STRUCTURAL, ELECTRONIC, AND MAGNETIC PROPERTIES OF SMMCON ($M + N \leq 3$) MICROCLUSTERS: DENSITY FUNCTIONAL THEORY CALCULATIONS

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submitted by **NAZAN KARA** in partial fulfillment of the requirements for the degree of **Master of Science in Physics Department, Middle East Technical University** by,

Prof. Dr. Canan Özgen
Dean, Graduate School of **Natural and Applied Sciences** _____

Prof. Dr. Mehmet T. Zeyrek
Head of Department, **Physics** _____

Prof. Dr. Şakir Erkoç
Supervisor, **Department of Physics, METU** _____

Assoc. Prof. Dr. Hüseyin Oymak
Co-supervisor, **Elec.and Electronics Eng Dept., Atılım University** _____

Examining Committee Members:

Prof. Dr. Ümit Kızıloğlu
Department of Physics, METU _____

Prof. Dr. Şakir Erkoç
Department of Physics, METU _____

Prof. Dr. Enver Bulur
Department of Physics, METU _____

Assoc. Prof. Dr. Hüseyin Oymak
Elec.and Electronics Eng Dept., Atılım University _____

Assoc. Prof. Dr. Hande Toffoli
Department of Physics, METU _____

Date: _____

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Name, Last Name: NAZAN KARA

Signature :

ABSTRACT

STRUCTURAL, ELECTRONIC, AND MAGNETIC PROPERTIES OF SMMCON ($M + N \leq 3$) MICROCLUSTERS: DENSITY FUNCTIONAL THEORY CALCULATIONS

Kara, Nazan

M.S., Department of Physics

Supervisor : Prof. Dr. Şakir Erkoç

Co-Supervisor : Assoc. Prof. Dr. Hüseyin Oymak

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Performing density functional theory calculations with many possible exchange correlational energy functionals, the most stable structures, symmetries, electronic, and magnetic properties of Sm_MCo_N ($M + N \leq 3$) microclusters have been studied in a systematic and statistical manner. Starting from the atoms of cobalt and samarium, dimers and trimers have been investigated in their ground states. The optimum geometries, binding energies, vibrational properties, possible dissociation channels, local magnetic moments and their enhancements with the growing size of the microclusters under study have been obtained. The calculations have been performed by using 13 DFT methods in the scope of present study.

Keywords: Density Functional Theory (DFT), Transition Metal Clusters, Rare Earth Elements, Cobalt, Samarium

ÖZ

SMMCON ($M + N \leq 3$) MİKROTOPAKLARININ YAPISAL,
ELEKTRONİK VE MANYETİK ÖZELLİKLERİ:
YOĞUNLUK FONKSİYONELİ TEORİSİ HESAPLARI

Kara, Nazan
Yüksek Lisans, Fizik Bölümü
Tez Yöneticisi : Prof. Dr. Şakir Erkoç
Ortak Tez Yöneticisi : Doç. Dr. Hüseyin Oymak

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Sm_MCo_N ($M + N \leq 3$) mikrotopaklarının en kararlı yapısı, simetrisi, elektronik ve manyetik özellikleri muhtemel birçok yerdeğiştirme-korelasyon enerji fonksiyonelleri ile yoğunluk fonksiyonel teorisi (YFT) hesapları kullanılarak sistematik ve istatistiksel olarak çalışılmıştır. Kobalt ve Samaryum atomlarından başlayarak, ikili ve üçlü yapıları sıfır enerji seviyesinde çalışılmıştır. Çalışılan bu topakların optimum geometrileri, bağ enerjileri, titreşim özellikleri, mümkün ayrışma kanalları, yerel manyetik momentleri ve bu momentlerin topağın yapısı ile ilgili değişimleri elde edilmiştir. Bu çalışma kapsamında, hesaplar 13 YFT metodu kullanılarak gerçekleştirilmiştir.

Anahtar Kelimeler: Yoğunluk Fonksiyoneli Teoremi (YFT), Geçiş Metali Topakları, Nadir Toprak Elementleri, Kobalt, Samaryum

To my family...

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DFT	Density Functional Theory
SCF	Self Consistent Field
ECP	Effective Core Potential (pseudopotential)
Xα	A local density method, α is a parameter
GGA	Generalized Gradient Approximation
LDA	Local Density Approximation
LSDA	Local Spin Density Approximation
XC	Exchange–Correlation
HF	Hatree–Fock
RHF	Restricted Hartree–Fock
HFS	Hatree–Fock–Slater
HFB	Hatree–Fock–Becke
LYP	Lee–Yang–Parr
PBE	Perdew–Burke–Ernzerhof
PW	Perdew–Wang
mPW	Modified Perdew–Wang

CHAPTER 1

INTRODUCTION

In industry and technology, the applications of transition metal (TM)–rare earth (RE) alloys, offer a significant amount of research opportunities, since they have remarkably high magnetocrystalline anisotropy which causes a large coercivity [1]. For the scope of the present study samarium (Sm)–cobalt (Co) alloys have been chosen. In order to try, for the first time to the best of our knowledge, to give an insight into the building blocks of the Sm-Co system, we investigate its smallest microclusters, namely Sm, Co, Sm_2, Co_2, SmCo, Sm_3, Co_3, Sm_2Co, and $SmCo_2$.

1.1 Sm-Co Systems

In the literature, some binary alloys of Sm and Co are available in different phases. These are $SmCo_2$, $SmCo_3$, $SmCo_5$, Sm_2Co_7, Sm_2Co_{17}, Sm_3Co, Sm_5Co_2, Sm_5Co_{19}, and Sm_9Co_4 which have been investigated by many researchers from several fields [1, 2]. Especially, $SmCo_5$ and Sm_2Co_{17} are of great importance, since they are known to belong to the strongest permanent magnet class. In the room temperature, their magnetocrystalline anisotropy constant is of the order of 10^7 J/m^3 [3–6]. The Curie temperature of these alloys are very high that give them an advantage over other magnets in the same category for high temperature applications. In addition, coercivities of these magnets are very high, which means that they cannot be demagnetized easily [7].

Because of these high magnetocrystalline anisotropy, coercivity, and high Curie temperature, Sm-Co alloys have an important place in many applications; examples are high-performance permanent magnets [4, 8], high-density data storage media [5, 8], high performance thin films

[5, 7], and high-resolution nuclear magnetic resonance spectroscopy [9].

The scope of the present study comprises the ground state investigations of Cobalt and Samarium atoms, their dimers (Co_2, Sm_2, and SmCo), and trimers (Co_3, Sm_3, $SmCo_2$, and Sm_2Co). These investigations will also contain some spectroscopic and electronic properties of the atoms and their compounds.

1.2 Transition Metals

Transition metals have unfilled d-subshells or easily give rise in ions with incomplete d-subshells. They have relatively small atomic radii, so that they have strong atomic bonds. On this account, TMs have high densities and high melting and boiling points. Since the electrons in d-subshells are loosely bounded, they exhibit high electrical and heat conductivity and malleability. Another valuable property of TMs is that they show a wide range of oxidation state because their valence electrons are usually distributed more than one subshell. The compounds of TMs are mostly paramagnetic because of their incompletely filled d-subshells [10–12].

Another important point about TMs is their orbital energies. It is known that the energy of the 4s orbital is lower than that of the 3d orbitals. Thus, it might be expected that when forming a compound TM will lose its electron from its more energetic 3d-subshell. But this is not true because electrons are first lost from its 4s-subshell [12]. Therefore, the electron configuration of Co^{2+} ion is $[Ar]\ 3d^7$ instead of $[Ar]\ 3d^5 4s^2$. The reason of this situation can be explained by the stability of the orbitals that 3d-subshells are more stable than 4s-subshells in TM ions [10].

1.3 Rare Earth Elements (Lanthanides)

Rare earth elements are the series of elements which have atomic numbers 57 through 71. Except lutetium (a d-block element with atomic number 71), RE elements are f-block elements, in other words, their 4f-orbitals are gradually filled. The history of these elements do not date back so long, until their analysis with the help of x-ray spectra in 1907, they could not be grouped or placed in the periodic table correctly [13]. Rare earth elements also known as

inner transition metals, although they differ from TMs in various features. For example, REs are more reactive than TMs; they do not form multiple bonds like TMs, etc. [10, 11, 13, 14].

Compounds of the RE elements are generally ionic and most of them are strongly paramagnetic. They have high melting and boiling points in accordance with TMs. They are relatively soft metals and their hardness increases with increasing atomic number. The coordination number of REs are high, generally 8 or 9 [13].

Rare earth elements are located in 5d-block of the periodic table and their electron configuration is generally written as $[Xe]6s^2 4f^n 5d^0$. Lanthanium, cerium, gadolinium, and lutetium have exceptional electron configurations of the form $[Xe]6s^2 4f^n 5d^1$. The energy spacing of the 5d- and 4f-orbitals are very close, so that for some configurations electron enters into the 5d-orbital instead of staying at the expected 4f-orbital. For instance, gadolinium has $[Xe]6s^2 4f^7 5d^1$ because it gains extra stability from the half-filled subshell 5d. Another similarity between REs and TMs is about forming the positive ions. Electrons are lost first from 6s and 5d, instead from 4f. As a result, all the 3+ ions have the configuration $[Xe]4f^n$ [10,11,13].

Rare earths have many scientific and industrial uses. For instance, their compounds are utilized as catalysts in the production of petroleum and some synthetic products. They are essential in lamps, lasers, magnets, phosphors, motion picture projectors, and x-ray intensifying screens [13]. As a result, it is not surprising at all that there have been innumerably many researches carried out nowadays trying to explore the chemical and physical properties of REs, and their possible industrial applications. The present study is such a small example to this end.

CHAPTER 2

DENSITY FUNCTIONAL THEORY

Density functional theory (DFT) brought a fresh breath to physics and chemistry in 60s. Number of studies about the field increased rapidly at 80s and now reach to a huge number [15]. The new approach that brings DFT such popularity is its basis on electron density instead of wave function. In other words, DFT provides an alternative computational method to examine many body systems such as atoms, molecules or larger systems, for which it is impossible to obtain exact solution of the Schrödinger equation.

