rangle; E_2 = \langle \psi_2 | \hat{H}_2 | \psi_2 \rangle \quad (1.83)$$

Next step in the demonstration is to evaluate the energy of the two wavefunctions using the hamiltonian that is not associated to it. Of course we do not know the exact value of that energy but we do know that it is larger than the original one, based in the variational principle, for each one of the wavefunctions:

$$E_1 < \langle \psi_2 | \hat{H}_1 | \psi_2 \rangle = \langle \psi_2 | \hat{H}_2 | \psi_2 \rangle + \langle \psi_2 | \hat{H}_1 - \hat{H}_2 | \psi_2 \rangle = E_2 + \int \rho(\vec{r}) [v_1(\vec{r}) - v_2(\vec{r})] d\vec{r} \quad (1.84)$$

$$E_2 < \langle \psi_1 | \hat{H}_2 | \psi_1 \rangle = \langle \psi_1 | \hat{H}_1 | \psi_1 \rangle + \langle \psi_1 | \hat{H}_2 - \hat{H}_1 | \psi_1 \rangle = E_1 + \int \rho(\vec{r}) [v_2(\vec{r}) - v_1(\vec{r})] d\vec{r} \quad (1.85)$$

Adding (1.84) and (1.85):

$$E_1 + E_2 < E_1 + E_2 \quad (1.86)$$

Expression that lacks of any sense. Returning to the statement of the demonstration there not exist two or more external potentials that define a single electron density (except for an additive constant). The consequences of this theorem are that considering that:

$$\int \rho(\vec{r}) d\vec{r} = N \quad (1.87)$$

And that $\rho(\vec{r})$ also fix the external potential, $\rho(\vec{r})$ defines an unique Hamiltonian for the system. And given a Hamiltonian, given the wavefunction that by the first postulate of quantum mechanics contains all the information about the system.

This theorem can be applied to N-representable and v-representable ground states. N representability is fulfilled if the density is positive in all the space and integrates to the total number of electrons of the system.

A state is v representable if there exists an external potential for the system. This seems also trivial but it is not since hypothetical densities not always can be derived from a external potential.

Fulfilling these two conditions, the energy of a molecular system can be expressed:

$$E[\rho] = T[\rho] + V_{Ne}[\rho] + V_{ee}[\rho] + V_m \quad (1.88)$$

The terms that not depend on the external potential are normally grouped in this demonstration to a new functional named Hohenberg-Kohn functional $F_{HK}[\rho]$ and the energy can be rewritten as:

$$E_v[\rho] = \int \rho(\vec{r}) v(\vec{r}) d\vec{r} + F_{HK}[\rho] \quad (1.89)$$

As we will see later, if $F_{HK}[\rho]$ is known, the exact solution of the energy for a system will be known but $F_{HK}[\rho]$ is not known and approximate methods must be used.

The second Hohenberg-Kohn theorem, which can be seen as a generalization of the variational principle in a DFT framework theorem reads:

"The electron density of a non-degenerate ground state can be calculated theoretically, obtaining the density that minimizes the ground state"

Again, this theorem is fulfilled if the electron density is N and V representable. Taking $\tilde{\rho}(\vec{r})$ as trial density, this theorem can be stated as:

$$E_0 \leq E_v[\tilde{\rho}(\vec{r})] \quad (1.90)$$

Applying the variational principle to the evaluation of the trial density with the exact Hamiltonian the theorem is proved:

$$E_v[\tilde{\rho}(\vec{r})] = \langle \tilde{\psi} | \hat{H} | \tilde{\psi} \rangle \geq \langle \psi | \hat{H} | \psi \rangle = E_0 \quad (1.91)$$

Where E_0 is the exact energy of the considered ground state and the inequality is a consequence of the variational principle. Under this principle lies the practical application of DFT since for obtaining the density of the ground state it suffices with the minimization of the energy functional with respect to the density. In this way we have the differential equation:

$$\frac{\delta E_v[\rho]}{\delta \rho} = 0 \quad (1.92)$$

(1.92) must be minimized under a basic restriction. This is, maintaining the N representability of the density. In the same way that in HF this restriction is doing constructing the Lagrange function for the problem.

The Lagrange function is constructed adding to the original function a restriction multiplied by a certain multiplier. The restriction in our case is:

$$\int \rho(\vec{r}) d\vec{r} - N = 0 \quad (1.92)$$

The Lagrange function therefore:

$$E_v[\rho(\vec{r})] - \mu \left[\int \rho(\vec{r}) d\vec{r} - N \right] \quad (1.93)$$

The minimization:

$$\delta \left[E_v[\rho(\vec{r})] - \mu \left[\int \rho(\vec{r}) d\vec{r} - N \right] \right] = 0 \quad (1.94)$$

The differentiation and rearrangement of the expression leads to:

$$\int \left\{ \frac{\delta E_v[\rho]}{\delta \rho(\vec{r})} \right\} \delta \rho(\vec{r}) d\vec{r} = 0 \quad (1.95)$$

Operating we arrive to the fundamental equation of DFT:

$$\mu = \frac{\delta E_v[\rho]}{\delta \rho(\vec{r})} = v_n(\vec{r}) + \frac{\delta F_{HK}[\rho]}{\delta \rho(\vec{r})} \quad (1.96)$$

Where μ can be proved to be the chemical potential of the system.

iv) KOHN-SHAM METHOD

So far we have derived the equation for the minimization of the energy and for the determination of the ground state density, opening a tremendous usage for a great number of applications. As promised, the equations contracts the number of variables of the system to the three spatial coordinates reducing the complexity of the problem. However, eq (1.96) needs the knowledge of F_{HK} to be evaluated, and surprisingly these functional is not known. In particular the unknown variable is $T[\rho]$. Ironically, in wavefunction theory the calculation of the kinetic energy is considered trivial in comparison with the interelectronic terms. In this way Kohn and Sham [27] proposed to construct a set of orbitals (just the same as in HF) from the electron density taking into consideration that the exact density can be constructed as:

$$\rho(\vec{r}) = \sum_{i=1}^{N_{occ}} |\chi_i(\vec{r})|^2 \quad (1.97)$$

And the kinetic energy therefore can be evaluated applying the kinetic energy operator:

$$T_s[\rho] = \sum_{i=1}^{N_{occ}} \left\langle \chi_i \left| -\frac{1}{2} \nabla^2 \right| \chi_i \right\rangle \quad (1.98)$$

Once it is determined how the kinetic energy is evaluated, we can add the potential terms, that in this context is grouped as an external potential energy and an electron-electron interaction potential. The total energy can be written as:

$$E_v[\rho] = T_s[\rho] + \int \rho(\vec{r}) v_n(\vec{r}) d\vec{r} + V_{ee}[\rho] \quad (1.99)$$

It is important to point out that in the transition from (1.98) to (1.99) we have lost the exact kinetic energy on the way since it is only exact when HF energy is exact. It can be defined an "excess" of kinetic energy due to the inclusion of interelectronic repulsion:

$$T_c[\rho] = T[\rho] - T_s[\rho] \quad (1.100)$$

Which is called correlation kinetic energy. The total energy can be grouped as:

$$E_v[\rho] = T_s[\rho] + \int \rho(\vec{r}) v_n(\vec{r}) d\vec{r} + J[\rho] + T_c[\rho] + (V_{ee}[\rho] - J[\rho]) \quad (1.101)$$

$\int \rho(\vec{r}) v_n(\vec{r}) d\vec{r}$ represents the interaction of the electronic density with the external potential i.e the electron nucleus interaction.

$J[\rho]$ can be extracted from (1.82) :

$$J[\rho] = \frac{1}{2} \iint \frac{\rho(\vec{r}_1)\rho(\vec{r}_2)}{|\vec{r}_1 - \vec{r}_2|} d\vec{r}_1 d\vec{r}_2 \quad (1.102)$$

The term $(V_{ee}[\rho] - J[\rho])$ is normally grouped as

$$W_{xc} = (V_{ee}[\rho] - J[\rho]) \quad (1.103)$$

And represent the exchange-correlation energy of the electronic-part of the system. (1.100) and (1-103) can be grouped as:

$$E_{xc}[\rho] = T_c[\rho] + W_{xc}[\rho] \quad (1.104)$$

E_{xc} can be expressed if we know the external potential that fix it as:

$$E_{xc}[\rho] = \int \rho(\vec{r}) v_{xc}(\vec{r}) d\vec{r} \quad (1.105)$$

Upon all these reorganizations we obtain the following energy equation:

$$E_v[\rho] = T_s[\rho] + \int \rho(\vec{r}) v_n(\vec{r}) d\vec{r} + \frac{1}{2} \iint \frac{\rho(\vec{r}_1)\rho(\vec{r}_2)}{|\vec{r}_1 - \vec{r}_2|} d\vec{r}_1 d\vec{r}_2 + E_{xc}[\rho] \quad (1.106)$$

Now, making use of (1.96):

$$\frac{\delta E_v[\rho]}{\delta \rho(\vec{r})} = \frac{\delta T_s[\rho]}{\delta \rho(\vec{r})} + v_n(\vec{r}) + \int \frac{\rho(\vec{r}_2)}{|\vec{r}_1 - \vec{r}_2|} d\vec{r}_2 + \frac{\delta E_{xc}[\rho]}{\delta \rho(\vec{r})} = \mu \quad (1.107)$$

For the sake of simplicity, let us group similar terms in the equation:

$$v_n(\vec{r}) + \int \frac{\rho(\vec{r}_2)}{|\vec{r}_1 - \vec{r}_2|} d\vec{r}_2 = \phi(\vec{r}) \quad (1.108)$$

named Coulomb potential and:

$$\frac{\delta E_{xc}[\rho]}{\delta \rho(\vec{r})} = v_{xc}(\vec{r}) \quad (1.109)$$

As exchange-correlation potential, (1.107) becomes:

$$\frac{\delta E_v[\rho]}{\delta \rho(\vec{r})} = \frac{\delta T_s[\rho]}{\delta \rho(\vec{r})} + (\phi(\vec{r}) + v_{xc}(\vec{r})) = \mu \quad (1.110)$$

Or:

$$\frac{\delta T_s[\rho]}{\delta \rho(\vec{r})} + v_{eff} = \mu \quad (1.111)$$

In which $v_{eff} = (\phi(\vec{r}) + v_{xc}(\vec{r}))$. Once we have v_{eff} defined, we can express the Kohn-Sham hamiltonian as:

$$\hat{h}_{KS} = -\frac{1}{2}\nabla^2 + v_{eff}(\vec{r}) \quad (1.112)$$

And, the system energy would be obtained applying the pseudo Schrodinger equation:

$$\hat{h}_{KS}\chi_i = \varepsilon_i\chi_i \quad (1.113)$$

The orbitals are chosen orthonormal and in a way that reconstruct $\rho(\vec{r})$ as seen in (1.97)

Just as in Hartree-Fock, an initial guess of orbitals is needed to reconstruct the electron density and to calculate the kinetic energy. With this density, the terms corresponding to $v_{eff}(\vec{r})$ are known and can be evaluated to know the energy of the system and the associated eigenfunctions. This step must be done N times up to convergence.

So, we have determined how to obtain the exact energy of a system, but since $v_{xc}(\vec{r})$ is not known, the energy will be always an approximation that tend to the exact energy with the quality of the exchange-correlation potential. Next subsection is devoted to the construction of the so-called exchange-correlation functionals for the evaluation of that term.

Some comments on the KS and HF approaches to the problem. Whereas the usage of a single Slater determinant in Hartree-Fock is always an approximate method, in KS it is not since we can reconstruct the exact density with a single determinant. In KS the problem lies in the definition of the hamiltonian, not in the trial wavefunction. Another difference lies in the physical interpretation of the molecular orbitals obtained by both methods. HF occupied orbitals do have a physical meaning as monoelectronic delocalized wavefunctions of a molecule. In DFT only the density has a meaning and the orbitals are a fictitious construction used for the evaluation of the energy so they do not have any physical meaning. By extension, neither Ψ_{KS} nor its square have any physical meaning and it is not suitable for the evaluation of observables, with some exceptions.

Finally it is important to remark that just as HF theory KS method is solved making use of the LCAO approximation and the orbitals are expanded in terms of a certain basis set.

v) SOME APPROXIMATIONS TO THE EXCHANGE-CORRELATION FUNCTIONAL

The next subsections are devoted to the definition of the exchange-correlation functionals (up to hybrid functionals).

Equations (1.105) and (1.109) provides the relationship between the exchange correlation potential and the exchange correlation energy.

Defining ε_{xc} as the exchange-correlation energy per particle, other useful variable that we can define is:

$$e_{xc}[\rho] = \rho(\vec{r}) \varepsilon_{xc} \quad (1.114)$$

Which represents the exchange correlation energy per unit volume.

Local Density Approximation and local spin density approximation (and functionals).

This approximation relies in considering that ε_{xc} only depends on the density itself and not in related variables to it. In this way exchange and correlation part can be treated separately :

$$\varepsilon_{xc}^{LDA}[\rho] = \varepsilon_x^{LDA}[\rho] + \varepsilon_c^{LDA}[\rho] \quad (1.115)$$

For the exchange part, a conceptual model such as the uniform electron gas (or jellium) is taken into consideration. In this model positive charges are distributed in an uniform way in the space and therefore the electron density is uniformly distributed as well. Slater [28] provides an expression for this contribution, per particle ($\alpha = 2/3$):

$$\varepsilon_x^{LDA}[\rho] = -\frac{9}{4} \alpha \left(\frac{3}{8\pi} \right)^{1/3} \rho^{1/3} \quad (1.116)$$

Total exchange energy is calculated upon integration:

$$E_x^{LDA}[\rho] = -\frac{9}{4} \alpha \left(\frac{3}{8\pi} \right)^{1/3} \int \rho^{4/3} d\vec{r} \quad (1.117)$$

Correlation part has no a fix recipe and the most used is the one developed by Vosco, Wilk and Nusair [30].

Just as in HF, open shell systems are not as simple as closed shell systems and even in densities that are uniformly distributed α and β densities do not coincide, so just as in UHF both densities have to be minimized separately. Kohn-Sahm kinetic energy and external potential interaction can be calculated separately and independently for each one of both densities. However, J and E_c have terms that are not independent of one of both densities and the expression to calculate them are:

$$J^\alpha [\rho^\alpha, \rho^\beta] = \frac{1}{2} \iint \frac{\rho^\alpha(\vec{r}_1) \rho^\alpha(\vec{r}_2)}{|\vec{r}_1 - \vec{r}_2|} + \frac{1}{2} \iint \frac{\rho^\alpha(\vec{r}_1) \rho^\beta(\vec{r}_2)}{|\vec{r}_1 - \vec{r}_2|} \quad (1.118)$$

$$J^\beta [\rho^\alpha, \rho^\beta] = \frac{1}{2} \iint \frac{\rho^\beta(\vec{r}_1) \rho^\beta(\vec{r}_2)}{|\vec{r}_1 - \vec{r}_2|} + \frac{1}{2} \iint \frac{\rho^\beta(\vec{r}_1) \rho^\alpha(\vec{r}_2)}{|\vec{r}_1 - \vec{r}_2|} \quad (1.119)$$

$$E_C^{LSDA,\alpha} [\rho^\alpha, \rho^\beta] = \int \rho^\alpha(\vec{r}) \varepsilon_C [\rho^\alpha, \rho^\beta] dr \quad (1.120)$$

$$E_C^{LSDA,\beta} [\rho^\alpha, \rho^\beta] = \int \rho^\beta(\vec{r}) \varepsilon_C [\rho^\alpha, \rho^\beta] dr \quad (1.121)$$

It is important to remark that the spin polarization in DFT is a consequence of the usage of approximate functionals (Kohn-Sham method) and it is only a tool for the resolution of open shell systems. Once known the exact functional, the exact density can be derived and thus no spin treatments are needed

Generalized Gradient Approximations: GGA Functionals and Meta-GGA ones

Considering the conceptual simplicity of the LDA (or LSDA) one can imagine that is not a suitable model for complex systems. This is only partially true since it performs quite well for predicting geometries or calculating vibrational frequencies, nevertheless this approximation fails when the system under consideration has a weakly bounded profile. There exist other problems related to the inhomogeneous nature of the regions near the nuclei and therefore is imperative to refine the model.