2.1 Theoretical Background

Many information about any molecular system can be obtained from the solution of time-independent non-relativistic wave function, $\psi(\vec{x_1}, ..., \vec{x_N})$. To obtain the wave function, time-independent Schrödinger equation has to be solved.

$$\hat{H}\Psi_e = E_e\Psi_e \tag{2.1}$$

In computational physics, we focus on atoms, molecules, and solids, on their structural and cohesive properties, and on how they interact with each other. For an M-nuclei and N-electrons system the Hamiltonian is given by,

$$\hat{H} = -\frac{1}{2}\sum_{i=1}^{N}\left(\nabla_i^2\right) - \frac{1}{\mathbf{M_A}}\sum_{A=1}^{M}\left(\nabla_A^2\right) - \sum_{i=1}^{N}\sum_{A=1}^{M}\frac{Z_A}{\mathbf{r_{iA}}} + \sum_{A=1}^{M}\sum_{A<B}^{M}\frac{Z_A Z_B}{\mathbf{R_{AB}}} + \sum_{i=1}^{N}\sum_{i<j}^{N}\frac{1}{\mathbf{r_{ij}}}, \tag{2.2}$$

where r_{iA} is the distance between electrons and the nuclei, R_{AB} indicates distance between each nuclei, and r_{ij} is distance between each electrons. The first term indicates total kinetic

energy of electrons and the second term indicates kinetic energy of the nuclei. Next three are the potential energy terms, based on the Coulombic interactions. First potential term due to interaction among nuclei and electrons, second one due to nucleus–nucleus interaction and the last one electron–electron interaction [16–18].

It is well known that the electrons are very tiny particles with respect to nuclei. As an approximation we can assume that the nuclei move much more slowly than electron. Now, only related terms are the kinetic energy term of electrons with electron-electron and electron-nuclei interaction of the potential terms. The effect of all nuclei can be written as an external potential exerted on ith electron:

$$V_{ext}(\vec{r}) = -\sum_{i} \frac{Z_i}{|\vec{r} - \vec{r}_i|}. \tag{2.3}$$

At least the Hamiltonian of the N-electron system reduces to;

$$\hat{H} = -\frac{1}{2}\sum_{i=1}^{N}\left(\nabla_i^2\right) + \sum_{i=1}^{N} V_{ext}(\vec{r}_i) + \sum_{i=1}^{N}\sum_{j>i}^{N} \frac{1}{\mathbf{r_{ij}}}. \tag{2.4}$$

As the solution of Schrödinger equation for many particle system, we obtain a many body wave functions;

$$\Psi = \Psi\left(\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_N\right). \tag{2.5}$$

It is not possible to solve Schrödinger equation exactly for many body systems because the eigen function depends on 3N position coordinates. We need to use some approximation methods to overcome the problem and attain the solution. One of the simplest examples of these approaches is Hartree Fock method.

2.2 Hartree–Fock Method

The assumption is that the wavefunctions of the electrons are written as a product of N orthonormal spin orbitals $\psi_i(\vec{x}_i)$, as if they do not interact with each other. Each spin orbital is assumed to be a combination of spatial orbital $\phi_i(\vec{r})$ and a spin function $\sigma(\mathbf{s})$. Since we deal with fermions, there are only two types of spin function, spin up $\alpha(\mathbf{s})$ or spin down $\beta(\mathbf{s})$.

The Hartree product which is the simplest application to a many-body wave function can be written as,

$$\Psi = \psi_1(\vec{r}_1)\,\psi_2(\vec{r}_2)\cdots\psi_N(\vec{r}_N)\,. \tag{2.6}$$

The Hartree product does not satisfy some properties of a fermionic wave function, i.e. the antisymetry principle. If the product written as Slater determinant, single electron wave functions can be stated to obtain N-electron wavefunction satisfying the antisymetry principle [19–21]. For N electrons, the Slater determinant is

$$\psi(\vec{x}_1,\vec{x}_2,\ldots,\vec{x}_N) = \frac{1}{\sqrt{N!}}\begin{vmatrix} \psi_1(\vec{x}_1) & \psi_2(\vec{x}_1) & \cdots & \psi_N(\vec{x}_1) \\ \psi_1(\vec{x}_2) & \psi_2(\vec{x}_2) & \cdots & \psi_N(\vec{x}_2) \\ \vdots & \vdots & & \vdots \\ \psi_1(\vec{x}_N) & \psi_2(\vec{x}_N) & \cdots & \psi_N(\vec{x}_N) \end{vmatrix}. \tag{2.7}$$

Another advantage of the Slater determinant is satisfying the Pauli exclusion principle. If the single electron wave functions of two or more electrons are same, it vanishes. This result is in accordance with the claim of exclusion principle that the two electrons can not be located to same orbital with the same spin. As a solution of the Schrödinger equation, Slater determinant includes exchange term however Hartree Fock method does not describe electron interaction, so correlation term. It is well known that electrons are interacting, so HF method does not fulfill the solution of the Schrödinger equation, on the other hand DFT calculations are similar to the HF calculations in some ways [15].

2.3 Electron Density

As stated above, exact solution of the Schrödinger equation is hard to achieve. The electron density is an important quantity for a given state, since it provides an alternative solution method instead of wave function. The electron density for an electronic system, can be defined as the number of electrons in the infinitesimal volume element $d\vec{r}$ and denoted by $\rho(\vec{r})$. In terms of the wave function, the electron density is,

$$\rho(\vec{r}) = N\int\ldots\int|\psi(\vec{x}_1,\vec{x}_2,\ldots,\vec{x}_N)|^2 ds_1 d\vec{x}_2\ldots d\vec{x}_N. \tag{2.8}$$

By the definition, integration over all space of electron density gives the total number of electrons.

$$\int\rho(\vec{r})d\vec{r} = N. \tag{2.9}$$

The many body wave functions has 3N spatial coordinates, whereas by using electron density it can be decreased to only three variables. If all the energy terms can be written in terms of electron density, there is no need to use wave funtions.

2.4 The Hohenberg–Kohn Theorem

The DFT lays the foundations especially by the theorem of the Hohenberg and Kohn published in 1964 [22]. As mentioned before, to obtain the observables of any system, we need to solve Schrödinger equation. For an N–electron system, the external potential $V_{ext}(\vec{r})$ determines the hamiltonian, given by Eqn. 2.4, by this means determine all the electronic properties of a system with N electrons.

Hohenberg and Kohn brought a new approach that the external potential $V_{ext}(\vec{r})$ could be determined by the electron density. The first Hohenberg-Kohn theorem provides a simple proof to show that the external potential $V_{ext}(\vec{r})$ is uniquely determined by $\rho(\vec{r})$ [22]. Since external potential fixes the Hamiltonian, the full many particle system can be expressed as a functional of electron density $\rho(\vec{r})$ [17].

The total energy is expressed with respect to electron density,

$$E[\rho] = T[\rho] + V_{ne}[\rho] + V_{ee}[\rho] = \int \rho(\mathbf{r})\, v(\mathbf{r})\, d\mathbf{r} + F_{HK}[\rho], \tag{2.10}$$

with Hohenberg–Kohn functional,

$$F_{HK}[\rho] = T[\rho] + V_{ee}[\rho], \tag{2.11}$$

which includes $T[\rho]$, the kinetic energy of the real system and $V_{ee}[\rho]$ is the potential energy of the electron–electron interactions. The functional for the electron–electron interaction is given as

$$V_{ee}[\rho] = J[\rho] + \text{nonclassical term}, \tag{2.12}$$

where $J[\rho]$ is the well known classical Coulombic electrostatic interactions between the electrons,

$$J[\rho] = \frac{1}{2} \int \int \frac{\rho(\mathbf{r})\ \rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}\, d\mathbf{r}\, d\mathbf{r}', \tag{2.13}$$

and the nonclassical term includes all self interaction correction effects, exchange and Coulomb correlation. It is not surprising that $F_{HK}[\rho]$ is the major problem in DFT, which consists of completely or partly unknown $T[\rho]$ and $V_{ee}[\rho]$ functionals.

The second theorem of the Hohenberg–Kohn is about to provide an electron density that minimizing the total energy $E[\rho]$. It is well known that only ground state electron density satisfies the ground state energy. This theorem specifies that to obtain ground state energy, true ground state electron density has to be searched by variatonal principle,

$$E_0 \leq E[\tilde{\rho}] = T[\tilde{\rho}] + V_{ne}[\tilde{\rho}] + V_{ee}[\tilde{\rho}]. \tag{2.14}$$

For any trial density $\tilde{\rho}(\vec{r})$, there are necessary boundary conditions which has to be satisfied, such as

$$\tilde{\rho}(\vec{r}) \geq 0, \tag{2.15}$$

and

$$\int \tilde{\rho}(\vec{r}) d\vec{r}_1 = N. \tag{2.16}$$

The proof of the second Hohenberg–Kohn theorem is obtained by using the variational principle to form ground state wave function [23] and can be found in various sources about the theorem.

2.5 The Kohn–Sham Method

After Hohenberg–Kohn theorem, another massive and the most powerful brick was put on the wall by Kohn–Sham in 1965 [24]. The Kohn–Sham method suggests a way to obtain kinetic energy in terms of electron density. We start with variational principle one more time, $E[\rho]$ and the ground state density need to satisfy the equation;

$$\delta \left(E[\rho] - \mu \left[\int \rho(\vec{r}) d\vec{r} - N \right] \right) = 0, \tag{2.17}$$

where μ is the Langrange multiplier related to obtain density for acquiring the correct number of electrons N. μ associated with the chemical potential and following equation is obtained by differentiation of functional,

$$\mu = \frac{\delta E[\rho]}{\delta \rho(\vec{r})} = V_{ext}(\vec{r}) + \frac{\delta F_{HK}[\rho(\vec{r})]}{\delta \rho(\vec{r})}. \tag{2.18}$$

If the exact form of $F_{HK}[\rho(\vec{r})]$ can be obtained, ground state electron density is also acquired by Eqn. 2.17. The main point here is to determine $F_{HK}[\rho(\vec{r})]$ which is equal to $T[\rho(\vec{r})]$, for

non-interacting electrons, but T is also unknown. The kinetic energy term is written for an N–electron non-interacting reference system as following

$$T = \sum_{i}^{N} n_i \left\langle \psi_i \right| - \frac{1}{2}\nabla_i^2 \left| \psi_i \right\rangle , \tag{2.19}$$

where ψ_i are spin orbitals and n_i are the corresponding occupation numbers. All physically accepted densities of the non-interacting N-electron system can be expressed as

$$\rho(\mathbf{r}) = \sum_{i}^{\infty} n_i \sum_{s} \left| \psi_i(\mathbf{r}, s) \right|^2 \tag{2.20}$$

The valuable part of this theorem is the simplification of these equations by assuming $n_i = 1$ for N orbitals and $n_i = 0$ for the remaining. The equations reduce to

$$T_s = \sum_{i}^{N} \left\langle \psi_i \right| - \frac{1}{2}\nabla_i^2 \left| \psi_i \right\rangle \tag{2.21}$$

and

$$\rho(\mathbf{r}) = \sum_{i}^{N} \sum_{s} \left| \psi_i(\mathbf{r}, s) \right|^2 \tag{2.22}$$

The following Hamiltonian of N–noninteracting electrons is obtained

$$\hat{H}_S = -\frac{1}{2}\sum_{i=1}^{N} \nabla_i^2 + \sum_{i=1}^{N} V_S(\vec{r}_i) \tag{2.23}$$

without electron–electron repulsion terms and with exact ground state density ρ.

The exact determinantial wave function of the system is

$$\Psi_s = \frac{1}{\sqrt{N!}} \left| \psi_1 \, \psi_2 \, \ldots \psi_N \right| , \tag{2.24}$$

where ψ_i reflects the N lowest eigenstates of the one electron Hamiltonian h_s;

$$h_s \, \psi_i = \left[-\frac{1}{2}\nabla^2 + V_s(\mathbf{r}_i) \right] \psi_i = \varepsilon_i \, \psi_i. \tag{2.25}$$

Now, the kinetic energy functional turns to

$$T_s[\rho] = \sum_{i}^{N} \left\langle \Psi_s \right| - \frac{1}{2}\nabla_i^2 \left| \Psi_s \right\rangle . \tag{2.26}$$

For isolating kinetic energy term, we write $F[\rho]$ again as,

$$F[\rho] = T_s[\rho] + J[\rho] + E_{xc}[\rho] \tag{2.27}$$

where

$$E_{xc}[\rho] = T[\rho] - T_s[\rho] + V_{ee}[\rho] - J[\rho]. \tag{2.28}$$

The $E_{xc}[\rho]$ is known as exchange-correlation energy and in definition it originates by the difference between $T[\rho]$ and $T_s[\rho]$ and the non-classical part of the potential energy of electron-electron interaction.

Now, let us turn to Euler equation again, that becomes

$$\mu = v_{\text{eff}}(\mathbf{r}) + \frac{\delta T_s[\rho]}{\delta \rho(\mathbf{r})}, \tag{2.29}$$

where the effective potential is,

$$v_{\text{eff}}(\mathbf{r}) = v(\mathbf{r}) + \frac{\delta J[\rho]}{\delta \rho(\mathbf{r})} + \frac{\delta E_{xc}[\rho]}{\delta \rho(\mathbf{r})} = v(\mathbf{r}) + \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}\, d\mathbf{r}' + v_{xc}(\mathbf{r}), \tag{2.30}$$

where the exchange–correlation potential define as,

$$v_{xc}(\mathbf{r}) = \frac{\delta E_{xc}[\rho]}{\delta \rho(\mathbf{r})}. \tag{2.31}$$

We still try to obtain the explicit form of $T_s[\rho]$. We can rewrite Eqn. 2.25 by replacing V_s with V_{eff} given in Eqn. 2.30;

$$[-\frac{1}{2}\nabla^2 + v_{\text{eff}}(\mathbf{r})]\psi_i, = \varepsilon_i\, \psi_i \tag{2.32}$$

and the following expression can be obtained for electron density given by Eqn.2.22.

The procedure begins with a trial density, than V_{eff} is obtained by Eqn.2.30, and then one finds a new electron density by using Eqn.2.22 and Eqn.2.32. The total energy can be computed as,

$$E = \sum_i^N \epsilon_i - \frac{1}{2} \int \int \frac{\rho(\mathbf{r})\, \rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}\, d\mathbf{r}\, d\mathbf{r}' + E_{xc}[\rho] - \int v_{xc}(\mathbf{r})\, \rho(\mathbf{r})\, d\mathbf{r}, \tag{2.33}$$

where

$$\sum_i^N \epsilon_i = \sum_i^N \langle \psi_i | - \frac{1}{2}\nabla^2 + v_{\text{eff}}(\mathbf{r})\, |\psi_i\rangle = T_s[\rho] + \int v_{\text{eff}}(\mathbf{r})\, \rho(\mathbf{r})\, d\mathbf{r}. \tag{2.34}$$

2.6 Exchange-Correlation Functionals

There are dozens of functionals developed and used, particularly for calculations with isolated molecules. Some of the widely used exchange functionals are Becke's 1988 functional **B** [25],

Perdew and Wang's 1991 functional **PW91** [26], and Perdew, Burke and Ernzerhof's 1996 functional **PBE** [27] which are also the components of the functionals that used in previous study. Similarly, correlation functional of Lee, Yang, and Parr **LYP** [28], Perdew and Wang's gradient-corrected correlation functional **PW91** [26, 27], and Perdew, Burke, and Ernzerhof's correlation function **PBE** [27] constitude the functionals of used methods. The combinations of these functionals and similar ones are used to form methods for DFT calculations.

It is necessary to specify what functional was used in any particular calculation because different functionals will give somewhat different results for any particular configuration of atoms. In the scope of previous study 13 DFT methods have been used and only one of them, HFB is an only exchange functional, the remaining 12 are hybrid functionals. HFB is named by Hartre–Fock–Becke, important for the study since it will reflect the contribution of the correlational effects by distinction from other methods.

Hybrid Functionals

The hybrid functionals includes both exchange–correlation affect, with the exact exchange from Hartree-Fock theory and changing proportion of exchange and correlation effects from other sources. The explanations about these methods can be listed as follows.

- B1LYP: It is one parameter hybrid density functional that was designed by Becke in 1996 [29]. The form of the functional is

$$E_{XC} = E_{XC}^{DFT} + a_0(E_X^{HF} - E_X^{DFT}), \tag{2.35}$$

  where a_0 takes a value in the range of 0.16-0.28 and changes according to the chosen correlation functional [30].

- B3P86: An example of hybrid functional with three parameters. The following equation was developed;

$$E_{XC} = E_{XC}^{LSDA} + a_0(E_X^{HF} - E_X^{LSDA}) + a_x\Delta E_X^{B88} + a_c\Delta E_C^{P86}, \tag{2.36}$$

  where a_0, a_x, and a_c are the parameters were determined by fitting to the G1 database which is a set of thermochemical data and obtained as 0.20, 0.72, and 0.81 a.u. respectively [29, 31].

- B3LYP: It is also a three parameters hybrid functional which uses Eqn.2.36 with the LYP correlation functional in stead of the P86 functional [25, 28].

- B3PW91: This method also uses Eqn.2.36 with the PW91 correlation functional [32].

  The following three methods are the revisions of Becke's 1997 functional τ dependent gradient-corrected correlation functional, defined as part of this one parameter hybrid functional [33].

- B98: The revision of Becke's B97 functional in 1998 [34].

- B971: The revision of B97 by Handy, Tozer, and co-workers in 1998 [35].

- B972: Another modification of B97 by Wilson, Bradley, and Tozer in 2001 [36].

- PBE1PBE: The PBE functional is a modification of PW91 correlation functional, which can satisfy only significantly energetic conditions, unlike PW91 which is for all exact conditions [30]. The one parameter combination of functionals form this method and the parameter is not empirical [27]. PBE1PBE method gives appropriate results for electronic, magnetic, and vibrational properties of molecules in comparison to other functionals with extensive parametrization [37].

- mPW1PW91: It includes the modification of PW exchange functional by Adamo and Barone [38]. Similar to PBE1PBE, it also gives satisfactory results by combining one parameter approach.

- O3LYP: Similar to B3LYP, O3LYP also a three-parameter functional and the parameters were defined by Cohen and Handy [39].

  Half and half functionals use a combination that includes equal ratio of DFT and exact exchange energies.

- BHandH: The related equation of the functional is,

$$0.5E_X^{HF} + 0.5E_X^{LSDA} + E_C^{LYP}. \tag{2.37}$$

- BHandHLYP: Similarly, the equation of the funtional is as follows,

$$0.5E_X^{HF} + 0.5E_X^{LSDA} + 0.5\Delta E_X^{Becke88} + E_C^{LYP}. \tag{2.38}$$

- HFB: As mentioned before, the method named from Hartre–Fock–Becke and does not include correlational functional. Namely, it is Becke's 1988 functional that also contains the Slater exchange with the gradient of the density [25]. It was chosen to determine the affect of correlation in comparison to other methods.

CHAPTER 3

RESULTS AND DISCUSSION

The calculation part of the present study consists of three main sets. The first of these sets includes calculations of minimum energy values with corresponding multiplicity values of cobalt and samarium atoms and their ions. Out of curiosity, we also wondered if the DFT methods we used are successful in spotting the correct multiplicity values for Co and Sm elements and their cations and anions. To this end, we have carried out some further atomic calculations for Co^{1+}, Co^{2+}, Co^{3+}, Co^{1-}, Sm^{1+}, Sm^{2+}, Sm^{3+}, and Sm^{1-}. The second set includes calculations of SmCo, Sm_2, and Co_2 dimers in the same way and single-point (sp) self-consistent field calculations (SCF) were performed. The third set includes Co_3, Sm_3, $SmCo_2$, and Sm_2Co trimers calculations. All parts have been carried out by 13 DFT methods to control their usefulness and convenience. In the scope of this study 38.000 calculations have been achieved.

At the begining, it will be essential to point out that the present study is based on a pre-study that has been covered the calculations about samarium (Sm) and cobalt (Co) elements and SmCo by using 21 DFT methods [5]. The idea of the previous study was the determination of the well-behaved and useful methods; which give appropriate results for Co and Sm atoms and SmCo dimer, so that they might also work properly for the higher order alloys of these atoms. As a conclusion, it was claimed that the only exchange functionals and the standalone functionals cannot fulfill the sufficient performance although hybrid functionals usually show great success [5]. According to this conclusion, 13 hybrid functionals have been chosen and calculations were performed by them in the scope of present study. The common purpose of both studies is forming preknowledge for investigation of higher order Sm–Co alloys.

In this chapter of the study, calculated spectroscopic constants (binding energy D_e, equilib-

rium interatomic separation r_e, and fundamental frequency w_e) of the dimers and trimers, the minimum energy configurations of the trimers (bond lengths and bond angle, as well as their fundamental frequencies wn) are reported. For all the microclusters considered, the possible dissociation channels and the corresponding dissociation energies, the calculated HOMO (highest occupied molecular orbital), LUMO (lowest unoccupied molecular orbital), and HOMO–LUMO gap energies are presented. The calculated dipole moments and excess charges on the atoms of the trimers are also given.

The structure of higher order clusters of transition metals are generally investigated experimentally by photoelectron spectroscopy or chemical probe experiments [40,41]. Due to these familiar methodologies it is possible to find information in the literature about higher order clusters, unfortunately this is not the case for smaller ones. This is why small clusters of transition metals still have not been well identified. At this point of view, it is clear that the theoretical studies come into prominence.

The present work exhibits the results of density functional theory calculations within the effective core potential (ECP) level, for small Sm-Co clusters up to trimers. The DFT calculations were carried out by using the GAUSSIAN 03 package [42]. For this study, the basis Cep-121G has been prefered and used for all calculations. Alternatively, UGBS and SDD would be used as basis, however much more works and effort will be needed for SDD, and UGBS has not been attempted.