Whereas the LDA considers that the exchange-correlation effects depend only on the electron density at the considered point, the GGA approach includes also information and contributions related to the gradient of the electron density, this is the rate of change of the electron density with a change of coordinates. This breaks the concept of locality introducing information on different places of the system but this approach only can be considered as semi-local since the exchange-correlation energy per volume only depends on the electron density at each point and of its derivative at this point.

Defining a certain function that acts as a exchange correlation energy per unit volume $f(\rho, \nabla\rho)$.

The exchange correlation energy is calculated, as always upon integration:

$$E_{XC}^{GGA}(\rho) = \int f(\rho, \nabla\rho) d\vec{r} \quad (1.122)$$

In this type of functionals the separation of exchange and correlation energies is still valid and:

$$E_{XC}^{GGA} = E_C^{GGA} + E_X^{GGA} \quad (1.123)$$

The philosophy behind the construction of this type of functionals is to take a LDA functional and, after the inclusion of gradient corrections make it has a correct asymptotic behaviour (a correct description of the points near cusps or holes in the electronic density) and correct scaling properties.

Lots of attempts have been done for this idea, but in the present work two of them need to be mentioned since will constitute the basis for the theoretical basis of the preliminary isomer search. These two functionals, one for the exchange part and the other for the correlation part are named B88 [30] and LYP [31] respectively.

B88 functional was proposed by Axel Becke, and works around the idea of the inclusion of a correction term to the LDA approximation instead of the calculation of a whole new term. In this way, he considered that exchange energy was a sum of local contributions and non local ones.

$$E_X^{GGA} = E_X^{LDA}(\rho) + E_X^{NLDA}(\rho) \quad (1.124)$$

The non local spin density proposed by Becke:

$$E_X^{NLDA}(\rho) = \int \rho^{\frac{4}{3}}(r) f^{NLDA}(x) d\vec{r} \quad (1.125)$$

With:

$$x = -\frac{|\nabla\rho|}{\rho^{\frac{4}{3}}} \quad (1.126)$$

The function that appears in (1.125) can be either one of these three functions:

$$f^{NLDA}(x) = -\frac{x}{6 \ln x} \quad f^{NLDA}(x) = -\frac{\beta x^2}{1 + 6\beta x \ln x} \quad f^{NLDA}(x) = -\frac{\beta x^2}{1 + 6\beta x \sinh^{-1} x} \quad (1.126)$$

Although each one of these three functions is suitable for our purposes, Becke also found that the latter with a parameter $\beta = 0.0042$ is the best one.

LYP correlation functional (that states for Lee Yang Parr functional) has a complex expression and it is directly presented below:

$$f^{LYP} = a \int \frac{\rho}{1 + d\rho^{1/3}} dr - ab \int \omega \rho^2 \left[C_F \rho^{8/3} + |\nabla|^2 \left(\frac{5}{12} - \delta \frac{7}{72} \right) \right] - \frac{11}{24} \rho^2 |\nabla\rho|^2 dr \quad (1.127)$$

In which a,b,c,d, are parameters to be fitted.

The combination of Becke and Lee-Yang-Parr functionals gives rise to the BLYP functional, a widely used GGA functional that gives great frequency and geometries predictions. However, this kind of functionals do not reproduce well dispersion forces and are not as reliable as other that will be presented later.

It is advisable to include a brief note on meta GGA functionals that are functionals that include not only the gradient of the energy but also its laplacian giving rise to a more coherent calculation since the functional does not only contains information of the rate of change of the density but also on how that rate of change varies.

So:

$$E_{XC}^{metaGGA}\rho = \int f(\rho, \nabla\rho, \nabla^2\rho) d\vec{r} \quad (1.128)$$

Hybrid Functionals

Finally we have arrived to the description of the exchange correlation functionals that will be used for the study of our Plutonium tricarbide. This kind of functionals are classified as hybrid functionals because they include a part of the exact exchange from a HF calculation. This addition can be done thanks to the adiabatic-connection formula for the exchange correlation energy.

For the derivation of such formula let us consider a system that contains two electron interaction of Coulombic type λ/r . In this system an external potential $v_s^\lambda(r)$ can be adjusted in a way that for any value of λ , the density $\rho(r)$ corresponding to $\lambda=1$ is obtained.

λ is a modulable parameter that accounts for the "degree of two electron interactions" that is present in a system ($\lambda=0$ corresponds to a system without electron-electron interactions). In this way the parameter can be used to know how far of the real system the model system is. The hamiltonian for the system including this parameter:

$$\hat{H}^\lambda = \sum_{i=1}^N -\frac{1}{2}\nabla^2(i) + \sum_{i=1}^N v_s^\lambda(i) + \sum_{i=1}^N \sum_{j>1}^N \frac{\lambda}{r_{ij}} \quad (1.129)$$

The energy for the system when $\lambda=0$:

$$E(0) = T_s[\rho] + \int \rho(\vec{r}) v_s(\vec{r}) d\vec{r} \quad (1.130)$$

And for $\lambda=1$:

$$E_v[1] = T_s[\rho] + \int \rho(\vec{r}) v_n(\vec{r}) d\vec{r} + \frac{1}{2} \iint \frac{\rho(\vec{r}_1)\rho(\vec{r}_2)}{|\vec{r}_1 - \vec{r}_2|} d\vec{r}_1 d\vec{r}_2 + E_{xc}[\rho] \quad (1.131)$$

We can now isolate the term corresponding to the exchange and correlation part:

$$E_{xc}[\rho] = E(1) - E(0) + \int \rho(\vec{r}) (v_s(\vec{r}) - v_n(\vec{r})) d\vec{r} + \frac{1}{2} \iint \frac{\rho(\vec{r}_1)\rho(\vec{r}_2)}{|\vec{r}_1 - \vec{r}_2|} d\vec{r}_1 d\vec{r}_2 \quad (1.132)$$

Let us apply the Hellmann-Feynman theorem to the energy using λ as a parameter:

$$\frac{dE^\lambda}{d\lambda} = \left\langle \psi^\lambda \left| \frac{dH^\lambda}{d\lambda} \right| \psi^\lambda \right\rangle = \left\langle \psi^\lambda \left| \sum_i^N \frac{dv_s^\lambda}{d\lambda} + \sum_i^N \sum_{j>1}^N \frac{1}{r_{ij}} \right| \psi^\lambda \right\rangle \quad (1.133)$$

Also, we have:

$$\int_0^1 \frac{dE^\lambda}{d\lambda} d\lambda = E(1) - E(0) \quad (1.134)$$

Recalling (1.80) and regrouping the above equations:

$$E(1) - E(0) = \int_0^1 \frac{dE^\lambda}{d\lambda} d\lambda = \int_0^1 \left\langle \psi^\lambda \left| \sum_i^N \frac{dv_s^\lambda}{d\lambda} \right| \psi^\lambda \right\rangle d\lambda + \frac{1}{2} \int \int \int_0^1 \frac{\gamma_2^\lambda(r_1, r_2)}{r_{12}} dr_1 dr_2 d\lambda \quad (1.135)$$

From the definition of the two electron density:

$$\gamma_2(r_1, r_2) = \rho(\vec{r}_1)\rho(\vec{r}_2) + \rho(\vec{r}_1)\rho_{xc}(\vec{r}_1, \vec{r}_2) \quad (1.136)$$

Combining (1.136) and (1.135):

$$E(1) - E(0) = \int \int_0^1 \rho(\vec{r}) \frac{dv_s(\vec{r})}{d\lambda} d\vec{r} d\lambda + \frac{1}{2} \int \int \int_0^1 \frac{\rho(\vec{r}_1)\rho(\vec{r}_2)}{r_{12}} dr_1 dr_2 d\lambda + \frac{1}{2} \int \int \int_0^1 \frac{\rho(\vec{r}_1)\rho_{xc}(\vec{r}_1, \vec{r}_2)}{r_{12}} dr_1 dr_2 d\lambda \quad (1.137)$$

The integration with respect the λ parameter the variables that do not depend on it:

$$E(1) - E(0) = \int \int_0^1 \rho(\vec{r}) (v_s(\vec{r}) - v_n(\vec{r})) d\vec{r} + \frac{1}{2} \int \int \frac{\rho(\vec{r}_1)\rho(\vec{r}_2)}{r_{12}} dr_1 dr_2 + \frac{1}{2} \int \int \int_0^1 \frac{\rho(\vec{r}_1)\rho_{xc}(\vec{r}_1, \vec{r}_2)}{r_{12}} dr_1 dr_2 d\lambda \quad (1.138)$$

Comparing (1.138) and (1.132) we can obtain the exchange-correlation energy as a function of the parameter:

$$E_{xc}[\rho] = \frac{1}{2} \int \int \int_0^1 \frac{\rho(\vec{r}_1)\rho_{xc}(\vec{r}_1, \vec{r}_2)}{r_{12}} dr_1 dr_2 d\lambda = \frac{1}{2} \int \int_0^1 \rho(\vec{r}) v_{xc}^\lambda(\vec{r}) d\vec{r} d\lambda \quad (1.139)$$

Which can be written as:

$$E_{xc}[\rho] = \int_0^1 W_{xc}^\lambda[\rho] d\lambda \quad (1.140)$$

The above expression reads for the so called adiabatic connection formula for the exchange correlation energy. $W_{xc}^\lambda[\rho]$ is the exchange-correlation energy of the electronic part for a system with pair electron interactions. The total exchange correlation can be obtained upon integration over the λ parameter. Since the exchange-correlation energy makes sense from a wide range of λ parameter from 0 to 1, it has a

physical meaning when $\lambda = 0$ and therefore it can be extracted a certain energy from it, justifying the existence of hybrid methods for the calculation of W_{XC}^0 .

Once shown the possibility of using hybrid methods it is time to construct some functionals. The most primitive one, developed by Becke, is the so called Half&Half method, in which, considering a linear dependence between W_{XC}^λ and λ the expression for the exchange-correlation energy reads:

$$E_{XC}[\rho] = \frac{1}{2}W_{XC}^{\lambda=1}[\rho] + \frac{1}{2}W_{XC}^{\lambda=0} \quad (1.141)$$

In which $W_{XC}^{\lambda=0}$ corresponds to the exact Hartree-Fock exchange energy and $W_{XC}^{\lambda=1}$ to the exchange correlation energy derived from a GGA functional, as explained before.

Even it exists a large amount of hybrid functionals described in the literature, the one used in the DFT section of this work, used for the exploration of the potential energy surface of the isomers is the widely known Becke-3-Lee-Yang-Parr functional (B3LYP) [32]. In this functional, the exchange correlation part is fitted to three parameters that read:

$$E_{XC}^{B3LYP} = E_{XC}^{LSDA} + a(E_X^{HF} - E_X^{LSDA}) + b(E_X^{B88} - E_C^{LSDA}) + c(E_C^{LYP} - E_C^{LSDA}) \quad (1.142)$$

The fitted parameters are optimized to the values $a=0.20$, $b=0.72$ and $c=0.81$. This kind of hybrid functionals performs quite good in predicting geometrical structures, vibrational frequencies and gives in general trustable thermochemical data. Even the B3LYP functional is the only one that will be used in this work, it is convenient to name some of the most important ones such as PBE0, MPW1K or B3PW91.

Exchange correlation functionals can be even more refined, with the inclusion of hybrid-meta GGA functionals, in which meta-GGA functionals are used in the hybrid functional. Notable examples of these kind of functionals are the ones from the Minnesota group M05, M06-2X, M06-L and so on.

As a final note it is important that the new generation of functionals also include part of the correlation energy from a wavefunction method in its expression. This kind of functionals are named double-hybrid functionals (in a way that both exchange and correlation energies are DFT, WFT hybrids). Some examples are B2PLYP, MPW2PLYP, D-BLYP etc

g) WAVEFUNCTION THEORY CORRELATED METHODS.

It is common to hear in the context of the Hartree-Fock theory in quantum chemistry that it gives solutions of around 99% of the total electronic energy. However the remaining 1% can be really important in a chemical context since it involves energies which are typical of bond formation/break. The energy which is the difference between the total energy and the Hartree-Fock limit is called correlation energy and is associated to the correlated movement of the electrons, this is, to the energy that arises from motions that at some extent are determined from the position of other particles, in this case electrons. Correlation between electrons has to be considered within a spin context, and, in this way we can find Coulomb correlation, or correlation between opposite spin electrons, and Fermi correlation if it implies electrons of the same spin. Now, if we look at the electron density we can find places where the probability of finding an electron is very low, not surprisingly these holes in the electron density function are called Coulomb and Fermi holes.

Next sections are devoted to present methods that are adequate to calculate electron correlation energy.

i) FIRST ATTEMPTS: CONFIGURATION INTERACTION AND PERTURBATION THEORY.

In this section two general strategies for the calculation of the correlation energy are presented. Both of them represent two different ways of tackling the problem: the variational and the perturbative one.

The philosophy behind the Configuration interaction (CI) method is that the exact wavefunction of the system can be obtained as an expansion in the basis of the determinants representing a single configuration. In this way, as was mentioned before a HF calculation is needed to "initialize" a CI calculation. The general CI wavefunction can be expressed as:

$$\Phi = \sum_i c_i \psi_i = c_0 \psi_{HF} + c_S \psi_a^r + c_D \psi_{ab}^{rs} + c_T \psi_{abc}^{rst} + \dots \quad (1.143)$$

Where the first term of the expansion represents the HF wavefunction and the other ones correspond to all the possible "excitations" of one electron to a virtual orbital, two electrons to two orbitals etc. Just as in HF the minimization has to be done with some constraints, in this case the normalization of the total CI wavefunction. The Lagrange multiplier in this case:

$$L = \langle \Phi | H | \Phi \rangle - \lambda [\langle \Phi | \Phi \rangle - 1] \quad (1.144)$$

The evaluation of both terms of the Lagrange function:

$$\langle \Phi | H | \Phi \rangle = \sum_{i=0} \sum_{j=0} c_i c_j \langle \psi_i | H | \psi_j \rangle = \sum_{i=0} c_i^2 E_i + \sum_{i=0} \sum_{j \neq 0} c_i c_j \langle \psi_i | H | \psi_j \rangle \quad (1.145)$$

$$\langle \Phi | \Phi \rangle = \sum_{i=0} \sum_{j=0} c_i c_j \langle \psi_i | \psi_j \rangle = \sum_{i=0} c_i^2 \langle \psi_i | \psi_i \rangle = \sum_{i=0} c_i^2 \quad (1.156)$$

If Slater determinants are chosen orthonormal.