3.1 Co and Sm Atoms

3.1.1 Calculations of Co Atoms

Co atom has 27 electrons and the electron configuration of the Co atom is $[Ar]3d^7 4s^2$. There are three unpaired electrons in the 3d orbital, so its expected multiplicity is four (by the formula 2S+1). For the sake of thoroughness we searched self consistent energies for all possible values of the multiplicity, from 2 to 18. These results are demonstrated in the Table 3.1. The first step is to control the methods which give the expected multiplicity value, can be controlled by corresponding total energy if it is minimum or not. Only nine of the methods give multiplicity value four for the minimum total energy. These methods are B1LYP, B3LYP, B3P86, B971, B98, BHandHLYP, HFB, O3LYP, and PBE1PBE. For other four methods,

the minimum energy values noted for $m = 2$. These are B3PW91, B972, BHandH, and MPW1PW91.

For values of m between 6 and 18, energies calculated using all methods increase monotonically with m. The difference between E_{10} and E_{12} is remarkably greater than the others, because there are nine electrons in the outer shells of the Co atom, except than the nearest noble gas (Ar) configuration. To obtain E_{12}, the electron from close shell configuration has to be excited that needs much more energy than the other outer-shell electrons.

At the end of the discussion about Co atom, we should claim that the functionals, B3PW91, B972, BHandH, and MPW1PW91 are the controversial functionals, and the remaining nine functionals (with minimum E_4 value) can be marked as the suitable functionals. The evaluation of the results continues by ions of Co atom. The expected electron configurations and the corresponding multiplicity values for Co are as the following: Co^{1+}: [Ar] $3d^7$ $4s^1$, $m = 5$; Co^{2+}: [Ar] $3d^7$, $m = 4$; Co^{3+}: [Ar] $3d^6$, $m = 5$; and Co^{1-}: [Ar] $3d^8$ $4s^1$, $m = 3$. Tables 3.2–3.5 tabulate the total energies for the all possible multiplicities, of course, in accord with the number of electrons used by GAUSSION03.

As is seen from Table 3.2, only B3PW91, BHandH, BHandHLYP, HFB, and MPW1PW91 have ended up with the correct multiplicity value $m = 5$ for Co^{1+}. All the others have spotted the $m = 3$ energies as their minima, which is logically unexplainable. Fortunately, the energy differences ΔE_{5-3} between E_5 and E_3 values for the cases in which $m = 5$ is not spotted as the minimum are always so small, at most 0.026 Hartrees for B3P86. What we want to say is that the incorrect results are not as bad as they look, for GAUSSIAN package have originally been designated for the ground-states of elements and/or molecules, not for excited states.

Now comes the interesting, and equally surprising part of the story. If we look at the corresponding situations for Co^{2+}, Co^{3+}, Co^{1-} from Tables 3.3, 3.4, and 3.5, respectively, all the 13 DFT methods have flawlessly resulted in the correct multiplicity values for the minimum energies: $m = 4$ for Co^{2+} and $m = 5$ for Co^{3+}. A quick glance at Tables 3.3–3.5 reveals that there exists always a definite pattern in energy values from the smallest to highest multiplicity values: they have only one minimum and that minimum is the correct one; put in another way, there is no fluctuation in energy values as we have witnessed previously in Co and Co^{1+} tables.

Table3.1: Total energies, E_m, in Hartrees, for a Co atom for different multiplicities, m $(2S+1)$. The starred ones show the lowest energy.

method	$-E_2$	$-E_4$	$-E_6$	$-E_8$	$-E_{10}$	$-E_{12}$	$-E_{14}$	$-E_{16}$	$-E_{18}$
B1LYP	145.0030	145.0132*	144.9096	144.6152	144.1686	141.1180	137.6516	133.8410	128.4115
B3LYP	145.1134	145.1244*	145.0147	144.7172	144.2683	141.2179	137.7551	133.9518	128.5384
B3P86	145.4932	145.5072*	145.3901	145.1187	144.6658	141.6178	138.1715	134.3714	129.0535
B3PW91	145.1410*	145.1409	145.0533	144.7809	144.3313	141.2912	137.8531	134.0831	128.7404
B971	145.0425	145.0665*	144.9369	144.6505	144.1864	141.1359	137.6889	133.9122	128.5915
B972	145.2484*	145.2443	145.1342	144.8514	144.3931	141.3251	137.8715	134.0965	128.7823
B98	145.0828	145.1068*	144.9791	144.6943	144.2310	141.1827	137.7371	133.9606	128.6327
BHandH	144.5442*	144.5432	144.4701	144.2183	143.7920	140.7446	137.2904	133.4822	128.1243
BHandHLYP	144.9438	144.9525*	144.8712	144.5948	144.1651	141.1081	137.6382	133.8326	128.4049
HFB	144.4087	144.4330*	144.3401	144.0880	143.6643	140.6998	137.3359	133.6450	128.4204
MPW1PW91	145.1156*	145.1153	145.0339	144.7652	144.3189	141.2794	137.8426	134.0733	128.7404
O3LYP	145.2852	145.2965*	145.1795	144.8936	144.4298	141.3670	137.9078	134.1159	128.7118
PBE1PBE	145.0443	145.0576*	144.9612	144.6939	144.2493	141.2115	137.7772	133.9877	128.6859

Table3.2: Similar to Table 3.1 for Co^{1+}.

method	$-E_1$	$-E_3$	$-E_5$	$-E_7$	$-E_9$	$-E_{11}$	$-E_{13}$	$-E_{15}$	$-E_{17}$
B1LYP	144.6309	144.7330*	144.7254	144.3903	143.8654	141.0078	137.5239	133.7030	128.2480
B3LYP	144.7357	144.8366*	144.8251	144.4862	143.9586	141.1015	137.6209	133.8068	128.3670
B3P86	145.0950	145.2020*	145.1756	144.8520	144.3288	141.4806	138.0156	134.2264	128.8496
B3PW91	144.7628	144.8562	144.8603*	144.5306	144.0137	141.1724	137.7159	133.9341	128.5570
B971	144.6836	144.7771*	144.7533	144.4095	143.8756	141.0241	137.5580	133.7694	128.4146
B972	144.8879	144.9765*	144.9534	144.6109	144.0834	141.2164	137.7440	133.9532	128.6032
B98	144.7220	144.8167*	144.7940	144.4511	143.9182	141.0699	137.6052	133.8166	128.4544
BHandH	144.1818	144.2751	144.2882*	143.9789	143.4876	140.6388	137.1676	133.3591	127.9389
BHandHLYP	144.5790	144.6837	144.6865*	144.3682	143.8598	141.0012	137.5145	133.6890	128.2421
HFB	nc	144.1503	144.1599*	143.8538	143.3651	140.5865	137.2044	133.5020	128.2544
MPW1PW91	144.7388	144.8343	144.8410*	144.5018	144.0013	141.1615	137.7060	133.9252	128.5578
O3LYP	144.9195	145.0203*	144.9950	144.6518	144.1212	141.2563	137.7779	133.9701	128.5365
PBE1PBE	144.6674	144.7781*	144.7698	144.4317	143.9332	141.0938	137.6408	133.8644	128.4812

Table3.3: Similar to Table 3.1 for Co^{2+}.

method	$-E_2$	$-E_4$	$-E_6$	$-E_8$	$-E_{10}$	$-E_{12}$	$-E_{14}$	$-E_{16}$
B1LYP	144.0025	144.1012*	143.8917	143.2966	140.3619	137.1811	133.2990	127.7709
B3LYP	144.0961	144.1934*	143.9819	143.3833	140.4488	137.2708	133.3960	127.8827
B3P86	144.4369	144.5283*	144.3250	143.7273	140.7995	137.6365	133.7860	128.3357
B3PW91	144.0985	144.2335*	144.0226	143.4320	140.5117	137.3560	133.5134	128.0629
B971	144.0931	144.1441*	143.9126	143.3035	140.3726	137.2025	133.3534	127.9268
B972	144.2206	144.3514*	144.1155	143.5123	140.5649	137.3883	133.5415	128.1143
B98	144.0944	144.1817*	143.9515	143.3435	140.4154	137.2484	133.4000	127.9652
BHandH	143.5393	143.6758*	143.4830	142.9189	139.9914	136.8304	132.9800	127.5053
BHandHLYP	143.9684	144.0730*	143.8689	143.2893	140.3532	137.1729	133.2909	127.7835
HFB	143.4839	143.5405*	143.3614	142.8011	139.9462	136.8601	133.0982	127.8006
MPW1PW91	144.0802	144.2174*	144.0072	143.4203	140.5014	137.3470	133.5054	128.0644
O3LYP	144.3133	144.3761*	144.1536	143.5500	140.6057	137.4247	133.5611	128.0690
PBE1PBE	144.0374	144.1474*	143.9388	143.3542	140.4358	137.2832	133.4460	128.0120

Table3.4: Similar to Table 3.1 for Co^{3+}.

method	$-E_1$	$-E_3$	$-E_5$	$-E_7$	$-E_9$	$-E_{11}$	$-E_{13}$	$-E_{15}$
B1LYP	142.6897	142.7386	142.8568*	142.4395	139.4134	136.1416	132.6207	127.0347
B3LYP	142.7738	142.8217	142.9391*	142.5198	139.4935	136.2242	132.7097	127.1389
B3P86	143.0897	143.1550	143.2689*	142.8406	139.8184	136.5620	133.0711	127.5606
B3PW91	142.7392	142.8567	142.9857*	142.5648	139.5507	136.3022	132.8182	127.3079
B971	142.7540	142.7928	142.8946*	142.4480	139.4234	136.1598	132.6649	127.1799
B972	142.8627	142.9739	143.1074*	142.6581	139.6162	136.3452	132.8524	127.3671
B98	142.7878	142.8709	142.9294*	142.4851	139.4629	136.2022	132.7094	127.2170
BHandH	142.2000	142.3201	142.4599*	142.0645	139.0436	135.7571	132.3076	126.7558
BHandHLYP	142.6652	142.7181	142.8447*	142.4316	139.4038	136.1317	132.6141	127.0300
HFB	142.1570	142.2544	142.3317*	141.9495	139.0034	135.8270	132.4180	127.0405
MPW1PW91	142.7235	142.8429	142.9728*	142.5541	139.5416	136.2943	132.8113	127.3112
O3LYP	142.9329	142.9954	143.1266*	142.6936	139.6558	136.3815	132.8737	127.3057
PBE1PBE	142.7108	142.7724	142.9059*	142.4904	139.4785	136.2329	132.7534	127.2599

Table3.5: Similar to Table 3.1 for Co^{1-}.

method	$-E_1$	$-E_3$	$-E_5$	$-E_7$	$-E_9$	$-E_{11}$	$-E_{13}$	$-E_{15}$	$-E_{17}$	$-E_{19}$
B1LYP	144.9423	145.0402*	144.9957	144.9027	144.6523	144.0943	141.0478	137.5836	133.7823	128.3710
B3LYP	145.0607	145.1574*	145.1069	145.0134	144.7602	144.1999	141.1535	137.6915	133.9002	128.5046
B3P86	145.4532	145.5551*	145.4981	145.4140	145.1759	144.6187	141.5726	138.1272	134.3731	129.0425
B3PW91	145.0784	145.1817*	145.1287	145.0572	144.8167	144.2656	141.2339	137.7944	134.0427	128.7107
B971	144.9922	145.0841*	145.0355	144.9325	144.6804	144.1125	141.0694	137.6249	133.8681	128.5563
B972	145.1903	145.2888*	145.2333	145.1278	144.8772	144.3165	141.2585	137.8119	134.0425	128.7422
B98	145.0344	145.1252*	145.0776	144.9763	144.7231	144.1585	141.1167	137.6728	133.9172	128.5986
BHandH	144.4746	144.5723*	144.5477	144.4624	144.2410	143.7137	140.6711	137.2260	133.4518	128.0274
BHandHLYP	144.8727	144.9738*	144.9514	144.8648	144.6323	144.0873	141.0369	137.5700	133.7694	128.3609
HFB	nc	128.3609*	144.3957	144.3318	144.1109	143.5932	140.6305	137.2773	nc	128.3808
MPW1PW91	145.0513	145.1533*	145.1126	145.0369	144.7993	144.2518	141.2169	137.7833	134.0326	128.7100
O3LYP	145.2221	145.3188*	145.2627	145.1738	144.9189	144.3545	141.2983	137.8493	134.0686	128.6750
PBE1PBE	144.9759	145.0820*	145.0415	144.9635	144.7275	144.1818	141.1480	137.7253	133.9711	128.6551

After the calculation of the anions and cations of Co atom, what naturally comes is the performances of the DFT methods in the prediction of the first, second, and third ionization energies and the (first) electron affinity of Co atom. In Table 3.6 are shown the calculated first ionization energies of Co for the process Co $\rightarrow$ $Co^{1+} + e^{-}$. The experimental value is 7.881 eV [43]. The calculations were performed following the recipe $IE_1 = E_5(Co^{1+}) - E_5(Co)$. (Similar calculations were performed for the other Co ions and for Sm ions.) First of all, the errors produced by the methods are not so large, usually acceptably reasonable. The biggest errors for IE_1 are seen for B3P86 and then for BHandH methods. The smallest ones are for B972, PBE1PBE, and B1LYP, which are all nearly zero. B3LYP needs more attention at this point because researchers usually believe that it is the best one among the other DFT methods. As we see from Table 3.6, its first ionization energy prediction is only about 3 percent; so that B3LYP deserves its fame. (In Tables 3.7 and 3.8 we see that the predictions of B3LYP are nearly zero and around 1 percent for the second and third ionization energies; solidifying further its glory.) We can speak well also of PBE1PBE and B1LYP methods. The former is also distinguished among the researchers for its prominent performances. As we notice from Tables 3.7—3.9, PBE1PBE have produced better results than expected for all kinds of ions of Co we considered in this work: the errors for all ionization energies and the electron affinity of Co are all nearly zero. If its results happen to be in this accuracy also for Sm, we would choose PBE1PBE method as the best and most appropriate method in studying all Sm-Co type clusters. As we will see shortly, this is not the case, unfortunately.

In Table 3.7 we show the results for the second ionization energies, for which the experimental value is 17.080 eV [43]. Here all the methods lead to very small errors; among them B1LYP, B3LYP, B3PW91, MPW1PW91, and PBE1PBE (as we mentioned above) have produced IE_2 with nearly zero errors. It is interesting to note also that HFB method, which does not include electron correlation energy in its formulation, have given somehow unexpectedly a result with about 1 percent error. The fact here that O3LYP method has generated a similar 1-percent error is also noticeable.

Some similar words can be said about the third ionization energy given in Table 3.8. The experimental value of IE_3 is 33.497 eV [43]. The results in this table are the best ones compared to the first and second ionization energies, for the errors here are so small: except B3P86, all are about 1 percent. BHandHLYP and PBE1PBE methods resulted in the best

Table3.6: The first ionization energy IE_1 of Co atom for the process IE_1+Co $\rightarrow$ $Co^{1+}+e^-$, calculated as $IE_1 = E_5(Co^{1+}) - E_4(Co)$. The experimental value is 7.881 eV [43]. Δ in the second column gives the error between the experimental and the calculated results; the last column is for the corresponding percentage error.

method	IE_1 (eV)	Δ (eV)	% error
B1LYP	7.831	0.050	0
B3LYP	8.147	0.266	3
B3P86	9.023	1.142	14
B3PW91	7.636	0.245	3
B971	8.522	0.641	8
B972	7.916	0.035	0
B98	8.512	0.631	8
BHandH	6.939	0.942	11
BHandHLYP	7.236	1.645	8
HFB	7.433	0.448	5
MPW1PW91	7.464	0.417	5
O3LYP	8.206	0.325	4
PBE1PBE	7.833	0.048	0

values.

Finally about Co atom is its electron affinity EA values for each method, which are listed in Table 3.9. The process to define EA is Co + e^- $\rightarrow$ Co^{1-} and the calculation were carried out according to the formula $EA = E_4(Co) - E_3(Co^{1-})$. (A similar calculation was done for the electron affinity of Sm element.) The experimental value EA of Co is 0.662 eV [43]. As we said previously, the best result has been produced by PBE1PBE nearly flawlessly. The other satisfactory results were from O3LYP, B1LYP, and BHandHLYP. All the other methods generated outcomes with much bigger errors. These are all expected. Notice that the three experimental ionization energies of Co are all on the order of 10. But its experimental electron affinity is on the order of only 1. In another words, ionization energies are roughly 10 times bigger than electron affinity value. The conclusion we may therefore draw vaguely is that it is very unlikely that we could reach an EA value as accurate as IE_i values for Co. As we shall witness below, the situation for the electron affinity of Sm is much worse than that for Co. Be prepared to see an error about 700 percent which was produced by PBE1PBE! What we want to say here that the zero error generated by PBE1PBE method is probably only an incident, so that should not be taken into account seriously.

Table3.7: The second ionization energy IE_2 of Co atom for the process $IE_2 + \mathrm{Co}^{1+} \rightarrow \mathrm{Co}^{2+} + e^-$, calculated as $IE_2 = E_4(\mathrm{Co}^{2+}) - E_5(\mathrm{Co}^{1+})$. The experimental value is 17.080 eV [43]. Δ in the second column gives the error between the experimental and the calculated results; the last column is for the corresponding percentage error.

method	IE_2 (eV)	Δ (eV)	% error
B1LYP	16.987	0.093	0
B3LYP	17.190	0.110	0
B3P86	17.613	0.533	3
B3PW91	17.055	0.025	0
B971	16.579	0.501	2
B972	16.380	0.700	4
B98	16.661	0.419	2
BHandH	16.666	0.414	2
BHandHLYP	16.694	0.386	2
HFB	16.854	0.226	1
MPW1PW91	16.970	0.110	0
O3LYP	16.839	0.241	1
PBE1PBE	16.936	0.144	0

3.1.2 Calculations of Sm Atoms

The discussion continues with 62-electrons Sm atom. The ground state electron configuration of Samarium is $[Xe]4f^6 6s^2$. It has 6 unpaired electrons in the 4f shell that causes expected multiplicity of 7. In accordance with Co atom, Sm also investigated in terms of self-consistent energy values and among all possible multiplicity values from 1 to 17 are indicated in the Table 3.10. It can be easily recognized, all methods give the minimum energy for multiplicity value 7.

Even when CEP-121G basis is used some of the calculations do not complete substantially since Sm is a large atom. Although there are some non-convergent results, all 13 functionals indicate perfect consistence to accept lowest energy as E_7. B3P86, BHandH, and HFB produce the non-convergent results but they may not be so problematic since these non-convergent results do not belong to minimum energy column, they are E_3, E_1, and E_9, respectively.

Another interesting result arises while energy values are put in order. Other than a few exceptions, the general inclination is destroyed by E_9. Corresponding multiplicity to E_9 can be obtained by unpaired eight electrons in the outer shells, needs to transfer one of the paired 6s

Table3.8: The third ionization energy IE_3 of Co atom for the process IE_3+$Co^{2+} \rightarrow Co^{3+}$+ e^-, calculated as $IE_3 = E_5(Co^{3+}) - E_4(Co^{2+})$. The experimental value is 33.497 eV [43]. Δ in the second column gives the error between the experimental and the calculated results; the last column is for the corresponding percentage error.

method	IE_3 (eV)	Δ (eV)	% error
B1LYP	33.861	0.364	1
B3LYP	34.130	0.633	1
B3P86	34.272	0.775	2
B3PW91	33.953	0.456	1
B971	34.000	0.503	1
B972	33.850	0.353	1
B98	34.076	0.579	1
BHandH	33.085	0.412	1
BHandHLYP	33.425	0.072	0
HFB	32.892	0.605	1
MPW1PW91	33.867	0.370	1
O3LYP	34.002	0.505	1
PBE1PBE	33.783	0.286	0

electron to unoccupied 4f energy level. The O3LYP method turn out the E_9 value with a great difference, means that it excepts this situation with a little possibility however others do not allocate this condition.

The energy difference between the E_9 and E_{11} values are remarkably greater than the others. Since the posibility of obtaining E_{11} is due to excitation of an electron from Xe noble gas configuration, it needs more energy than needed for smaller multiplicity values.

A discussion can be carried out about the total energy values of Sm cations and anion, similar to the evaluation of Co ions. The results of energy calculations for every possible multiplicity values have been indicated to the Tables 3.11—3.18. The expected electron configurations of these ions and their corresponding multiplicity values can be given as Sm^{1+}: [Xe] $6s^1$ $4f^6$, $m = 8$; Sm^{2+}: [Xe] $4f^6$, $m = 7$; Sm^{3+}: [Xe] $4f^5$, $m = 6$; and Sm^{1-}: [Xe] $6s^2$ $4f^7$, $m = 8$.

If we start from Sm^{1+} ion whose energies are given in Table 3.11, most of the methods complete the calculations with expected multiplicity values, only B98 and O3LYP fail, they give $m = 6$. As mentioned above, it is known that for rare earth elements, the given electrons to form a cation, lost from the 6s-subshell instead of 4f. To obtained $m = 6$ case for minimum energy, Sm has to lost its electron from 4f, so we can claim that B98 and O3LYP gives the wrong multiplicity values. Other 11 methods can be described as successful since they give

Table3.9: The electron affinity EA of Co atom for the process $\mathrm{Co} + e^- \rightarrow \mathrm{Co}^{1-}$, calculated as $EA = E_4(\mathrm{Co}) - E_3(\mathrm{Co}^{1-})$. The experimental value is 0.662 eV [43]. Δ in the second column gives the error between the experimental and the calculated results; the last column is for the corresponding percentage error.

method	EA (eV)	Δ (eV)	% error
B1LYP	0.735	0.073	11
B3LYP	0.896	0.234	35
B3P86	1.303	0.641	96
B3PW91	1.111	0.449	67
B971	0.478	0.184	27
B972	1.212	0.550	83
B98	0.502	0.160	24
BHandH	0.792	0.130	19
BHandHLYP	0.579	0.083	12
HFB	-0.021	0.683	103
MPW1PW91	1.034	0.372	56
O3LYP	0.606	0.056	8
PBE1PBE	0.664	0.002	0

expected multiplicity 8. If we scan the energy values closely, the pattern can be observed for most of the methods, which have only one minimum corresponding to $m = 8$, except B1LYP, B3PW91, and HFB. The E_2 and E_4 energies break down the pattern for latter methods by interchanging the sequence from smaller to greater.