For the evaluation of the coefficients we must minimize the Lagrange function:

$$\frac{\partial L}{\partial c_i} = 2 \sum_j c_j \langle \psi_i | H | \psi_j \rangle - 2\lambda c_i = 0$$

$$c_i (\langle \psi_i | H | \psi_i \rangle - \lambda) + \sum_{j \neq i} c_j \langle \psi_i | H | \psi_j \rangle = 0$$

$$c_i (E_i - \lambda) + \sum_{j \neq i} c_j \langle \psi_i | H | \psi_j \rangle = 0 \quad (1.157)$$

The problem then can be expressed in matrix form and reduced to the solution of a certain secular equation:

$$\begin{pmatrix} H_{00} - E & H_{01} & H_{02} & \dots \\ H_{10} & H_{11} - E & H_{12} & \dots \\ H_{20} & H_{21} & H_{22} - E & \dots \\ \dots & \dots & \dots & \dots \end{pmatrix} \begin{pmatrix} c_0 \\ c_1 \\ c_2 \\ \dots \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ 0 \\ \dots \end{pmatrix} \quad (1.158)$$

Diagonalization of this matrix will give the eigenvalues, in which the correlation energy is the lowest one as stated by the variational principle, and eigenvectors with the corresponding weights of the expansion.

As can be seen the CI has a quite simple formulation, which can be simpler if we attend to the Brillouin[33] theorem that states that the matrix elements resulting from the interaction of the HF reference and a single excited state is zero and the Slater-Condon rules that say that any excitation between two determinants in which both determinants differ between them in more than two electrons have a null contribution.

Considering this, the resulting matrix of a CI expansion is block diagonal and therefore easy to diagonalize.

The main problem associated to the CI method is that for a system with N electrons evaluated with M basis functions each, the scaling of the method is estimated as [34]. $O(n^{m+2})$ which is quite unaffordable for the vast majority of chemical systems. This is why "full CI" as the complete CI expansion is named is not commonly used, and instead contractions of this full CI such as CISD (only including single and double excitations) are used.

CISD method refines the energy to some extent and therefore some properties but the improvement does not worth the extra time needed in a great number of cases because the method has a big disadvantage, the size-consistency, this is, the method does not

give the same results for one system composed of N non interacting particles with respect to N isolated systems each one with one particle, and this is why truncated CI methods reduce its accuracy when the size of the system tends to be higher. Full CI however is size consistent as the error arises from coupled excitations between the non interacting systems that are not considered in the truncated scheme. It serves as a theoretical basis for other correlated methods.

Perturbation theory presents a different approach to the calculation of the correlation energy. The main philosophy behind this approach relies in the fact that the correlated system only differs slightly from the non-correlated one, and therefore the solution for both systems should be enough close to define a reference Hamiltonian for the non-correlated system, H_0 , and a perturbation Hamiltonian H' that accounts for the differences between them.

The total Hamiltonian is therefore:

$$H = H_0 + \lambda H' \quad (1.159)$$

λ is a parameter that determines the strength of the perturbation and takes values from 0 to 1.

Non-perturbed Schrodinger equation reads:

$$H_0 |\Phi\rangle = E_i |\Phi_i\rangle \quad (1.160)$$

For a time-independent and a non-degenerate reference state, we can write:

$$H |\Psi\rangle = W |\Psi\rangle \quad (1.161)$$

When $\lambda = 0$, $H = H_0$, $\Psi = \Phi_0$ and $W = E_0$. The variation of both the energy and wavefunction with the λ parameter can be written as a Taylor expansion:

$$W = \lambda^0 W_0 + \lambda^1 W_1 + \lambda^2 W_2 + \dots \quad (1.162)$$

$$\Psi = \lambda^0 \Psi_0 + \lambda^1 \Psi_1 + \lambda^2 \Psi_2 + \dots \quad (1.163)$$

It is convenient to choose the perturbed wavefunction to be intermediately normalized, this is it is orthonormal with respect the reference wavefunction. All the correction terms, therefore are orthogonal to the reference wavefunction. Now, let us develop the Schrodinger equation making use of the perturbed hamiltonian:

$$(H_0 + \lambda H') (\lambda^0 \Psi_0 + \lambda^1 \Psi_1 + \dots) = (\lambda^0 W_0 + \lambda^1 W_1 + \dots) (\lambda^0 \Psi_0 + \lambda^1 \Psi_1 + \dots) \quad (1.164)$$

Terms from the same power of λ can be collected giving:

$$\begin{aligned}
\lambda^0 : H_0 \Psi_0 &= W_0 \Psi_0 \\
\lambda^1 : H_0 \Psi_1 + H' \Psi_0 &= W_0 \Psi_1 + W_1 \Psi_0 \quad (1.165) \\
\lambda^2 : H_0 \Psi_2 + H' \Psi_1 &= W_0 \Psi_2 + W_1 \Psi_1 + W_2 \Psi_0
\end{aligned}$$

The power of the lambda parameter is usually called order in this context. And, in general:

$$\lambda^n : H_0 \Psi_n + H' \Psi_{n-1} = \sum_{i=0}^{n-1} W_i \Psi_{n-i} \quad (1.166)$$

For the resolution of the equations we will make use of the Rayleigh-Schrodinger formulation of the perturbation theory, that states that, since the resolution of the zero-order gives us a complete set of eigenfunctions, these eigenfunctions can serve as a basis for a n-th order correction wavefunction. Mathematically:

$$\Psi_i = \sum_i c_i \Phi_i \quad (1.167)$$

The equation for the first order correction becomes:

$$(H_0 - W_0) \left(\sum_i c_i \Phi_i \right) + (H' - W_1) \Phi_0 = 0 \quad (1.168)$$

Projection of $\langle \Phi_0 |$ into (1.168) and integration yields:

$$\begin{aligned}
\sum_i c_i \langle \Phi_0 | H_0 | \Phi_i \rangle - W_0 \sum_i c_i \langle \Phi_0 | \Phi_i \rangle + \langle \Phi_0 | H' | \Phi_0 \rangle - W_1 \langle \Phi_0 | \Phi_0 \rangle &= 0 \\
\sum_i c_i E_i \langle \Phi_0 | \Phi_i \rangle - c_0 E_0 + \langle \Phi_0 | H' | \Phi_0 \rangle - W_1 &= 0 \\
c_0 E_0 - c_0 E_0 + \langle \Phi_0 | H' | \Phi_0 \rangle - W_1 &= 0 \\
W_1 = \langle \Phi_0 | H' | \Phi_0 \rangle &
\end{aligned} \quad (1.169)$$

The first order correction to the wavefunction is obtained projecting an arbitrary function different from Φ_0 and integrating:

$$\begin{aligned}
\sum_i c_i \langle \Phi_j | H_0 | \Phi_i \rangle - W_0 \sum_i c_i \langle \Phi_j | \Phi_i \rangle + \langle \Phi_j | H' | \Phi_0 \rangle - W_1 \langle \Phi_j | \Phi_0 \rangle &= 0 \\
\sum_i c_i E_i \langle \Phi_j | \Phi_i \rangle - c_j E_0 + \langle \Phi_j | H' | \Phi_0 \rangle &= 0 \\
c_j E_j - c_j E_0 + \langle \Phi_j | H' | \Phi_0 \rangle &= 0 \\
c_j = \frac{\langle \Phi_j | H' | \Phi_0 \rangle}{E_0 - E_j} &
\end{aligned} \quad (1.170)$$

A similar treatment for the equation for λ^2 yields the mostly used equations of second order perturbation theory:

$$W_2 = \sum_{i \neq 0} \frac{|\langle \Phi_0 | H' | \Phi_i \rangle|^2}{E_0 - E_i} \quad (1.171)$$

$$c_j = \sum_{i \neq 0} \frac{\langle \Phi_j | H' | \Phi_i \rangle \langle \Phi_i | H' | \Phi_0 \rangle}{(E_0 - E_j)(E_0 - E_i)} - \frac{\langle \Phi_j | H' | \Phi_0 \rangle \langle \Phi_0 | H' | \Phi_0 \rangle}{(E_0 - E_j)^2} \quad (1.172)$$

Higher order formulas can be developed in the same way but they are progressively increasing its complexity. Finally, the final total energy and wavefunction is obtained as a sum over all the terms included in the corrections, as stated in (1.162) and (1.163)

Until now all the perturbation theory is developed for a general system with whichever hamiltonians are used. A procedure to define the hamiltonian for molecular system is the next step needed in the methodology. One of the choices, which is mostly the one used in all the computational applications is the Moller-Plesset [35] perturbation theory in which the unperturbed Hamiltonian is taken as a sum over Fock operators. In this way the unperturbed Hamiltonian counts twice the average SCF electron-electron interaction energy and the perturbed hamiltonian is taken as the exact interelectron energy minus two averaged electron-electron repulsion.

$$H = \sum_{i=1}^N F_i = \sum_{i=1}^N \left(h_i + \sum_{j=1}^N (J_{ij} - K_{ij}) \right) = \sum_{i=1}^N h_i + 2 \langle V_{ee} \rangle \quad (1.173)$$

$$H = \sum_{i=1}^N h_i + \sum_{i=1}^N \sum_{j=1}^N \langle g_{ij} \rangle$$

$$H' = V_{ee} - \sum_{i=1}^N \sum_{j=1}^N (J_{ij} - K_{ij}) = V_{ee} - 2 \langle V_{ee} \rangle \quad (1.174)$$

$$H' = \sum_{i=1}^N \sum_{j=1}^N g_{ij} - \sum_{i=1}^N \sum_{j=1}^N \langle g_{ij} \rangle$$

The zero order wavefunction is taken as the HF determinat and the zero order energy is the sum of the MO energies. Developing the equations of the Rayleigh-Schrodinger formulation into this context we obtain that the first order energy correction equals to:

$$W_1 = -\langle V_{ee} \rangle \quad (1.175)$$

Which is the exact term that recovers the Hartree-Fock energy. This is the same as to say that MP1 energy is the HF energy.

Just as the same that with CI theory, given that the basis is not complete the perturbation functions, chosen as excited Slater determinants is not infinite as needed and the procedure must be truncated.

By virtue of Brillouin's theorem and the orthogonality of the orbitals chosen during the calculation, the second order correction only depend on the interactions between the doubly excited determinants and the unperturbed one. The perturbation energy is given by:

$$W_2 = \sum_{i < j} \sum_{a < b} \frac{|\langle \Phi_0 | H | \Phi_{ij}^{ab} \rangle|^2}{E_0 - E_{ij}^{ab}} \quad (1.176)$$

And the MP2 energy in terms of the basis functions and basis functions energies then:

$$E(MP2) = \sum_{i < j} \sum_{a < b} \frac{[\langle \phi_i \phi_j | \phi_a \phi_b \rangle - \langle \phi_i \phi_j | \phi_b \phi_a \rangle]^2}{\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b} \quad (1.177)$$

In this way we are able to recover 80-90% of the correlation energy with a reasonable accuracy/time ratio. More improvements such as MP3 or MP4 can be formulated, but most of the times is not worth the effort for the same reason that with CI, Slater-Condon rules applies for the interaction between determinants and to recover all the small contributions between different excited determinants need a very big expansion of the Taylor series only in order to recover a small part of what we have recovered with MP2 at the prize of a very high computational time. MP2 method usually provides very good geometries and frequencies and furthermore is a size consistent method. However its main limitation is the fact that the procedure is not variational which means that neither an expansion of the basis set used nor an increase of the order of the method should necessarily improve the energy since we are not covered by the variational theorem anymore. The energies are not always an upper bound of the energy. This can be summarized saying that continuous improve of the quality of the calculation not always conduce to a convergent behavior of the energy. Another main limitation arises from the problem of the MP theory to handle multiconfigurational systems even at infinite order.

ii) COUPLED CLUSTER METHODS

Whereas perturbation theory and configuration interaction give good correlation energies, they have some limitations and these limitations are inherent to the methods, for example the size consistency in CI and the order truncation in Moller-Plesset perturbation theory.

For improving the results of this kind of calculations Coupled Cluster [36] theory is used. In this type of calculations all types of corrections (singles, doubles, triples etc) are included in the treatment to an infinite order. The CC wavefunction, comparing it with both MP and CI wavefunctions, is not composed by a linear expansion but by a exponential one. The CC wavefunction:

$$\Psi_{CC} = e^T \Phi_0 \quad (1.178)$$

The cluster operator T is given by:

$$T = T_1 + T_2 + T_3 + \dots + T_N \quad (1.179)$$

The T operators acting on a reference wavefunction:

$$\begin{aligned} T_1 \Phi_0 &= \sum_i^{\text{occ}} \sum_a^{\text{vir}} t_i^a \Phi_i^a \\ T_2 \Phi_0 &= \sum_{i < j}^{\text{occ}} \sum_{a < b}^{\text{vir}} t_{ij}^{ab} \Phi_{ij}^{ab} \end{aligned} \quad (1.180)$$

In where the lower case t defines the amplitude of the expansion which is a coefficient similar to c_i in other theories.

If we expand in a Taylor series the exponential of the cluster operator:

$$e^T = 1 + T + \frac{1}{2}T^2 + \frac{1}{6}T^3 + \dots = \sum_{k=0}^{\infty} \frac{1}{k!} T^k \quad (1.181)$$

And develop the cluster operator expression:

$$e^T = 1 + T_1 + \left(T_2 + \frac{1}{2}T_1^2 \right) + \left(T_3 + T_2T_1 + \frac{1}{6}T_1^3 \right) + \left(T_4 + T_3T_1 + \frac{1}{2}T_2^2 + \frac{1}{2}T_2T_1^2 + \frac{1}{24}T_1^4 \right) \quad (1.182)$$

In this development we can find a very interesting point and the key for the Coupled Cluster improvement with respect to other theories. This is that even though a T_N operator can generate the N-th excited Slater determinant, a product of N single operators also generate a N-th excited Slater determinant. The "direct" operators are named connected ones whereas the product of operators are named disconnected ones. In this way for example for a triple excited Slater determinant can be either be obtained directly applying T_3 or by products of single and double operators T_1T_2, T_1^3 . Just to remark, physically the difference between a connected transition and a disconnected one can be seen as the excitation of either the electrons simultaneously or the electrons being promoted alone, by pairs, trios etc.