The cases for Sm^{2+} and Sm^{3+} ions seem more succesful, that all the methods give the minimum energy at expected multiplicity values 7 and 6 respectively. This situation is also surprising as well as that mentioned for Co^{2+} and Co^{3+} ions. According to Table 3.12, the sequences of the energies also appear more smooth. Only B972 and HFB ruin the pattern, however the differences of these energy values are very small, numerically 0.0526 Hartrees for B972 and 0.0181 for HFB, so it is not so disturbing. A similar situation occurs for Table 3.13 and the related methods are B1LYP, B3P86, and BHandHLYP.

Unfortunately, Sm^{1-} ions results which are tabulated in Table 3.14 are not so regular as previous two tables. The methods B3P86, B3PW91, MPW1PW91, and PBE1PBE fail to give minimum total energy at expected multiplicity value 8. They conclude the calculations with $m = 6$ which is inadmissible, because it means one of the valence electrons paired with imported electron; strictly banned situation according to Hund's Rule. In addition, even for other methods, which are successful to present correct multiplicity value, any pattern has not

Table3.10: Total energies, E_m, in Hartrees, for a Sm atom for different multiplicities, m $(2S+1)$. The starred ones show the lowest energy. 'nc' indicates a 'not completed' calculation due to a non-convergent- or confused-SCF process.

method	$-E_1$	$-E_3$	$-E_5$	$-E_7$	$-E_9$	$-E_{11}$	$-E_{13}$	$-E_{15}$	$-E_{17}$
B1LYP	80.9767	81.1066	81.1206	81.2383*	81.1420	80.4743	79.8524	79.2364	77.9589
B3LYP	79.5032	81.1449	81.3103	81.4139*	81.3185	80.6690	80.0493	79.4370	78.1700
B3P86	81.4817	nc	81.6812	81.7856*	81.7021	81.0606	80.4737	79.8724	78.6599
B3PW91	81.1579	81.1520	81.3673	81.4599*	81.3867	80.7493	80.1630	79.5667	78.3541
B971	81.1207	81.0281	81.2394	81.3568*	81.2664	80.6228	80.0243	79.4236	78.2404
B972	81.1733	81.0886	81.3451	81.4633*	81.3542	80.7323	80.1307	79.5299	78.3487
B98	81.1252	81.0567	81.2724	81.3809*	81.2887	80.6471	80.0514	79.4506	78.2610
BHandH	nc	80.2748	80.3698	80.5407*	80.4614	79.8222	79.1646	78.5562	77.2856
BHandHLYP	80.4282	80.5762	80.7436	80.8219*	80.7413	80.0052	79.4284	78.7822	77.4875
HFB	80.9420	81.0298	81.1741	81.2689*	nc	80.4295	80.0775	79.5262	78.4046
MPW1PW91	81.0418	81.0819	81.2709	81.3640*	81.2813	80.6570	80.0509	79.4643	78.2611
O3LYP	81.2874	81.2518	81.4755	81.6235*	70.0165	80.9413	80.3365	79.7183	78.4574
PBE1PBE	80.9665	80.9867	81.2189	81.3171*	81.2317	80.5978	79.9987	79.4168	78.2160

Table3.11: Similar to Table 3.1 for Sm^{1+}.

method	$-E_2$	$-E_4$	$-E_6$	$-E_8$	$-E_{10}$	$-E_{12}$	$-E_{14}$	$-E_{16}$
B1LYP	80.9345	80.9266	81.0393	81.0523*	80.3532	79.7173	79.0405	77.7428
B3LYP	81.0664	81.1164	81.2172	81.2223*	80.5507	79.9082	79.2406	77.9445
B3P86	81.3845	81.4061	81.5555	81.5766*	80.9243	80.2596	79.6505	78.4080
B3PW91	81.1034	81.0408	81.2698	81.2811*	80.6298	80.0033	79.3645	78.1229
B971	80.9380	80.9985	81.1506	81.1622*	80.5110	79.8768	79.2303	78.0169
B972	80.9782	81.0819	81.2575	81.2677*	80.6219	79.9831	79.3371	78.1287
B98	80.9622	81.0166	81.1822*	81.1797	80.5323	79.9001	79.2544	78.0357
BHandH	79.5234	80.1900	80.3497	80.3579*	79.6705	78.9724	78.3643	77.1125
BHandHLYP	80.5141	80.5540	80.6272	80.6425*	79.9430	79.2351	78.5901	77.3156
HFB	80.8805	80.8296	81.0967	81.1054*	80.5280	79.9432	79.3485	78.1877
MPW1PW91	81.0109	81.0531	81.1736	81.1781*	80.4937	79.8656	79.2531	78.0323
O3LYP	81.2048	81.2790	81.4425*	81.4382	80.8288	80.1878	79.5290	78.2338
PBE1PBE	80.9330	80.9933	81.1157	81.1347*	80.4424	79.8177	79.1855	77.9885

Table3.12: Similar to Table 3.1 for Sm^{2+}.

method	$-E_1$	$-E_3$	$-E_5$	$-E_7$	$-E_9$	$-E_{11}$	$-E_{13}$	$-E_{15}$
B1LYP	80.4084	80.5279	80.5575	80.6446*	79.9602	79.2934	78.6073	77.2723
B3LYP	nc	80.6627	80.7046	80.8096*	80.1439	79.4771	78.7927	77.4668
B3P86	80.8529	80.9828	81.0204	81.1446*	80.5034	79.8432	79.1739	77.8978
B3PW91	80.5596	80.7140	80.7413	80.8783*	80.2282	79.5723	78.9084	77.6346
B971	80.5273	80.4747	80.5794	80.7703*	80.1207	79.4580	78.7866	77.5374
B972	80.5913	80.6383	80.7035	80.8687*	80.2384	79.5697	78.8974	77.6488
B98	80.3501	80.5583	80.6273	80.7872*	80.1407	79.4798	78.8089	77.5533
BHandH	79.5597	79.6932	79.7373	79.9643*	79.2419	78.5913	77.9073	76.6369
BHandHLYP	79.3709	79.9919	80.1646	80.2360*	79.4902	78.8314	78.1577	76.8416
HFB	80.3863	80.3682	80.4113	80.7079*	80.1343	79.5182	78.8959	77.7111
MPW1PW91	80.4544	80.5916	80.6432	80.7769*	80.1221	79.4688	78.8085	77.5449
O3LYP	80.7038	80.8385	80.8858	81.0331*	80.4287	79.7636	79.0781	77.7570
PBE1PBE	80.3770	80.5482	80.5994	80.7279*	80.0743	79.4220	78.7398	77.5024

Table3.13: Similar to Table 3.1 for Sm^{3+}.

method	$-E_2$	$-E_4$	$-E_6$	$-E_8$	$-E_{10}$	$-E_{12}$	$-E_{14}$
B1LYP	79.5062	79.4896	79.7154*	79.1542	78.5713	77.8438	76.4594
B3LYP	79.6694	79.7959	79.8556*	79.3155	78.7504	78.0243	76.6474
B3P86	80.0094	80.0041	80.1560*	79.6287	79.0917	78.3780	77.0469
B3PW91	79.7282	79.8262	79.9013*	79.4183	78.8393	78.1313	76.8048
B971	79.6395	79.6948	79.8230*	79.3282	78.7357	78.0196	76.7085
B972	79.6991	79.7398	79.8988*	79.4162	78.8479	78.1309	76.8255
B98	79.6604	79.7225	79.8223*	79.3457	78.7546	78.0391	76.7218
BHandH	78.8015	78.9162	78.9809*	78.5151	77.8613	77.1606	75.8078
BHandHLYP	79.1654	79.1460	79.3611*	78.7405	78.0982	77.3836	76.0113
HFB	79.5553	79.5772	79.7442*	79.3243	78.8149	78.1475	76.9065
MPW1PW91	79.6174	79.7359	79.7952*	79.3259	78.7338	78.0293	76.7143
O3LYP	79.8689	79.9583	80.0482*	79.5904	79.0399	78.3173	76.9389
PBE1PBE	79.5811	79.6688	79.7678*	79.2758	78.6881	77.9851	76.6729

been observed.

Now the order comes to mention about the first, second, and third ionization energy and electron affinity of Sm atom. The process of first ionization energy was given above for the Co atom. Similarly, $IE_1 + \text{Sm} \rightarrow \text{Sm}^{1+} + e^-$ is used for finding the first ionization energy of Sm with the recipe $IE_1 = E_8(\text{Sm}^{1+}) - E_7(\text{Sm})$ and the results demonstrated in Table 3.15. The same procedure was followed for second and third ionization energies. If we start with IE_1 of Sm, we will first call attention to the errors originating from the difference between experimental (5.643 eV [43])and the calculated results. HFB method is again discriminated from others by a great error of 21 percent. Except HFB, other methods have quite acceptable errors. Minimum errors are given by B3P86 (0 percent) and B98 (3 percent). The next discussion is about IE_2, which is based on Table 3.16. The error values are remarkably smaller than the IE_2, in fact half of them give values around zero and 1 percent. The worst result comes from B3P86 with the value 6 percent. The experimental values of second ionization energy is 11.090 eV [43]. For the third ionization energy error values are increase around 11 percent unlikely to Co case which errors have been decreased by increasing the ionization number. Only BHandHLYP and B1LYP indicate smaller error than others, numerically 1 and 7 percent respectively.

The electron affinity of the Sm atom can be demostrated by $\text{Sm} + e^- \rightarrow \text{Sm}^{1-}$ which is calculated with $EA = E_8(\text{Sm}) - E_7(\text{Sm}^{1-})$. In accordance with Co atom calculations, errors of electron affinity is very large for Sm atom. The reason was explained above by the small experimental value (which is 0.518 eV for Sm atom [43]). The interesting point here is that the energy values are so close to each other, in other words there is a consistancy among all methods. Maybe O3LYP can be excluded from this case with slightly smaller energy value 2.7 eV, since the others are changing in the range of 3.0–3.6 eV.