The energy is evaluated as always with the TISE:

$$He^T \Phi_0 = Ee^T \Phi_0 \quad (1.183)$$

Projecting $\langle \Phi_0 |$ into (1.183):

$$\langle \Phi_0 | He^T | \Phi_0 \rangle = E_{cc} \langle \Phi_0 | e^T | \Phi_0 \rangle \quad (1.184)$$

$$\langle \Phi_0 | He^T | \Phi_0 \rangle = E_{cc} \langle \Phi_0 | (1 + T_1 + T_2 + \dots) | \Phi_0 \rangle \quad (1.185)$$

And considering that the wavefunction is intermediate normalized:

$$\langle \Psi_{cc} | \Phi_0 \rangle = 1 \quad (1.186)$$

We have that:

$$E_{cc} = \langle \Phi_0 | H e^T | \Phi_0 \rangle \quad (1.187)$$

Since the hamiltonian operator contains only one and two electron operators:

$$E_{cc} = \left\langle \Phi_0 | H | (1 + T_1 + T_2 + \frac{1}{2} T_1^2) \Phi_0 \right\rangle \quad (1.188)$$

$$E_{cc} = \langle \Phi_0 | H | \Phi_0 \rangle + \langle \Phi_0 | H | T_1 \Phi_0 \rangle + \langle \Phi_0 | H | T_2 \Phi_0 \rangle + \frac{1}{2} \langle \Phi_0 | H | T_1^2 \Phi_0 \rangle \quad (1.189)$$

$$E_{cc} = E_0 + \sum_i \sum_a^{occ} t_i^a \langle \Phi_0 | H | \Phi_i^a \rangle + \sum_{i < j} \sum_{a < b}^{virt} (t_{ij}^{ab} + t_i^a t_j^b - t_i^b t_j^a) \langle \Phi_0 | H | \Phi_{ij}^{ab} \rangle \quad (1.190)$$

And, considering Brillouin's theorem:

$$E_{cc} = E_0 + \sum_{i < j} \sum_{a < b}^{occ} (t_{ij}^{ab} + t_i^a t_j^b - t_i^b t_j^a) \langle \Phi_0 | H | \Phi_{ij}^{ab} \rangle \quad (1.191)$$

And, considering the integrals over MO orbitals just as we did in HF:

$$E_{cc} = E_0 + \sum_{i < j} \sum_{a < b}^{occ} (t_{ij}^{ab} + t_i^a t_j^b - t_i^b t_j^a) (\langle \phi_i \phi_j | \phi_a \phi_b \rangle - \langle \phi_i \phi_j | \phi_b \phi_a \rangle) \quad (1.192)$$

The Coupled Cluster energy is completely defined by the singles and double amplitudes and the two-electron MO integrals. For obtaining the amplitudes we have to project an arbitrary single excited determinant $\langle \Phi_m^l |$ and integrate:

$$\langle \Phi_m^l | H e^T | \Phi_0 \rangle = E_{cc} \langle \Phi_m^l | e^T | \Phi_0 \rangle \quad (1.193)$$

$$\langle \Phi_m^l | H | (1 + T_1 + T_2 + \dots) \Phi_0 \rangle = E_{cc} \langle \Phi_m^l | (1 + T_1 + T_2 + \dots) \Phi_0 \rangle \quad (1.194)$$

Using the Slater-Condon rules for the evaluation of the integrals of both sides give us the result that on the left-hand side, determinants up to triple excited ones has a positive contribution and, on the right hand side only the single excited projected determinant remains giving us the equation for the evaluation of its amplitude:

$$\langle \Phi_m^l | H | (1 + T_1 + T_2 + T_3) \Phi_0 \rangle = E_{cc} t_m^l \quad (1.195)$$

As can be seen, in a single calculation every amplitude must be considered individually, as well the equations for the equation. In contrast, CI method obtains the

coefficients in a single step diagonalizing the CI matrix. Double excitations amplitudes are obtained projecting by a double excited determinant and so on.

Until now everything is exact (just as full CI for CI), but unaffordable. In order to reduce the cost of the calculation the cluster operator expansion can be truncated at some excitation level. The most used is the CCSD (coupled cluster single and double excited) level of truncation. In which the exponential operator is defined as expanded as:

$$e^T = e^{T_1+T_2} = 1 + T_1 + \left(T_2 + \frac{1}{2}T_1^2\right) + \left(T_2T_1 + \frac{1}{6}T_1^3\right) + \left(\frac{1}{2}T_2^2 + \frac{1}{2}T_2T_1^2 + \frac{1}{24}T_1^4\right) + \dots \quad (1.196)$$

The equation for the energy is (1.188) because we said that the energy of CC expansion only depends on single and double excitations, and the single and double amplitudes are given by:

$$\left\langle \Phi_m^l | H \left| \left(T_1 + T_2 + \frac{1}{2}(T_1^2 + 2T_1T_2) + \frac{1}{6}T_1^3 \right) \Phi_0 \right. \right\rangle = E_{cc} t_m^l \quad (1.197)$$

$$\left\langle \Phi_{mm}^{lk} | H \left| \left(T_1 + T_2 + \frac{1}{2}(T_1^2 + T_2^2 + 2T_1T_2) + \frac{1}{6}(T_1^3 + 3T_1^2T_2) + \frac{1}{24}T_1^4 \right) \Phi_0 \right. \right\rangle = E_{cc} t_m^{lk} \quad (1.198)$$

That the energy expression does not change do not imply that the energy is the same since the expression for the energy depends on the amplitudes that will be more refined with more terms of the expansion and improve when we increase the expansion.

One of the better points of the CC method is that it is size consistent as a result of the presence of disconnected terms in both sides of the equations to solve, furthermore the accuracy achieved with this kind of methods in applications such as geometries, vibrational analysis etc, makes this method a gold standard in the vast majority of the cases. The increase in the number of terms of the truncation can lead to CCSDT for example, but this method is already unaffordable except for model small systems. A slight improvement of this method can be given by the CCSD(T) method in which triple excitations are treated in a perturbative way.

The two main problems of these methods (CCSD and CCSD(T)) are that is very computationally expensive and calculation time can be too long if the size of the system or the basis is not taken into account, and that the method is not variational. The amplitudes are not minimized but calculated in system of equations and therefore we cannot grant that our energy is an upper bound of the correct energy not guaranteeing an improvement of the energy or other properties by changing other parameters such as the size of the basis (even though in most cases DO improve)

CCSD and CCSD(T) calculations are the ones that are used in the present job to characterize all the plutonium carbide isomers and only some considerations in the most contributive isomers energy must be done apart from the CC energy.

h) STATIC CORRELATION. MULTICONFIGURATIONAL SELF CONSISTENT FIELD

It has been briefly mentioned that the methods that have been discussed above are valid for systems in which the HF wavefunction has the largest contribution to the total wavefunction and it contains most of the information of the system.

$$\Phi = \sum_i c_i \psi_i = c_0 \psi_{HF} + c_S \psi_a^r + c_D \psi_{ab}^{rs} + c_T \psi_{abc}^{rst} + \dots$$

$$c_0 > \sum_{i>0} c_i \quad (1.199)$$

But there are some systems in which this requirement is not fulfilled. In this cases the single HF wavefunction can lead not only to quantitative wrong results but also qualitative ones. This problem is often associated with near degeneracy problems in which the energy of two near states is similar enough to consider that can be some couplings between both of them, resulting in a different description of the energetics of the problem. Far from equilibrium species (bond breaking processes, transition states), excited states and species involving d or f metals are candidates for this effect.

In a monoconfigurational correlated method the excited Slater determinants are not optimized and the occupancies came from a creation-annihilation process of electrons taking as a reference the HF wavefunction. And this description allows us to calculate the so called "dynamic correlation" whose interpretation is mainly related with the effect that the motion of an electron causes in other electron. In this way excited, non-optimized Slater determinants module the original HF wavefunction in a way that includes nodes in it at a certain extent (defined by the optimized coefficients of the expansion): as intuition dictates, defined nodes create an electron forbidden region in the wavefunction and this region "emulates" the interrepulsive behavior of the electrons.

However, when the wavefunction is qualitatively wrong, this improvement is not enough for the correct description of the system and the so called static correlation energy plays an important role. As has been said this correlation describes the system in near degeneracy cases and its physical explanation comes from the superposition of energetic near states. In this cases more than one configuration (and the associated Slater determinant) contains the vast majority of the information of the system.

For determining if our system has a multiconfigurational character many tests have been developed, but commonly the most used is the T1 [37] diagnostic test. The single excited determinants of a single reference wavefunction in a Coupled Cluster framework provides information of the multiconfigurational character of the system. The T1 diagnostic parameter is defined as:

$$T_1 = \frac{|t_1|}{\sqrt{N}} \quad (1.200)$$

In which t_1 represents the amplitude of the single excitations and N the number of electrons of the system. If this number is higher than a certain quantity (0.04 in most cases) the multiconfigurational character of the wavefunction starts to be important enough.

For the study of this kind of systems multiconfigurational self-consistent techniques have been used. These techniques involve the iterative optimization of both coefficients and determinants of the expansion of the CI wavefunction. The main problem associated with this procedure is that in the majority of the cases is very expensive.

Nowadays, the widely used method for the solution of this issue in medium to large size systems is the CASSCF [38] technique (complete active space self-consistent field). In this technique the original HF wavefunction is divided in three subsets of orbitals instead of the original two (occupied and virtual). These subsets are the a) inactive one in which we have doubly occupied orbitals that do not change in any of the configurations selected, it can be also referred as frozen or core orbitals. b) virtual one which includes all the orbitals that are similar in all configurations and are not populated and c) active part, including all the orbitals that are optimized through a variational procedure. The orbitals included in the active space are treated in a similar way that in full CI method, recovering all the static and dynamic correlation associated to that part of the wavefunction. Therefore, the main problem in a CASSCF calculation relies in the definition of the active space which also define the number of electrons that are included in it. In this way, all the CASSCF calculations are defined by a pair of numbers in a parenthesis (n,m) in which n defines the number of electrons of the active space and m the number of orbitals contained in that active space. Once the CASSCF wavefunction is known, the multiconfigurational energy can be obtained and compared with the single reference one. If further precision is needed the energy can be refined including dynamic correlation up to the entire wavefunction. This can be achieved by means of multireference correlated methods in which the multiconfigurational wavefunction is taken as the reference wavefunction for a CI or MP treatment. MRCI (multireference configuration interaction) and CASPT2 [39] (complete active space perturbation theory up to second order) methods are important examples of this kind of methods .

In the present work this kind of multiconfigurational methods will be used for elucidating possible inconsistencies between the two most contributive isomers once the single reference energy order of the plutonium carbide isomers has been done

i) ATOMS IN MOLECULES THEORY.

Until now we have discussed different methods for the evaluation of the energy and energy related properties, but more information can be extracted from the wavefunction of a system, or from its corresponding electron density as Hohenberg Kohn theorem states. Wavefunction analysis theories seek to interpret the information contained in the wavefunction in chemical systems in order to merge pure chemical and quantum mechanical concepts.

There are many methods for this kind of studies but in the present work the one that is used is the Quantum theory of Atoms in Molecules, developed by R.F.W.Bader and coworkers [40]. The main concept behind this theory is to characterize all the points that are relevant at some extent in the structure of a molecule, since commonly chemical models construct a molecule as a arrange of atoms linked by bonds, the theory try to find physical explanation to this intuitive idea. Furthermore, the theory allows the calculation of energetic properties based on the energies of these separated subsystems within the molecule.

The main tool for this work is the electron density once more, and concretely the topology of this electron density, or better said the critical points that define parts of this density. A critical point in a function is a point in the space in which the derivative of the function gets null, and considering that here we are working with the electron density, the points in $\nabla\rho(r)$ function that are zero. As were stated in the definition of a potential energy surface, there exist many types of critical points for a function, and they are characterized by the derivative of the gradient vector at that point, or better said by the second derivative of the density, which is a matrix called Hessian matrix, with a shape:

$$\begin{pmatrix} \frac{\partial^2 f(x)}{\partial x^2} & \frac{\partial^2 f(x)}{\partial x\partial y} & \frac{\partial^2 f(x)}{\partial x\partial z} \\ \frac{\partial^2 f(x)}{\partial y\partial x} & \frac{\partial^2 f(x)}{\partial y^2} & \frac{\partial^2 f(x)}{\partial y\partial z} \\ \frac{\partial^2 f(x)}{\partial z\partial x} & \frac{\partial^2 f(x)}{\partial z\partial y} & \frac{\partial^2 f(x)}{\partial z^2} \end{pmatrix} \quad (1.201)$$

This matrix is symmetric by virtue of the Clairaut theorem. Now, if we plug in the electron density of a system and diagonalize this matrix we obtain a set of three eigenvalues with its corresponding eigenvectors. Depending on the sign of this eigenvalues (commonly notated as $\lambda_1, \lambda_2, \lambda_3$) the critical point will be qualitatively different. A set of three positive values corresponds to a minimum, while a set of three negative ones to a maximum in the function and a saddle point has two negative values and a positive one. The morphology of a PES is obtained in a similar way but in this case the diagonalizable matrix do not have a fixed dimension anymore, the dimension of a hessian matrix used for the study of a potential energy surface depends entirely on

the number of degrees of freedom given to the system (or better said in the number of variables that are considered in a calculation).

In QTAIM, critical points are commonly labeled attending to two numbers. The first one, named rank, indicates the number of non zero eigenvalues in the hessian matrix. For the purposes of study of stationary species, this number is always three since numbers minor than three indicate a changing topology and therefore a different structure for the system. The second number is named signature, and corresponds to the sum of signs of the eigenvalues.

It can be demonstrated that the gradient at each point of the system, following the maximum gradient path constitutes a gradient vectorial field, and that this gradient vector field begin and end is located in the atomic positions. This is why, in the context of this theory, atomic positions are usually named as atomic basins, referring to the fact that the electron density accumulates in the region near to them. QTAIM theory is based in the separability of the molecular system into atomic basins. Since the density around the atomic basins decreases in every direction of the space, the point is characterized by three negative eigenvalues and the critical point is labeled (3,-3) and these critical points are usually named as NCP (nuclear critical point).

Between two NCP there exists a surface where the flux of electron density equals zero, and delimitates the region of the space that physically constitutes an atom in a molecule.

In a stationary, equilibrium geometry for a molecule, the gradient path linking two adjacent atoms define the atomic interaction line. Within this line a certain point have two negative eigenvalues of the hessian matrix, a logical thing considering the presence of two NCP, but also a positive eigenvalue corresponding to the interatomic surface between both atoms. In this way the critical point is labelled (3,-1) and this kind of points define the chemical bond within this theory's framework. This type of critical points are called BCP (bond critical points). The other critical points relevant for the chemistry of the problem that remain to be considered are the RCP (ring critical point) (3,+1) and the CCP (cage critical point) (3,+3).

When the entire electron density is evaluated and all the critical points are obtained, we can draw the arrange of critical points giving rise to the molecular graph, which is the mathematical representation of the shape of the molecule, and not surprisingly usually coincides with the structures obtained from a Lewis model.

Many values of the electron density or the eigenvalues of the hessian matrix in a certain point can be used to generalize commonly used chemical concepts such as the bond order, or the overlapping characteristics of a bond. Just as an example, the π character of a bond can be estimated looking at the ellipticity of that bond, or the measure of the preferential direction of the density near that bonding.

$$\varepsilon = \frac{\lambda_1}{\lambda_2} - 1 \quad (2.202)$$

An ellipticity equal 0 gives us the information that there is not any preferential plane for the electron density, reminding a sigma bond. When it is not, the pi character of a bond can be found checking at what axis the biggest accumulation of electron density is located.

Another useful function apart from the gradient of the density is the laplacian of the density, or better said the scalar given by the sum of the eigenvalues of the hessian matrix.. The Laplacian of the density whose value is normally given as the negative of this function, $L(r)$ gives information of the rate of change of the electron density, in this way, a positive $L(r)$ value corresponds to a concentration of density and a negative one to a density depletion. The qualitative information behind this affirmation is that a local depletion is usually matched with a ionic character in which the bond critical points accumulate, a very small electron density. In this way, a shared interaction will have a high density at the critical point and a positive $L(r)$ function (a negative laplacian).

Apart from all of that, QTAIM theory relies in the separability of the molecular properties or observables can be calculated of the sum over the observables calculated for every atomic basin:

$$\langle \hat{A} \rangle = \sum_i^{\text{atomic basin}} \langle \hat{A} \rangle_i \quad (2.203)$$

Some of the properties that can be discussed are the charge (using the atomic charges), the total energy density $H(r)$ (which also can be used as a measure of the degree of covalency of a bond) the potential and the kinetic energy $V(r)$, $G(r)$ the molecular dipole and so on. This procedure can also generalize other chemical important concepts such as electronegativity, using localization and delocalization indexes which are a measure of how many electrons belong to an atom in a specific bond. As can be seen, the theory allows to quantitatively demonstrating a lot of qualitative classical chemical concepts.

In the present work, QTAIM will be used to characterize the bond of all the isomers in order to evaluate their chemical nature remembering that these kind of species are very rare and therefore not easily classified.

3. METHODOLOGY.

This chapter will be devoted to explain the procedure and approaches made for the study of the different isomers along with an explanation on why these methods have been chosen. It is important to remark in the first place the computational facilities and capabilities used during this study, mentioning also the computer codes used during the research.

All the calculations were performed in the Barayo Cluster of the Grupo de Química Teórica y Computacional of the Universidad de Valladolid. This cluster has sixteen nodes (eight Dual Opteron 246 at 2.0GHz and eight Dual QuadXeon E5430 at 3.0 GHz). Other processors are devoted to login and fileserver jobs. Monoconfigurational and DFT calculations have been carried out with the Gaussian 09 package of programs, multiconfigurational calculations are done with the Molpro package of programs and the Bader analysis was done using the Aimall package of programs. [41-43]. Gaussian and Molpro calculations are performed in a Linux environment whereas Aimall calculations in a Windows based environment. Images and spectra are presented with both Gaussview and Aimall graphical utilities.

The general scheme of work for all the isomers presented in the work is:

a.) Exploration of the different potential energy surfaces available or potentially viable for the system at a DFT level.

For all the isomers a prior exploration in a DFT level (B3LYP functional) have been made, considering mainly three possible spin multiplicities for each isomer. Taking into account the number of electrons of the Plutonium atom, the most viable choices are the triplet, quintet and septet spin multiplicities. All the DFT calculations were performed with a Pople basis set (6-311G+3df) for the carbon atoms and a combined Stuttgart-Dresden pseudopotential and basis set for the Plutonium atom [19-22]. The exploration of the potential energy surface consists in a geometry optimization, this is to check for points in the PES in which the gradient of the energy and the root mean square deviation of that gradient is equal or very similar to zero. This procedure, that can be automated with Gaussian, firstly calculate the energy of a given guess point followed by a minimization of the unknown multivariate function by means of a certain algorithm, normally the Berny one [44].

b.) Validation of the wavefunction obtained in the optimization step.

Nothing has been said about the wavefunction of the system. Whereas the geometry obtained can correspond to the equilibrium one, not always the associated wavefunction is the one of lowest energy of the system. It is quite common to optimize a structure to a bad geometry due to the fact that the guessed wavefunction is not necessarily the most stable one. For evaluating the so called "Stability" of a wavefunction, the gradient of the energy with respect to a permutation of the molecular orbitals in such wavefunction is performed. Once again, this procedure can be automatically performed with Gaussian.

In this kind of calculations, permutations in the wavefunctions are performed according to what the gradient dictates, until this gradient reaches a certain negligible quantity. These calculations are performed over all the possible spin multiplicities of the system in order to ensure that the firstly obtained minimum energy state is truly a valid state.

c.) Reoptimization of the geometry.

Once given the correct wavefunction for the system and assuming that another geometry optimization normally only deals with very small displacements of the coordinates of the atoms, a refinement of the geometry is carried out, using as a guess for the wavefunction the one obtained from the stability calculation. In this way we ensure that the geometry is truly the most stable one that represents our isomer at the desired level of theory.

d.) Calculation of the harmonic vibration frequencies at DFT level.

By means of the diagonalization of the Hessian Matrix (second derivative of the energy matrix) we can determine the force constants associated to the bonds within the molecule. And a direct and simple transformation can give us the harmonic vibrational frequencies at the selected level of theory. These vibrational frequencies are used as an indicator of the chemical nature of the different isomers more than a quantitative tool for the prediction of the vibrational spectra. This is, if the molecule is truly a minimum in the PES or if it is a saddle point (transition state) to a different isomer. Thermochemical data can also be extracted from this output.

e.) Refinement of the geometry and vibrational frequencies at the CCSD level of theory.

Using the above calculated initial geometry, wavefunction and force constants, a CCSD optimization and vibrational analysis is performed. This step is the more time consuming one and must be planned carefully in order not to give wrong results. The geometries and vibrational frequencies obtained from this point are considered qualitatively and semi quantitatively good and therefore are used to predict the vibrational spectra that is one of the main goals for this work. These predicted spectra for the most stable isomers are used for establishing a discussion of the potential viability for experimental detection.

f.) Final electronic energy of the system. CCSD(T) calculations.

The final energy is calculated at the “gold pattern” level of theory, including a perturbative treatment of the triple excitations. T diagnostic is evaluated also at this level of theory for the most relevant isomers, in order to provide a guideline for multiconfigurational calculations.

g.) Multiconfigurational discussion of the two competitive isomers.

The final step in electronic structure calculation involves the evaluation of the non-dynamic correlation energy with the use of Molpro program. This study is restricted to

the two most contributive isomers in order to ensure that the prediction of the infrared spectra is correct. These calculations consist in a CASSCF optimization followed by a CASPT2 single point energy. The chosen active space for the calculation is (12,14) according with what was studied in the plutonium dicarbide study [45], tests with a (12,16) active space shown

h.) Study of the bonding in these isomers.

A separate study is performed over all the compounds, regarding the bonding characteristics of each isomer. These calculations are done taking as a reference the DFT electron density and were performed with the Aimall package of programs, taking as valuable information the molecular graph, the electron density distribution, the laplacian of that electron density and several energetic parameters used in the classification of the species according to their bond.

As can be seen, the procedure is designed taking into account the minimization of the problems that can arise from the use of a low level of theory method as only reference or the usage of a high level of theory calculation in the first place, without a prior knowledge of the characteristics of the system. The procedure also ensures that the main object study, which is the molecular structure vibrational spectrum of the most stable isomer is validated through a series of tests which guarantees that non dynamical and dynamical correlation contributions are taking into account in order to confirm the electronic state and molecular geometry of the system.

It is worth to point out that all the graphic analysis of the system, such as the label of the normal modes of vibration or the visualization of the molecular orbitals for the active space are done with the help of Molden [46] visualization program.

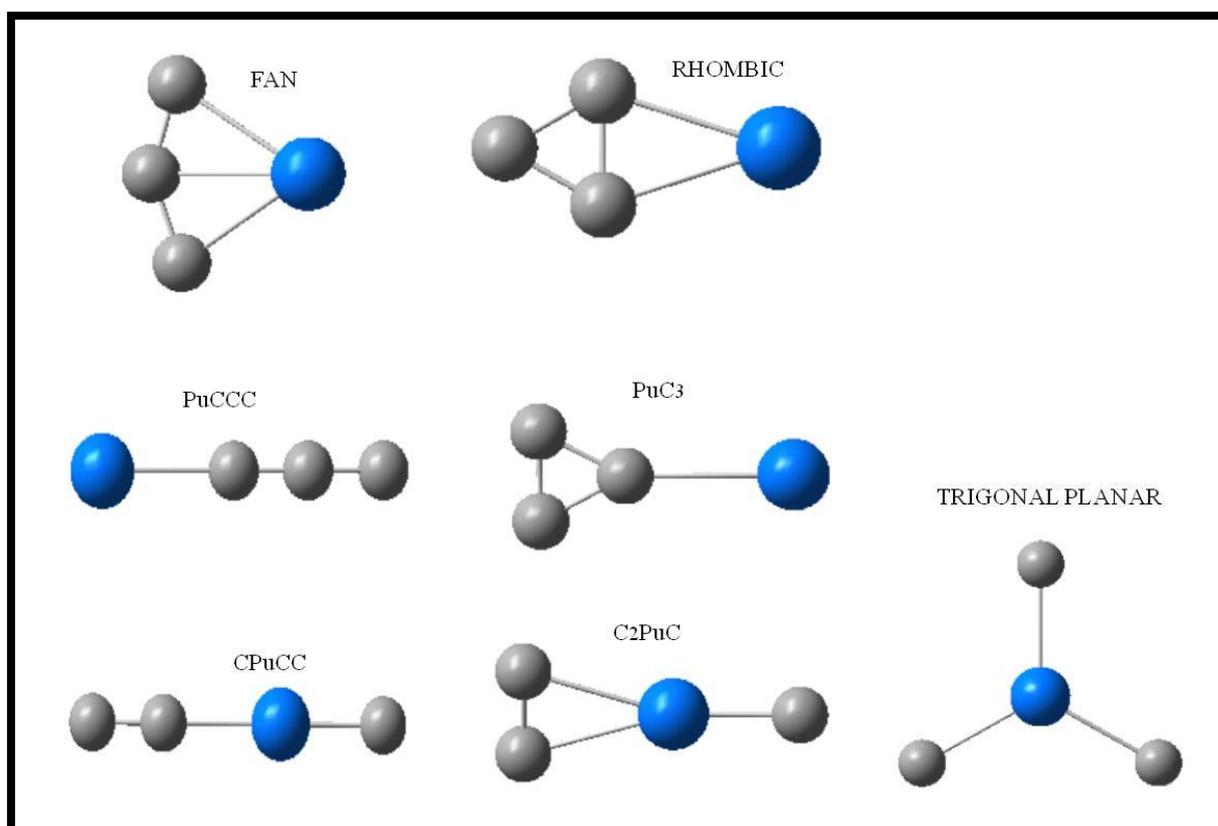
4. RESULTS

a) PRESENTATION OF THE ISOMERS.

An exhaustive study of a variety of isomer has been done, taking as a reference the isomers that arise from the study of the uranium tricarbide[7]. Several new isomers have been studied such as a pyramidal one, or a quasilinear one. However, these isomers are not competitive at all comparing them with the guidelines shown in the previous study. Taking into account the work on the Plutonium dicarbide, carried out by Pogany et al [45], we also have the intuitive idea, considering that a bend isomer will lie much lower in energy that a linear one. And therefore, considering the possible formation paths presented in [7], it is easy to generalize its conclusions to the plutonium analogue.

In this way, the isomers which are candidates for a study are:

Figure 4.1- Plutonium tricarbide isomers under study



All these isomers will be treated at a high level of theory for their correspondent ground states.

Regarding these isomers is important to remark that not always the most stable specie is the one found experimentally, and not always a discussion of the stability referred to the electronic energy provide the results used in laboratory detection. This is why, discussion of possible formation channels must be added to this study.

b) DFT DETERMINATION OF THE ISOMERS GROUND STATE

In every isomer multiple spin multiplicities have been considered in order to evaluate the ground state of the isomer. However triplet, quintet and septet multiplicities are always more stable than the others and are the ones presented along all the work.

The results arising from each one of these three multiplicities for every isomer are presented below. Zero point vibrational energy, defined as the residual vibrational energy that is present in quantum mechanical object at 0K is not included in these calculations. This contribution tends to be very low and, considering the unstable character of some states not always was possible to determine the vibrational modes of the molecules. In this way, for this preliminary organization only electronic energies are calculated. Vibrational analysis, and ZPE are provided once all the meaningful multiplicities are discarded.

The obtained results are presented in the table below:

Table 4.1: Most stable spin multiplicites for each isomer

Isomer	Fan	Rombic	PuCCC	Exocyclic Ring	CPuCC	C2PuC	Trigonal Planar
Multiplicity	Septet	Septet	Septet	Quintet	Quintet	Quintet	Quintet

Once the multiplicities of the ground state are determined, it is time to calculate the DFT vibrational frequencies along with the elucidation of the electronic ground state.

The first task is done constructing and diagonalizing the Hessian matrix for the system. The data obtained from this calculation allow us to determine the nature of our isomer in the PES for the system, (along with the multiplicity that determines in which PES we are working). Harmonic oscillator frequency for a normal mode is calculated:

$$\nu = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} \quad (4.1)$$

Where μ is the reduced mass of the fragments of the bond and k is the force constant defined as:

$$k = \left(\frac{\partial^2 E}{\partial r^2} \right) \quad (4.2)$$

which is an element of the Hessian Matrix for the system. Diagonalization of the Hessian matrix will give us the vibrational frequencies of the molecule, and considering that these calculations are performed over singular points of the PES, this is over global or local minima in the PES, depending on the sign of the eigenvalues of the Hessian matrix is possible to determine the nature of the isomer. This is, if it is a true minimum

it corresponds to a true isomer, or if it has one negative force constant (imaginary frequency) corresponds to a transition state to another isomer.

Table 4.2: Number of imaginary frequencies per isomer

Isomer	Fan	Rombic	PuCCC	Exocyclic Ring	CPuCC*	C2PuC	Trigonal Planar
N° Imaginary frequencies	0	0	0	1	2	0	0

(*double degenerate frequency)

The other important topic is the determination of the spatial symmetry of the ground state. These kind of systems with heavy metals have lots of states in a very narrow range of energies and the correct determination of the ground state is neither trivial nor easy. A well represented ground state allows us to guarantee that the isomer is fully characterized and that ensures the repeatability of the results. Normally, quantum chemistry software assigns the electronic state attending to symmetry criteria but, in the case in which heavy atoms are present is quite usual to lose the orbital symmetry making impossible to automate the process. In these cases, a visual inspection of the MO that defines the wavefunction is needed, and once these MO are obtained, a direct product following the rules of the molecular symmetry between the unpaired molecular orbitals must be done. The results of this process are presented below:

Table 4.3 Electronic Ground state for every isomer

Isomer	Fan	Rombic	PuCCC	Exocyclic Ring	CPuCC	C2PuC	Trigonal Planar
Electronic Ground State	7B_1	7A_2	${}^7\Pi$	5B_1	5B_1	${}^5\Phi$	${}^5A_2''$

It is important to point out that the three most stable isomers are septets which seems to give to this multiplicity an important role in the system. Once this preliminary study is done, it is time to optimize the given ground state with a more reliable method, as, for example CCSD. Next subsection will present quantitative results of the energies of the system at all levels of theory considered in this work, and will clearly define each isomer in a stability ladder, helping us to give a context to further calculations.

c) COUPLED CLUSTER CALCULATIONS: MONOCONFIGURATIONAL ENERGIES, GEOMETRIES AND STABILITY SEQUENCE

The immediate procedure after establishing the general features at a DFT level is to improve the results of electronic energies, geometries and frequencies. For doing so we must ensure that the electronic guess coincides with the wave function we have obtained at the DFT level and that the given geometries also correspond with that guess.

Once that point is ensured, the calculation is straightforward. After that, a CCSD(T) calculation of the electronic energy is also done for further improvement. Results are presented below including ZPE correction:

Table 4.4 Relative energies, referring to the most stable isomer. (kcal/mol)

	Fan 7B_1	Rhombic 7A_2	PuCCC ${}^7\Pi$	Pu(C ₃) 5B_1	CPu(C ₂) 5B_1	CPuCC ${}^5\Phi$	Trigonal planar ${}^5A_2''$
B3LYP/SDD+6-311+G(3dp)+ZPE	0.00	4.40	15.51	28.61	50.52	64.24	184.71
CCSD/SDD+6-311+G(3dp)+ZPE	0.00	5.61	29.49	40.74	48.43	64.77	189.47
CCSD(T)/SDD+6-311+G(3dp)	0.00	9.31	35.90	47.58	46.63	63.97	169,76

Given the energies some qualitative results can be extracted.