3.2 Dimers

3.2.1 SmCo Dimer Calculations

The SmCo dimer calculations can be explained into two parts and each one consists of approximately 6000 calculations. The first part of the calculations aim to determine the interaction between Sm and Co atoms, if it is Lennard-Jones type or not. So it includes three dimensions;

Table3.14: Similar to Table 3.1 for Sm^{1-}.

method	$-E_2$	$-E_4$	$-E_6$	$-E_8$	$-E_{10}$	$-E_{12}$	$-E_{14}$	$-E_{16}$	$-E_{18}$
B1LYP	80.8742	81.0447	81.1149	81.1327*	70.3971	80.3891	79.7224	79.1246	77.8979
B3LYP	81.0792	81.2035	81.2968	81.3123*	70.5189	80.5715	79.9258	79.3328	78.1167
B3P86	77.2028	81.5399	81.6916*	81.6847	70.8295	80.9810	80.3704	79.8004	78.6390
B3PW91	76.8817	81.2061	81.3580*	81.3460	70.5195	80.6494	80.0406	79.4747	78.3123
B971	80.9460	81.1005	81.2486	81.2631*	70.3525	80.5210	79.8899	79.3234	78.1932
B972	81.0153	81.2409	81.3377	81.3675*	81.2716	80.5881	80.0156	79.4289	78.3015
B98	80.9631	81.1689	81.2806	81.2835*	70.3537	80.5473	79.9198	79.3526	78.2165
BHandH	80.0259	80.2363	80.4198	80.4272*	80.3274	79.7053	79.0217	78.4478	77.2619
BHandHLYP	80.4732	80.6328	80.6992	80.7132*	80.6076	79.9831	79.2616	78.6722	77.4640
HFB	72.5404	80.9615	81.1416	81.1554*	69.9344	80.3339	nc	79.4142	78.3421
MPW1PW91	77.1460	81.0956	81.2708*	81.2500	70.5101	80.5571	79.9357	79.3719	78.2186
O3LYP	81.2048	81.4355	81.5311	81.5415*	70.5887	80.5800	80.2025	79.6193	78.4072
PBE1PBE	77.4614	81.0321	81.2131*	81.2024	70.5060	80.5026	79.8858	79.3227	79.3227

Table3.15: The first ionization energy IE_1 of Sm atom for the process $IE_1 + \text{Sm} \rightarrow \text{Sm}^{1+} + e^-$, calculated as $IE_1 = E_8(\text{Sm}^{1+}) - E_7(\text{Sm})$. The experimental value is 5.643 eV [43]. Δ in the second column gives the error between the experimental and the calculated results; the last column is for the corresponding percentage error.

method	IE_1(eV)	Δ (eV)	% error
B1LYP	5.059	0.585	10
B3LYP	5.214	0.430	7
B3P86	5.685	0.042	0
B3PW91	4.863	0.780	13
B971	5.292	0.351	6
B972	5.321	0.322	5
B98	5.472	0.171	3
BHandH	4.971	0.673	11
BHandHLYP	4.879	0.764	13
HFB	4.449	1.194	21
MPW1PW91	5.055	0.589	10
O3LYP	5.039	0.604	10
PBE1PBE	4.964	0.680	12

methods, multiplicity values, and interatomic separation. This part of the study is performed for all 13 DFT methods, to be sure if they are appropriate as predicted from previous calculations. The second dimension is the multiplicity for which each method is scanned for seven discrete values; from $m = 2$ to $m = 14$ since there are odd number of unpaired electrons and so multiplicity value is even. The last dimension is interatomic separation, so that the initial interatomic distance is varied from $r = 1.0$ Å to 7.0 Å, 0.1 Å added to r for each calculation (61 calculations for each method and each multiplicity value). By this means of calculation we can determine the multiplicity which gives the minimum total energy, the spectroscopic constants and some electronic properties for each method. These spectroscopic constants are binding energy D_e, equilibrium interatomic separation r_e, and fundamental frequency w_e and the electronic properties are the highest occupied molecular orbit (HOMO), the lowest unoccupied molecular orbit (LUMO), HOMO-LUMO gap energy, dipole moment, and excess charges on the atoms.

The first set of calculations includes the self-consistent energy values of SmCo dimer with respect to multiplicity values and resuls are listed in Table 3.19. It can be clearly seen that all functionals give the minimum energy value for the $m = 10$ condition. This distinctive determination means that both Sm and Co atoms do not lose their own electronic structure and keep their original multiplicity values four and seven. It is an expected situation since

Table3.16: The second ionization energy IE_2 of Sm atom for the process $IE_2 + Sm^{1+} \rightarrow Sm^{2+} + e^-$, calculated as $IE_2 = E_7(Sm^{2+}) - E_8(Sm^{1+})$. The experimental value is 11.090 eV [43]. Δ in the second column gives the error between the experimental and the calculated results; the last column is for the corresponding percentage error.

method	IE_2(eV)	Δ (eV)	% error
B1LYP	11.095	0.005	0
B3LYP	11.232	0.142	1
B3P86	11.757	0.667	6
B3PW91	10.963	0.127	1
B971	10.666	0.424	3
B972	10.859	0.231	2
B98	10.683	0.407	3
BHandH	10.713	0.377	3
BHandHLYP	11.062	0.028	0
HFB	10.817	0.273	2
MPW1PW91	10.920	0.170	1
O3LYP	11.027	0.063	0
PBE1PBE	11.071	0.019	0

the unpaired electrons of the Co atom are in the 3d orbitals and the Sm atom are in the 4f orbitals. By their nature, they are at different energy levels however by six 4f-electrons and seven 3d-electrons the interaction between the atoms can be defined as very strong. In this case we expect to determine interaction between Sm and Co atoms as the Lennard Jones type. If it is the case we can conclude that the values for binding energy D_e and the equilibrium separation distance r_e are in plausible range. We will turn to this point while discussing these variables.

If energy values are arranged in order, it is seen that the case $E_{10} < E_6 < E_4 < E_8 < E_{12} < E_2 < E_{14}$ is common for most of the methods. The methods B1LYP, B3LYP, HFB, and O3LYP has the same order with the interchange of E_{14} and E_2. Only B98 gives a different pattern, that is $E_{10} < E_4 < E_8 < E_6 < E_{12} < E_{14} < E_2$. There is only one not–completed calculation, E_2 of the method BHandH.

One of the important part of the study summarized on Table 3.20 by exhibiting the spectroscopic and electronic properties of each method according to multiplicity value that gives the minimum total energy. This part is important because there is no experimental data found in the literature about SmCo dimer. As mentioned before, these spectroscopic constants are binding energy D_e, equilibrium interatomic separation r_e, and fundamental frequency ω_e.

Table3.17: The third ionization energy IE_3 of Sm atom for the process IE_3 + $Sm^{2+} \rightarrow Sm^{3+} + e^-$, calculated as $IE_3 = E_6(Sm^{3+}) - E_7(Sm^{2+})$. The experimental value is 23.423 eV [43]. Δ in the second column gives the error between the experimental and the calculated results; the last column is for the corresponding percentage error.

method	IE_3 (eV)	Δ (eV)	% error
B1LYP	25.285	1.862	7
B3LYP	25.958	2.535	10
B3P86	26.901	3.478	14
B3PW91	26.585	3.162	13
B971	25.777	2.354	10
B972	26.391	2.968	12
B98	26.256	2.833	12
BHandH	26.761	3.338	14
BHandHLYP	23.809	0.386	1
HFB	26.225	2.802	11
MPW1PW91	26.714	3.291	14
O3LYP	26.798	3.375	14
PBE1PBE	26.123	2.700	11

The binding energy D_e can be defined as the energy required to decompose a molecule into its constituents. As a calculation example of binding energy, HFB can be shown as; $D_e = -C(E_{10}^{SmCo} - E_7^{Sm} - E_4^{Co})$, where C is the conversion constant of Hartrees to electronvolt, $C = 27.211383$ eV/Hartree. The energy values at the right hand side of the equation are obtained from tables of Co, Sm and SmCo calculations, Table 3.1, Table 3.10, Table 3.19 respectively. In the same way, to calculate binding energy of B3PW91, B972, BHandH, or MPW1PW91, $D_e = -C(E_{10}^{SmCo} - E_7^{Sm} - E_2^{Co})$ has to be used, since the minimum energy values are at $m = 2$ case for them.

The binding energy values are not so successful since the range is wide and values are spread between 0.9092 eV to 1.8315 eV for hybrid functionals. Unfortunately, even similar methods do not give close values for binding energy, i.e. B971 has 1.2402 eV where B972 has 1.6230 eV. (One more: BHandH has 1.5669 eV and BHandHLYP has 1.0493 eV). Although the D_e range is wide, the binding energy values of the $m = 10$ case are actually small.

The equilibrium interatomic separation r_e is the distance between the atoms where the possible energy is minimum, so the most stable state. Unlike D_e, r_e values are proper and the range is 2.95-3.09 Å for the $m = 10$ cases. This range can be defined as $r_e = 2.975 \pm 0.035$ Å for the $m = 10$ case of the SmCo bond length. In contrast to D_e, similar methods gives similar re-

Table3.18: The electron affinity EA of Sm atom for the process Sm $+ e^- \rightarrow$ Sm^{1-}, calculated as $EA = E_8(\text{Sm}) - E_7(\text{Sm}^{1-})$. The experimental value is 0.518 eV [43]. Δ in the second column gives the error between the experimental and the calculated results; the last column is for the corresponding percentage error.

method	EA (eV)	Δ (eV)	% error
B1LYP	-2.872	3.390	654
B3LYP	-2.765	3.283	633
B3P86	-2.745	3.263	629
B3PW91	-3.100	3.618	698
B971	-2.550	3.068	592
B972	-2.607	3.125	603
B98	-2.651	3.169	611
BHandH	-3.087	3.605	695
BHandHLYP	-2.957	3.475	670
HFB	-3.089	3.607	696
MPW1PW91	-3.100	3.618	698
O3LYP	-2.231	2.749	530
PBE1PBE	-3.121	3.639	702

sults for r_e. For example, B3LYP gives 2.9669 Å where B1LYP gives 3.0111 Å and another acceptable result is coming from Becke series; B98 gives 3.0077 Å, B971 gives 3.0061 Å, and B972 gives 2.9903 Å.

The calculated excess charge on Sm, $q(Sm)$ and dipole moment μ for SmCo also demonstrated in Table 3.20. Excess charge is written only for Sm, since it is known that $q(Co) = -q(Sm)$, for SmCo dimer. Again for the $m = 10$ case $q(Sm)$ and μ gives acceptable results. $q(Sm)$ values can be placed in the interval of $0.58|e|$ to $0.63|e|$, also represent as $q(Sm) = 0.60 \pm 0.03|e|$. Similarly, dipole moment change between 3.7 D and 4.5 D and can be represented as $\mu = 4.1 \pm 0.4$ D which has greater error value than $q(Sm)$.