The first and most important is that the most stable isomer is at all levels of theory the fan one being in this way the global minimum for the system, followed closely by the rhombic one, at least at the DFT level. The next isomer, the linear PuCCC one lies quite high in energy to consider it to be very contributive in equilibrium conditions, and therefore IR peaks associated to this isomer and the next ones are not expected to appear in a IR spectrum of the PuC₃ species.

It is important also to remark that the trend of stability is maintained through all the series of theoretical levels and for all the isomers except in one case in which Pu(C₃) and CPu(C₂) are permuted (at the CCSD(T) level), which in any case has very few or no implications to the main discussion. In this way, monoconfigurational calculations are in agreement with the results obtained in the uranium tricarbide paper. Regarding to the trend that appear when we vary the level of theory we can see that in general, the energy gap between Fan isomer and the other isomers, at least the most contributive ones, gets higher with the “increase” in the level of theory. This trend is inverted in CPu(C₂) but in any case these isomers lie so high in energy to even consider that an extrapolation from that energies could finally converge in something near the Fan isomer energy.

PuCCC isomer has been the most “controversial” one since the energy difference between it and the fan one is high but not as high to completely forget about a discussion about it. However, it holds the maximum change in energy with the inclusion of CCSD and CCSD(T) corrections, this is, the inclusion of progressively more dynamic correlation in the description of the system destabilizes the system, taking the Fan isomer as reference having at CCSD(T) level almost 40 kcal/mol of difference. This is why further improvements in the description of the non-dynamic correlation for the isomers only will include the Fan and the Rhombic isomers, T1 diagnostic for the rest of isomers are below the critical values and support this scheme.

All these results are in agreement with the ones obtained in previous works [1-7] in which the electronegativity of the heteroatom seems to be a good estimator of the trend of stability. In this way, electropositive species seem to give rise to fan and rhombic isomers, whereas electronegative atoms tend to favor linear or exocyclic species. However, this electronegativity factor only seems to be one of the two contributive factors for the establishment of a qualitative stability trend.

The other factor is the structure of the carbon chain, being the linear C_3 arrangement more stable than the cyclic one [47]. This trend qualitatively explains the difference between exocyclic and linear isomer, and once more points out that both fan and rhombic isomers are favored. Other arrangements with C_2 units, like in the case of CPuCC or CPu(C_2) are less stable, mainly to the lower interaction energy. Of course, the addition of a single carbon atom to the metal is a heavily disfavored process, and this explains why CPuCC, CPu(C_2) and the trigonal planar isomer are the most energetical ones. Finally, it is important to point out that the difference between CPuCC and CPu(C_2) should be due also to the different steric environments of both molecules. These two rules are useful to determine the structure of similar carbides but it can fail in some cases, like the CCSD(T) inversion of CPu(C_2) and PuC₃.

For the calculation of the non-dynamic correlation for the two most contributive isomers, which are expected to be the ones whose vibrations could eventually appear in an IR study, an improvement in both geometries and energies has been done, including partially the so called, non-dynamic correlation, associated to the multiconfigurational character of a wavefunction. CASSCF(12,14) and CASPT2(12,14) single state calculations have been carried out along with a optimization of the geometry in the CASSCF(12,14) case. T1 diagnostic for these systems are 0.040 for the Fan isomer and 0.027 for the Rhombic one which are reasonable values for systems containing heavy atoms.

Obtained electronic energies:

Table 4.5- Multireferential relative energies over the two most stable isomers (kcal/mol)

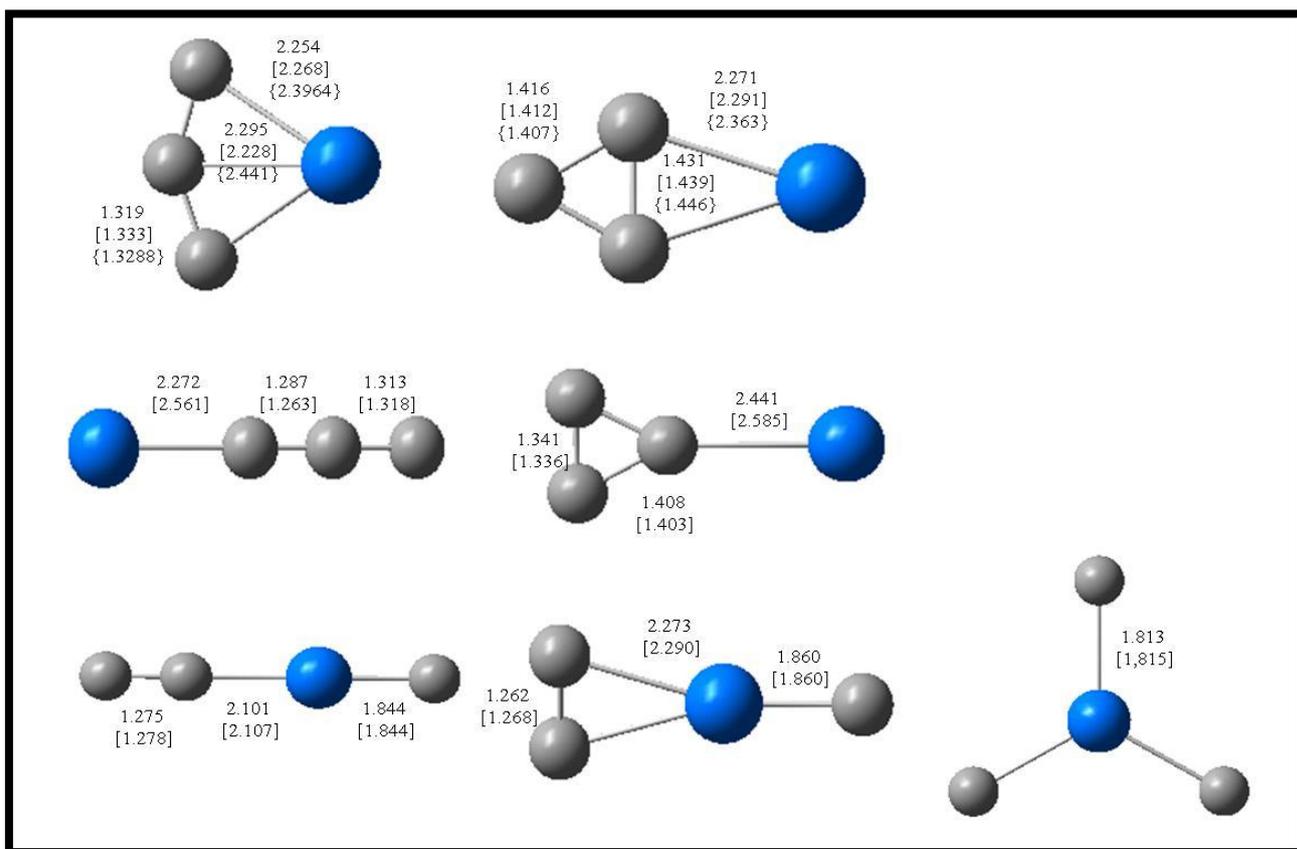
	Fan 7B_1	Rhombic 7A_2
CASSCF(12,14)/SDD+6-311+G(3dp)	36,52	0.00
CASPT2(12,14)/SDD+6-311+G(3dp)	0.00	3.22

The multiconfigurational calculation provides a very interesting result. These results show that Fan isomer is heavily shifted to higher energies by the non dynamic correlation, which is clearly shown by an inspection of the weight of the main configurations of the wave function. In the Fan case the weight of the single reference wave function is 0.9422 having other three major contributions of weights 0.1184, 0.098 and -0.098 along with much less contributive configurations. In the case of the rhombic one, the single reference wave function constitutes the 0.976 of the total wave function with no other configurations obtained in this active space. As can be seen it is expected due to the multiconfigurational character of the Fan isomer to be destabilized with this nature. However, the inclusion of a slight amount of dynamic correlation recovers the expected value from B3LYP calculations. Therefore we can conclude from a theoretical point of view that in this system dynamic correlation plays a major role in how this species could be found in nature.

It can be concluded that Fan isomer is the most stable one and the one expect to be found in experiments, however rhombic isomer should be quite contributive and it could be expected in an experimental detection to found some signals associated to it.

Energies and vibrational frequencies are calculated over optimized structures, whose geometric parameters are presented below (brackets and curly brackets represent CC and CASSCF distances respectively):

Figure 4.2- Plutonium tricarbide isomers bonding distances



The value of 1.333 Å for the case of the fan isomer points to a typical double bond behavior, (according to the typical 1.34 value), somewhat longer than the one provided by the CCDBD database [47] for the linear C₃ linear unit which in a CCSD(T)/ aug-cc-pVQZ calculation gives 1.298Å of distance, this data along with the CCC angle of ~140 degrees suggest that some of the electron density of the CC bond is accepted by the Plutonium atom, a viable consideration remembering that this atom have a similar electronic behavior that the electropositive heteroatom (alkaline, earth alkaline) carbides. As the QTAIM analysis will provide in a further section, looking at the Pu-C distance in the fan isomer we can say that there is not any bond between them and that the structure is a monocyclic specie. In the rhombic isomer C-C values are now much larger, with a distance that is comparable with a single CC bond, a very informative value for determining that the rhombic isomer comes from a distorted interaction with a linear C₃ unit, because if a cyclic unit were interacting with the Plutonium atom, as in the case of PuC₃ we should see that the peripheral CC interaction should retain the typical values for the cyclic C₃ molecule. Furthermore, both internal and peripheral CC bonds show similar geometric characteristics and suggest that rhombic isomer is a bicyclic one. The linear isomer, shows an interesting difference between both DFT and CCSD Pu-C bond distance, pointing that interelectronic interactions play an important role in this systems, this repulsion weakens this bond, strengthening the contiguous CC to an intermediate double/triple bond, being the other C-C bond similar to the ones

found in a linear C₃ specie, pointing that in these type of interactions only the contiguous neighbor to the Plutonium atom suffer an appreciable change in its electronic characteristics. Regarding the exocyclic isomer, as the frequency calculation dictates, the structure is a transition state, which in fact explains the abnormal Pu-C distance. The case of the CPuCC is particularly interesting since it is the only one in which the Plutonium atom is bonded along the same direction to two different chains, providing interesting data on how different is the C₂-Pu and C-Pu bond, pointing that the bond is weaker when the carbon atom is attached to another carbon atom. Qualitatively speaking this is due to the lower retrodonation in the PuC₂ bond comparing to the one in the C atom. In C₂PuC seems that the Plutonium atom strengthens the C₂ with a η^2 interaction, having the Pu-C bond a distance similar to the one observed in the previous isomer. Finally, concerning the trigonal planar isomer the only intra-atomic distance shows an abnormally short distance pointing to a possible true covalent compound.

d) VIBRATIONAL ANALYSIS OF ALL THE ISOMERS. INFRARED SPECTRA. WILL WE ABLE TO DETECT IT?

As we have mentioned, the main goal of this part of the work is to provide theoretical results for a potential experimental detection of this new molecule. Every step that has been taken until now has been guided to filter all the possible isomers detectable in the equilibrium. We have determined that both fan and rhombic isomers are the only viable isomers in the equilibrium from a theoretical point of view. And between them fan has been pointed as the equilibrium isomer, a simple Boltzmann ratio will help us to determine the ratio of Fan/Rhombic isomers at the equilibrium using the CCSD+ZPE values and 273K.

$$\frac{F(rho)}{F(fan)} = e^{\frac{(E_{fan} - E_{rho})}{kT}} \quad (4.3)$$

The numerical application of this expression yields:

$$\frac{F(rho)}{F(fan)} = 3.22 \cdot 10^{-5} \quad (4.4)$$

Obviously, the experimental conditions in which this kind of systems are found are heavier, and for example, at 1000K this ratio is 0.0594. It is expected therefore to obtain an increase in the rhombic signal with the temperature, along with a decrease in the fan signal. For linear and the other isomers the contribution is slow even at high temperatures.

Frequencies are listed by isomer in the table below:

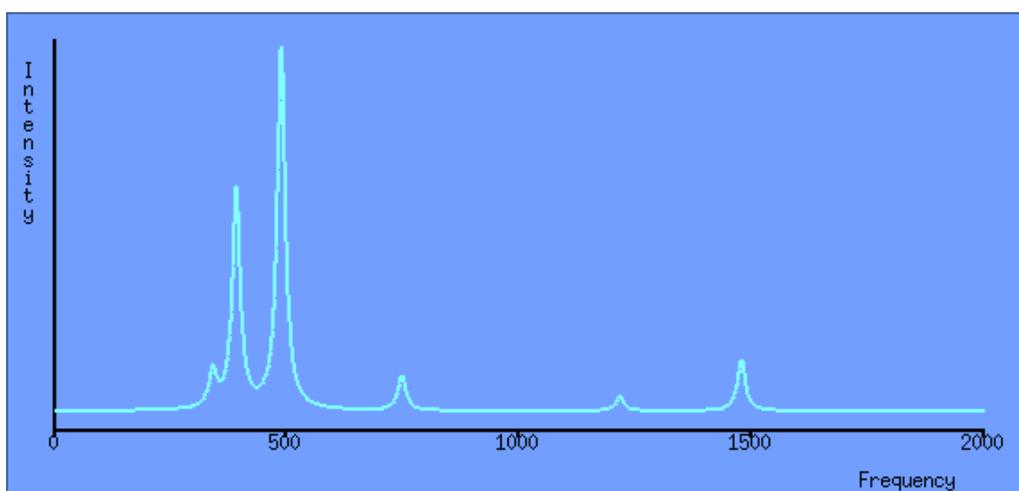
Table 4.6- Vibrational frequencies listed by isomer and theoretical method

Isomer	Method	Vibrational frequencies (cm ⁻¹) (Symmetry of the mode of vibration, intensity in km/mol)	μ (D)
Fan ⁷ B ₁	B3LYP/6-311+G(3df)+SDD	322 (b ₂ ,11), 391 (b ₁ ,60), 443(a ₁ ,67), 709 (a ₁ ,14), 1254 (a ₁ ,5), 1529(b ₂ ,6)	8,844
	CCSD/6-311+G(3df)+SDD	341 (b ₂ ,11), 391 (b ₁ ,69), 488(a ₁ ,114), 747 (a ₁ ,11), 1216 (a ₁ ,5), 1477(b ₂ ,16)	9,741
Rhombic ⁷ A ₂	B3LYP/6-311+G(3df)+SDD	229 (b ₁ ,2), 359 (b ₂ ,25), 408 (a ₁ ,96), 893 (b ₂ ,68), 1053(a ₁ ,2), 1424(a ₁ ,1)	9,206
	CCSD/6-311+G(3df)+SDD	238 (b ₁ ,4), 400 (b ₂ ,1), 454 (a ₁ ,104), 1009 (b ₂ ,6), 1125(a ₁ ,66), 1522(a ₁ ,4)	8,932
PuCCC ⁷ Π	B3LYP/6-311+G(3df)+SDD	79 (π,0), 95 (π,0), 210 (σ,4), 308 (π,17), 408(π,10), 1228(σ,9), 1822 (σ,716)	10,226
	CCSD/6-311+G(3df)+SDD	125(π,3), 140 (π,1), 242 (σ,4), 306 (π,142), 422(π,103), 1308(σ,147), 1915 (σ,1090)	10,257
Pu(C ₃) ⁵ B ₁	B3LYP/6-311+G(3df)+SDD	330 i(b ₂), 165 (b ₁), 179 (b ₂), 227 (a ₁), 1221(a ₁), 1590(a ₁)	6,286
	CCSD/6-311+G(3df)+SDD	391 i(b ₂), 160 (b ₁), 179 (b ₂), 230 (a ₁), 1305(a ₁),2018(a ₁)	8,450
CPu(C ₂) ⁵ B ₁	B3LYP/6-311+G(3df)+SDD	44 (b ₂ ,80), 112 (b ₁ ,52), 288 (b ₂ ,9), 492 (a ₁ ,175), 684(a ₁ ,3), 1827(a ₁ ,22)	1,884
	CCSD/6-311+G(3df)+SDD	118 (b ₂ ,75), 138 (b ₁ ,56), 329 (b ₂ ,16),513 (a ₁ ,253), 738(a ₁ ,10), 1825(a ₁ ,18)	2,371
CPuCC ⁵ Φ	B3LYP/6-311+G(3df)+SDD	123 i(π), -121 i(π), 107 (π), 109 (π), 465(σ), 740(σ), 1844(σ)	3,889
	CCSD/6-311+G(3df)+SDD	115 i(π), -113 i(π), 108 (π), 130 (π), 478(σ), 778(σ), 1852(σ)	4,348
Trigonal planar ⁵ A ₂ ''	B3LYP/6-311+G(3df)+SDD	84 i (e'), 192 (a ₂ '',38), 807 (a ₁ ',0), 815 (e',61)	0,000
	CCSD/6-311+G(3df)+SDD	141 (e',21), 245 (a ₂ '',27), 796 (a ₁ ',0), 876 (e',18)	0,000

It is noteworthy to point some key points in these results. Concerning linear isomers, we can observe a split in frequencies of the degenerate modes due to the Renner-Teller effect. Moreover, CCSD calculations over this isomer seems to give results slightly shifted to higher wavenumber values, which also appears in the CPu(C₂) isomer. Pu(C₃) isomer shows a clearly imaginary frequency, which points univocally to the transition state nature of the isomer. An impressive result arises when looking at the frequency values of the trigonal planar isomer, which at CCSD level loses the imaginary frequency, leading to a stationary specie from the PES point of view, this discrepancy between levels of theory seems interesting but, since the isomer is not stable enough to be contributive, a further investigation would not help to the purpose of the work. The spectral window for every isomer is very similar, suggesting that the nature of the vibrations implied in this analysis are of similar nature. Some of the possible vibrations present in this kind of systems include : out of plane bendings corresponding to PuCC twisting, in-plane C₃ bendings including rocking and scissoring, finally it is important to mention the PuC stretchings

A graphical view of both Fan and Rhombic spectra at 298K is represented in the next two images. In the first place, Fan spectrum is presented:

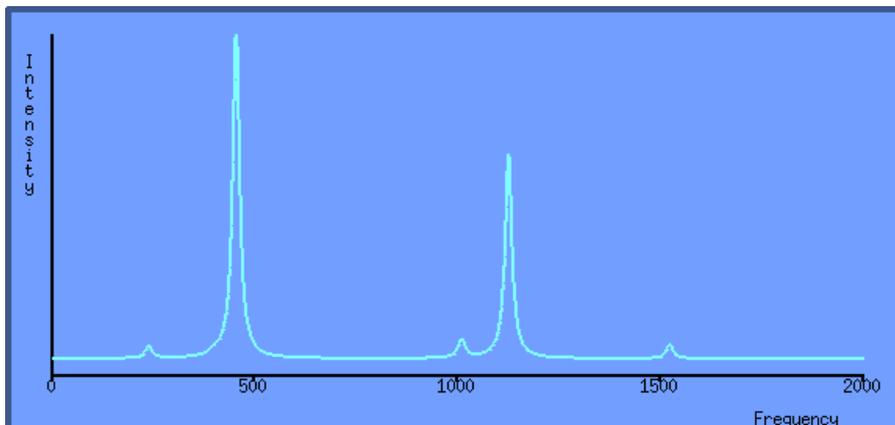
Figure 4.3. Fan isomer IR spectrum



This spectrum has been simulated applying a FWHM of 10 cm⁻¹ to a Lorentzian curve for every peak. The most intense peak correspond to the PuC_n stretching. The peak at 391 cm⁻¹ represent the symmetry bending of the C₃ unit. As it can be seen in the frequencies table, this peak is present in almost all isomers shifted in one or other way.

The rhombic isomer spectrum:

Figure 4.4. Rhombic isomer IR spectrum

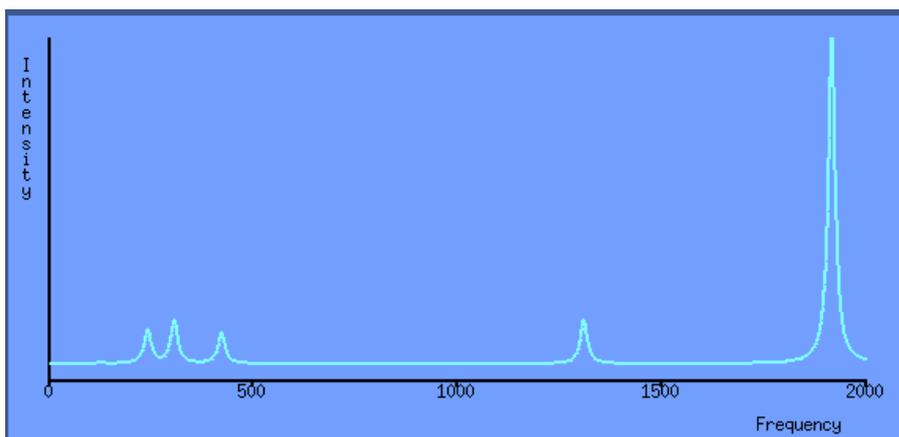


This spectrum has been simulated applying a FWHM of 10 cm^{-1} to a Lorentzian curve for every peak. The most intense peak correspond to the PuC_n stretching just as in the Fan spectrum, but we can distinguish both thanks to the in-plane asymmetric CC bending at 1125 cm^{-1}

Viewing the spectra we can confirm that it should be possible to distinguish them thanks to the rhombic 1125 cm^{-1} band.

This can be summarized as the most important conclusion in the whole thesis since from a thermodynamic point of view the isomers can be detected without the needing of an auxiliar isolation process. However, a qualitative description of formation schemes of the carbides must be done in order to ensure that both isomers are present in conditions far from equilibrium ones, just as in [7]. In our case triangular PuC_2 isomer is far more stable [45] and, if the precursor for the formation of PuC_3 is that molecule, C_{2v} isomers are expected. However, if the growth of the carbide is made starting with Pu, side interactions it can lead to linear PuCCC and if we perform our experiments far from equilibrium conditions is quite possible to measure an isomer which is not the thermodynamically stable one, which in this case is the fan isomer. Later in this document formation channels will be discussed in detail but for now it is important to say that certain experimental conditions can easily lead to the formation of PuCCC isomer and therefore the calculation of spectrum is needed just in case optimal conditions are not achievable.

Figure 4.5. Linear isomer IR spectrum



This spectrum has been simulated applying a FWHM of 10 cm^{-1} to a Lorentzian curve for every peak. The most intense peak corresponds to the CC asymmetric stretching. Luckily, if linear PuCCC is the experimentally detected one, the spectrum will be univocally assigned following these guidelines since it is completely different of the fan and rhombic one, which in fact can help to prove one of the main conclusions in formation channels that will be shown a few pages later

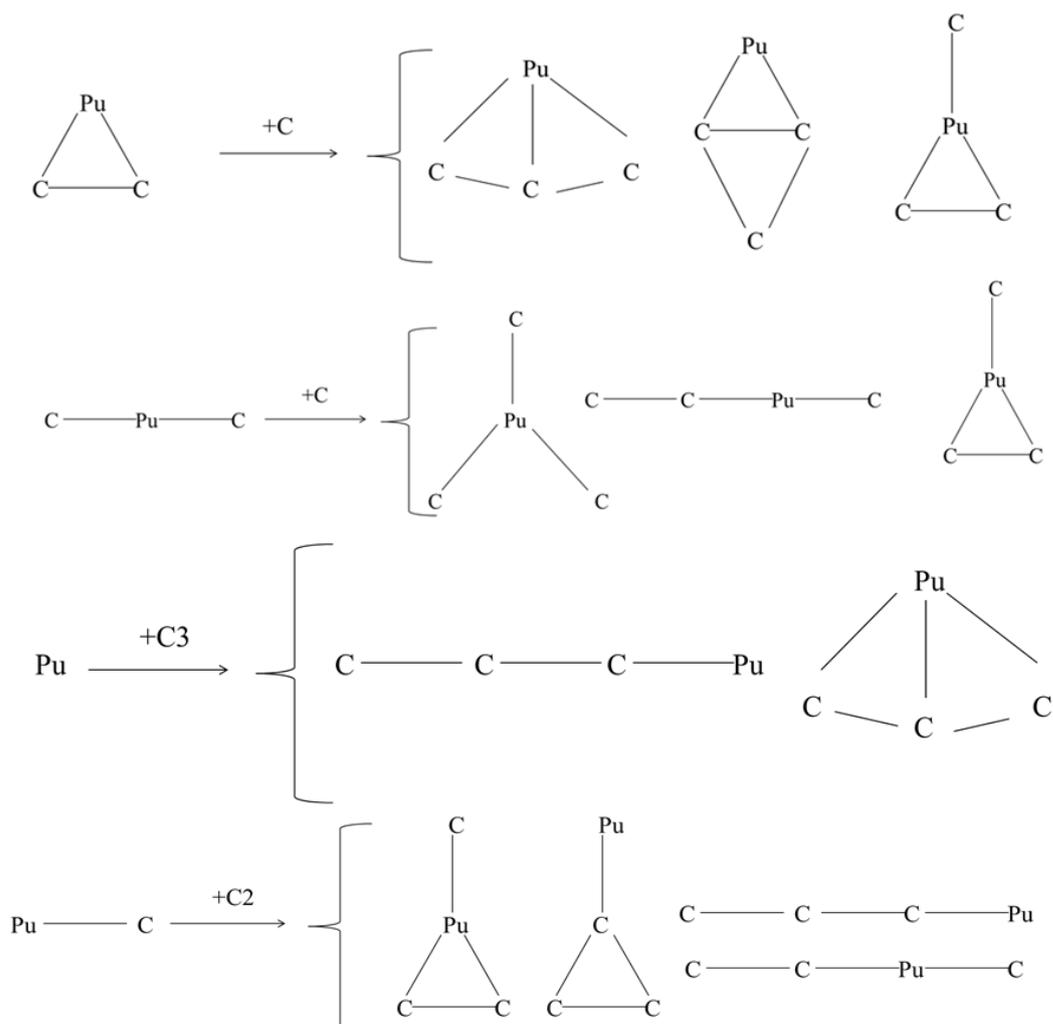
The prediction of more spectra is not necessary as will be shown in the next subsection.

A brief comment of the molecular dipole moments is now somewhat important, which is for the majority of the isomers impressively high. Only C_2PuC and CPuCC isomers have a low value, considering that symmetry forbids trigonal planar isomer to have dipole moment. For the rest of the isomers, dipole moment varies between 6-10 D, high values that help in different spectroscopical detections of the isomers. These values are indicators of the nature of the bonding suggesting a high ionic character, the QTAIM analysis will provide more data on this conclusions.

e.) FORMATION CHANNELS, WHERE ALL THESE ISOMERS CAME FROM?

A formation channel in this context refers to a possible elementary process to the formation of one of the considered isomers. This is not trivial; since different isomers can be formed in several ways and in a far from equilibrium condition and this has many implications in the bulk of reaction from a spectroscopical and chemical point of view. Elucidation of the main formation channels is a must have information for every experimental setup. Discussion in formation channels must be done considering firstly the precursor and the associated C_n unit that will grow the main molecular skeleton. Namely, these precursors are: bent plutonium dicarbide, linear plutonium dicarbide, Plutonium atom and plutonium monocarbide with the C , C , C_3 and C_2 units respectively. A graphic representation of the formation channels of plutonium tricarbide can be found below:

Figure 4.6. Possible plutonium tricarbide formation channels



As we can see, fundamentally we can predict 4 types of formation channels.

1) When an angular PuC_2 unit interacts with a Carbon atom via side interactions the fan isomer is formed, and considering that according with Pogany et al [45] triangular, PuC_2 is the most preferred dicarbide isomer, it seems that it in principle should be the most contributive channel over head interactions of C with both the C_2 unit or the Pu atom (Rhombic and CPuC_2 formation channels). 2) However, when linear PuC_2 is used as a precursor, less stable isomers are expected, each of them depending on the approximation paths followed by the last carbon atom, being possible to construct trigonal planar, CPuCC or CPuC_2 . These isomers will likely suffer isomerization processes to more stable isomers. In any case triangular isomer is $\sim 91\text{kcal/mol}$ below in energy with respect to the linear one, and therefore this formation channel should not be very contributive in usual experimental conditions. It can be argued that a hypothetical PuCC isomer can be used, but Pogany et al [45] discarded this isomer as contributive 3) When a linear C_3 unit approaches to a Plutonium atom, PuCCC or Fan isomer can be formed (it would be possible to postulate a cyclic C_3 unit giving rise to a exocyclic isomer but this process should not be favored). The formation of one or another would be dictated by the dynamics of the system, but, from a thermodynamical point of view Fan isomer should be preferred in this context. Like in the second channel, a cyclic C_3 unit can be used as reactant, but this isomer is disfavored comparing to the linear unit 4) When PuC is used as a precursor linear and “cyclic” isomers are formed, as expected (a QTAIM analysis will prove that in reality CPuC_2 is not a true cycle, but it is advisable to name it like that for visualization purposes).

These formation channels point out a main conclusion, qualitatively the Fan isomer is the one that should be detected, except if the formation path starts from a PuC unit. Other main conclusion is that, isomerization processes should be considered for an accurate description of the bulk of reaction.

The main discussion regarding formation channels arise from the competition between linear and fan isomer, depending on the substrate. Also, from this qualitative point of view, CPuC_2 can be formed as specified in the second formation channel, but this specie will likely suffer isomerization processes due to the high energy gap between it and the most competitive isomers. These isomerization will most likely lead to a fan isomer via CPuC bending mode. Once considered this step, the analysis of the formation channels concludes that linear isomer and differences in the spectrum with respect the fan isomer will only be perceived when linear PuC is used as a substrate. This hypothesis can be enforced using statistical or dynamical simulations along the reaction paths of the formation channels

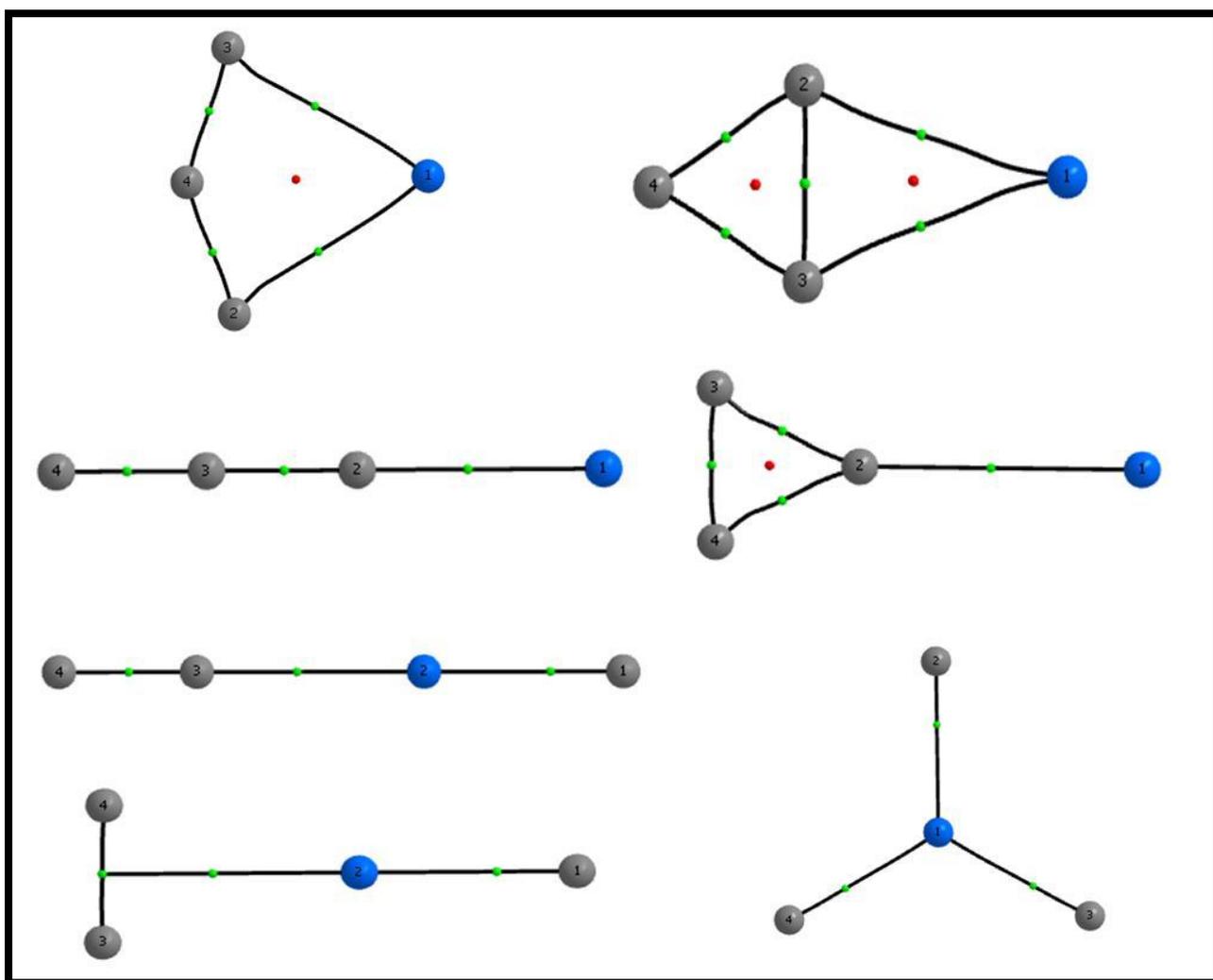
Finally, it is worth to point out that Rhombic isomer should not be preferentially formed with respect to the Fan isomer, and therefore the shape of the IR spectrum should remain as studied in the past subsection, with the possible exception of an hypothetical detection of the linear isomer when PuC precursor is used.

f) ATOMS IN MOLECULES: BONDING STUDY.

So far we have put our effort in the description of the arrangement of atoms forming all the isomers, and the inherent vibrational modes of that arrangement of atoms. Now it is time to discuss something about some characteristics of the bond between those atoms.

From the bond valuable theoretical information can be extracted, such as the ionicity or covalency, or if a certain disposition is truly a cycle or not. Main goals in this study are the cyclic/not cyclic nature of some isomers, along with their bonding nature. For this purpose topological analysis of the electron density has been done. Molecular graphs for every isomer are the first step to take:

Figure 4.7. Molecular graphs for the most relevant isomers



These graphs provide valuable information of the nature of each system and will be discussed next.

For the Fan isomer, the main feature we can observe that two peripheral BCPs connecting C and Pu atoms, and therefore a cycle is closed along the plane of the molecule. Being a true cyclic specie is quite important from a thermodynamical point of view and can explain to some extent the increased stability of both rhombic and fan isomer over the linear ones. Same conclusions can be extracted from the Rhombic

graph, adding that in this isomer, we can find two ring critical points, being a true bicyclic specie, this bicyclic behavior (even though a C3 ring does not provide as much stabilization as a PuCn) can be one explanation of the difference in stability order at low to moderate levels of theory, in which the non dynamic correlation inverts the sequence of stability.

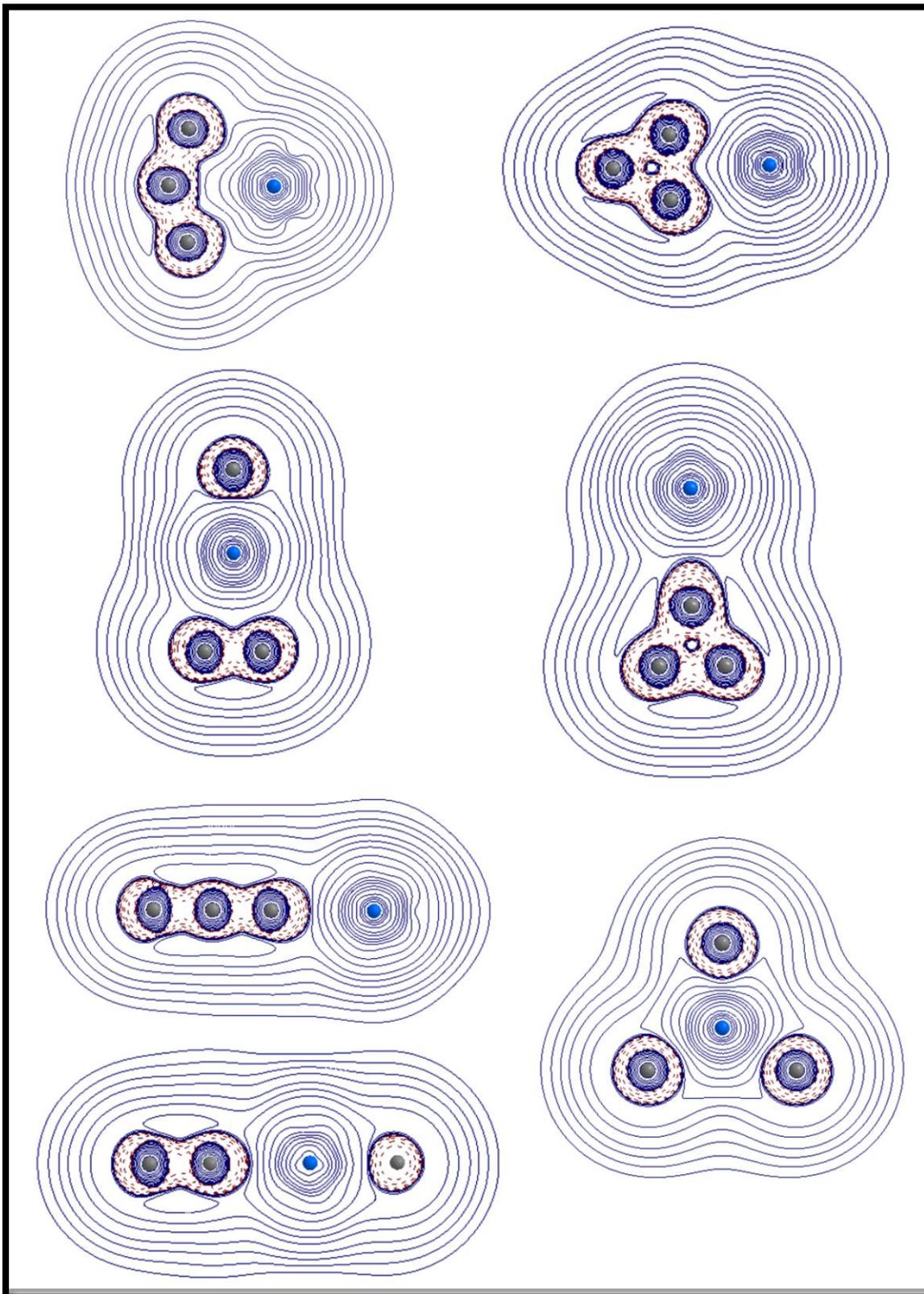
Regarding linear isomers the expected results are obtained, plutonium atom forms a true bond with the carbon atom (or atoms). Along with this general conclusion it is important to remark that a bond between plutonium and the carbon skeleton is formed and the PuCCC structure is not completely an ionic one, which is a valuable information regarding condensation processes. However, the bond is likely to be very weak.

An interesting discussion for the 3-ring and the C₂PuC isomers can be made, taking into account that the former has a true cycle from the interaction of the carbon atoms and the latter does not form a cycle at all with the Plutonium atom in a vertex. The appearance of this cycle can explain their “high” stability, near the most contributive isomers. However, the C₂PuC isomer, being a C_{2v} isomer, has a very high energy comparing with the other C_{2v} isomers, not stabilized by the cycle formation, having something similar to a T shape, due to the predominance of the π Pu – C₂, comparing them with the sigma contributions.

Finally, concerning the trigonal planar isomer, it is noteworthy to point out that no cycle is observed from C-C interactions, leaving a structure similar to the boron trifluorine one.

For a more quantitative study of the bond in the carbides it is convenient to present the Laplacian of the electron density for every isomer.

Figure 4.8 .Laplacian of the electron density for every of the PuC_3 isomers.



Numerical values for the laplacian at the bond critical points along with some other parameters are presented in the next table:

Table 4.7- Topological properties (in a.u) of the electronic electron density in the BCP points for each isomer

Isomer	Bond	ρ	$\nabla^2(\rho)$	$ V / G $	H
Fan 7B_1	Pu-C ₃ , Pu-C ₂	0,1144	0,1365	1,5819	-0,0475
	C ₃ -C ₄ , C ₂ -C ₄	0,3408	-0,9137	3,3512	-0,3975
Rhombic 7A_2	Pu-C ₃ , Pu-C ₂	0,0999	0,2187	1,3866	-0,0346
	C ₂ -C ₃	0,2692	-0,3639	2,5752	-0,2491
	C ₂ -C ₄ , C ₂ -C ₄	0,2788	-0,4889	2,8587	-0,2645
PuCCC ${}^7\Pi$	Pu-C ₂	0,1389	0,2185	1,5337	-0,0081
	C ₂ -C ₃	0,3559	-0,1094	3,8309	-0,4229
	C ₃ -C ₄	0,3863	-0,1299	4,5181	-0,4537
Pu(C ₃) 5B_1	Pu-C ₂	0,0822	0,1156	1,4639	-0,0251
	C ₂ -C ₃ , C ₂ -C ₄	0,2777	-0,3299	2,4585	-0,2624
	C ₃ -C ₄	0,3435	-0,8727	3,2794	-0,3887
CPu(C ₂) 5B_1	Pu-C ₁	0,1989	0,1523	1,8081	-0,1603
	Pu-CC	0,1058	0,1909	1,4428	-0,0379
	C ₃ -C ₄	0,3963	-1,2249	3,4502	-0,5174
CPuCC ${}^5\Phi$	Pu-C ₁	0,2097	0,1309	1,8445	-0,1776
	Pu-C ₃	0,1511	0,1056	1,7528	-0,0804
	C ₃ -C ₄	0,3861	-1,2354	3,7368	-0,4867
Trigonal planar ${}^5A_2''$	Pu-C ₁ , Pu-C ₂ , Pu-C ₃	0,2382	0,0272	1,9706	-0,2228

The way to interpret this data is as follows. Electron density and its Laplacian commonly are easy to interpret in a visual way, high electron densities and negative laplacian at the BCP intuitively gives the idea of a shared interaction, typical of covalent compounds. Ionic interactions therefore are characterized by low electron densities and positive values of the laplacian. H, which is the total energy density interpreted as the sum of kinetic and potential energy densities is also a estimator of the covalency of an interaction, just the same that the potential and kinetic energy $|V|/|G|$, positive values of H indicate a destabilization of the system [47] (positive energy) when electron is accumulated between both atoms, which could serve as a good analogy for indentify ionic interaction. Same ideas can be applied to the opposite case. The ratio however can, quantify in a way this concepts, with some ranges for every typical interaction, in this way values greater than 2 are typical of covalent interactions, smaller than one from ionic interactions, and values between 1-2 are an intermediate case between the two of them.

In the first place, let us take a quick look to the CC interactions, which follow the typical covalent CC behavior even in the most different case of the transannular carbon in the rhombic isomer with values of the potential/kinetic energy density ratio higher than the typical value of 2 for covalent compounds.

PuC interactions however, are not that easy to classify looking at its low electron density at the bond critical point and the sign of the laplacian of the electron density (positive). These two factors suggest an ionic nature of the bond, but, in an opposite way the total energy density remains negative, even though low comparing with other type of interactions. A possible label for this type of bonds is a highly polarized covalent bond, or maybe a partially covalent ionic bond, an intermediate bond in any case. Within this general trend some conclusions regarding the structure can be extracted, as for example the relation of the PuC bond length with the “covalency” of that bond. This can be observed in isomers that present two different bonds with the plutonium atom, as in the case of CPuC₂ or CPuCC isomers. In this case two different values of the total energy density are found, being one of them near to the CC ones. This variability is also observed in the bond lengths for those isomers, being the shorter one the more “covalent”, as expected.

Rhombic isomer present the most ionic character and the trigonal planar the least one. Considering this general discussion many conclusions can be taken, as for example, the covalent character of the different CC bonds that is not equal depending of the molecular vicinity or that the PuC interactions are very sensitive of the molecular electron density distribution. In general, conclusions that can be taken from this methodology are that this type of compounds are neither covalent nor ionic and that the bond can be interpreted as an ionic bond with a remarkable covalent character

5. CONCLUSION.

Main goals for the project have been achieved. We have been able to determine the stability order of the main isomers, discarding the ones that were enormously high in energy, from all of them their relative stability order along with the electronic state have been determined, confirming the general assumptions from previous works. The FAN isomer is still the most stable one as in the uranium tricarbide study but the rhombic one is in this case more contributive from a thermodynamic point of view. From this central conclusion, the IR detection can be predicted from the spectra, which luckily give, that in this case the two most contributive isomers are easily distinguishable. Along with this main goal, an understanding on how actinides bond with carbon chains has been resolved for the particular case of the plutonium atom, confirming that actually a true bond is formed.

Geometries patterns along the variation on the level of theory are consistent presenting slight variations between calculations, which are symptomatic of the goodness of the obtained electronic state. Frequencies for all the isomers have been characterized, showing that main isomers are true minima in the potential energy surface.

Regarding energetic criteria, this work presents an interesting discussion of the confrontation between non dynamic and dynamic correlation in this kind of systems, and how these two contributions have to be taken into account together in accurate calculations.

Various formation channels have been discussed concluding that only one formation channel will alter the final shape of the total spectrum, this is the formation of the tricarbide via the linear dicarbide one.

Some refinements for this work should include a multiconfigurational extension to all the isomers, the inclusion of spin-orbit effects that are important for these heavy systems, and finally a comparison between AIM method with other wavefunction analysis method. The study of the possible isomerization processes between isomers will be crucial to finally understand the system.

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