The charge separation and dipole moment values are based on unpaired electrons of the Sm and Co atoms. It can be claimed that the structure of the unpaired electrons in atoms are not degrade while composing the SmCo dimer. Also for $q(Sm)$ and μ values, similar methods give similar results; such as B3LYP ($0.6252|e|$ and 4.4947 D) and B1LYP ($0.6291|e|$ and 4.4694 D); and B98 ($0.5870|e|$ and 3.8195 D), B971($0.5846|e|$ and 3.7881 D), and B972 ($0.5752|e|$ and 3.7224 D).

In Table 3.21, HOMO and LUMO energy values and energy gap between HOMO-LUMO for SmCo dimer are represented for both alpha and beta energy terms. The energy gap corre-

Table3.19: Total energies, E_m, in Hartrees, for SmCo dimer for different multiplicities, m $(2S+1)$. The starred ones show the lowest energy.

method	$-E_2$	$-E_4$	$-E_6$	$-E_8$	$-E_{10}$	$-E_{12}$	$-E_{14}$	$-E_{16}$
B1LYP	226.1846	226.2942	226.2969	226.2898	226.2989*	226.2367	226.1454	225.8855
B3LYP	226.4338	226.5832	226.5862	226.5789	226.5888*	226.5234	226.4287	226.1652
B3P86	227.1681	227.3348	227.3371	227.3296	227.3398*	227.2785	227.1938	226.9362
B3PW91	226.4880	226.6633	226.6653	226.6580	226.6681*	226.6060	226.5304	226.2783
B971	226.2444	226.4631	226.4655	226.4592	226.4689*	226.3970	226.2952	226.0283
B972	226.5168	226.7612	226.7642	226.7570	226.7672*	226.6815	226.5826	226.3181
B98	226.2968	226.5220	226.5180	226.5183	226.5283*	226.4578	226.3594	226.0932
BHandH	nc	225.1359	225.1378	225.1303	225.1415*	225.0941	225.0073	224.7866
BHandHLYP	225.6693	225.7897	225.8099	225.7795	225.8129*	225.7688	225.6883	225.4487
HFB	225.6727	225.7303	225.7326	225.7234	225.7354*	225.6781	225.6162	225.3877
MPW1PW91	226.3690	226.5399	226.5414	226.5343	226.5445*	226.4897	226.4148	226.1667
O3LYP	226.8260	226.9734	226.9750	226.9677	226.9779*	226.9098	226.8165	226.5527
PBE1PBE	226.2321	226.4188	226.4205	226.4132	226.4236*	226.3686	226.2913	226.0441

Table3.20: Spectroscopic constants of the SmCo dimer calculated for the multiplicity, m $(2S+1)$, at which the total energy is minimum. Binding energy D_e is in eV, equilibrium interatomic separation r_e is in Å, and the fundamental frequency ω_e is in cm^{-1}. Also given are the calculated excess charge q(Sm) on the Sm atom (in units of electron charge $|e|$) and the dipole moment μ (in Debyes). Note that for the excess charge on the Co atom, we have $q(\text{Co}) = -q(\text{Sm})$.

method	m	D_e	r_e	ω_e	q	μ
B1LYP	10	1.2900	3.0111	120.7479	0.625214	4.4947
B3LYP	10	1.3725	2.9669	126.2534	0.629150	4.4694
B3P86	10	1.2799	2.9465	129.7313	0.622319	4.2417
B3PW91	10	1.8315	2.9686	126.8396	0.618716	4.2142
B971	10	1.2402	3.0061	117.7587	0.584616	3.7881
B972	10	1.6230	2.9903	120.5058	0.575191	3.7224
B98	10	1.1059	3.0077	117.5993	0.586995	3.8195
BHandH	10	1.5669	2.9705	122.0213	0.628273	4.2536
BHandHLYP	10	1.0493	3.0870	111.2646	0.609532	4.4178
HFB	10	0.9092	3.0718	118.5861	0.630904	4.7738
MPW1PW91	10	1.7757	2.9817	124.5935	0.619642	4.1843
O3LYP	10	1.5760	3.0097	120.2384	0.630045	4.0206
PBE1PBE	10	1.3294	2.9819	124.1326	0.619590	4.1239

sponds to an evaluation of the stability of the dimer. If the gap is large, means exitation probability is greater, in other words dimer is more stable and vice versa. The HOMO-LUMO gap also shows the interaction probability of the SmCo dimer with other atoms or species. For this situation, it gives an opportunity to make a comment about the structure of the higher order compound of Sm and Co atoms, such as industrially important, highly magnetized $SmCo_5$ and Sm_2Co_{17}. These will be the scope of future studies.

The main discussion in the scope of previous study is the validity and reliability of the methods. In this sense, it is easily pointed that HBF gives significantly lower value than the other methods for the $m = 10$ case. As known, HBF is an only-exchange method, so the reason of the result may be the cause of lack of correlation energy. Another exception is about half-and-half functionals; BHandH and BHandHLYP. These two functionals give much larger values than the other methods, that are $E_g(\alpha) = 3.7914$ eV and $E_g(\beta) = 4.1685$ eV for BHandH and $E_g(\alpha) = 3.9312$ eV and $E_g(\beta) = 4.0017$ eV for BHandHLYP. The other methods for the $m = 10$ case give similar results which spread out to an interval from 2.25 eV to 2.85 eV for $E_g(\alpha)$ values, in other representation; $E_g(\alpha) = 2.55 \pm 0.3$ eV. For $E_g(\beta)$ the situation includes a bit more uncertainity that the interval lays between 1.85 eV to 3.25 eV, can be written as $E_g(\beta) = 2.55 \pm 0.70$ eV.

Table3.21: HOMO and LUMO energies (in Hartrees), and HOMO-LUMO gap (E_g) energies (in eV) of the SmCo dimer, calculated for the multiplicity, m $(2S+1)$, at which the total energy is minimum.

method	m	HOMO(α)	LUMO(α)	$E_g(\alpha)$	HOMO(β)	LUMO(β)	$E_g(\beta)$
B1LYP	10	-0.11965	-0.01584	2.82481	-0.16135	-0.05294	2.94999
B3LYP	10	-0.12080	-0.02676	2.55896	-0.15661	-0.06062	2.61202
B3P86	10	-0.14301	-0.04713	2.60903	-0.17962	-0.07479	2.85257
B3PW91	10	-0.12384	-0.02705	2.63379	-0.15684	-0.05225	2.84604
B971	10	-0.11558	-0.02309	2.51678	-0.16070	-0.07328	2.37882
B972	10	-0.11442	-0.02238	2.50454	-0.15647	-0.07189	2.30154
B98	10	-0.11860	-0.02351	2.58753	-0.16484	-0.07175	2.53311
BHandH	10	-0.13529	0.00404	3.79136	-0.18174	-0.02855	4.16851
BHandHLYP	10	-0.13847	0.00600	3.93123	-0.17917	-0.03211	4.00171
HFB	10	-0.09223	-0.05521	1.00737	-0.07084	-0.04017	0.83457
MPW1PW91	10	-0.12675	-0.02208	2.84822	-0.16615	-0.04679	3.24795
O3LYP	10	-0.10715	-0.02436	2.25283	-0.12544	-0.05759	1.84629
PBE1PBE	10	-0.12529	-0.02224	2.80413	-0.16639	-0.04982	3.17203

3.2.2 Co_2 Dimer Calculations

The Co_2 discussion constitutes the second part of the dimer calculations. There are a few experimental and theoretical studies about electronic and structural properties of Co_2 dimer in the literature, however there are still inconsistencies in the results [40]. The number of studies are not sufficient for solving these inconsistencies. The results that are gathered from several studies in the literature, are demonstrated in the Table 3.22 [40]. The range of binding energy is wide enough to point out the inconsistency. The results for the bond length are better than binding energy, they are close to each other, change from 1.95 Å to 2.41 Å .

Table3.22: Results for Co_2 from previous works in literature.

method	D_e (eV)	r_e (Å)	ω_e (cm^{-1})
Ref. [44]	2.85	2.04	–
Ref. [45]	2.35	1.99	373
Ref. [46]	1.50	2.41	230
Ref. [47]	0.87	1.96	–
Ref. [48]	2.90	1.96	–
Ref. [49]	5.08	2.14	–
Ref. [50]	2.26	1.95	421
Ref. [51]	2.26	2.01	342
Ref. [40]-BLYP	1.71	2.13	329
Ref. [40]-PBE	2.03	2.10	271
Ref. [40]-exp	1.69	2.31	–

As mentioned before, Co atom has three unpaired electrons in the 3d orbitals. For Co_2 dimer, the number of unpaired electrons is 6, so expected multiplicity value is 7. According to Table 3.23, eight of the methods gives minimum potential at $m = 7$. Whereas five of them gives the minimum energy at $m = 5$, that are B3P86, B3PW91, B971, B972, and O3LYP. They can obtain the multiplicity 5 only by sharing the electrons by overlapping of the shells. It is an unexpected result whereas $-E_5$ and $-E_7$ values are close to each other. The five methods which indicate the minimum energy at $m = 5$, have the same sequence of energies; $-E_5 < -E_7 < -E_3 < -E_9 < -E_1 < -E_{11} < -E_{13} < -E_{15}$. Most of the methods that indicate minimum energy for the case $m = 7$ give the sequence as $-E_7 < -E_5 < -E_3 < -E_9 < -E_1 < -E_{11} < -E_{13} < -E_{15}$. Only for B98 and BHandH, the sequence of first three energies changes as $-E_7 < -E_3 < -E_5$.

Since there is not a concurence about minimum energy values we prefer to give corresponding variables both for $m = 5$ and $m = 7$ in Table 3.24. The binding energy values for $m = 5$ case, have not seen appropriate, since the range is so wide and even BHandH method gives a negative value. It seems much more convenient for $m = 7$. The values change from $0.5316\ eV$ to $1.9743\ eV$. The interatomic separation can be written as $r_e = 2.306 \pm 0.212$ Å for $m = 7$ and $r_e = 2.412 \pm 0.075$ Å for $m = 5$. The corresponding error part is smaller for $m = 7$, but the value when $m = 7$ is closer to the experimental one $r_e = 2.31$ Å given by Sebetci [40]. The vibrational frequency of Co_2 has been determined distinctively by researchers according to Table 3.22.

The frequency value given by B98 for $m = 5$ is 374.20 cm^{-1} that is remarkably greater than the others. If it is ignored, error can be decreased and value can be expressed as $\omega_e = 251 \pm 42$ cm^{-1}. The circumstance appears more acceptable for $m = 7$ case, given range is $\omega_e = 232 \pm 31$ cm^{-1}. The BHandH method gives a negative value for binding energy at $m = 5$ case, that is of course nonsense. The reason for this situation is not clear to comment on it, but we estimate that will be arised from the minimum energy values of Co atom which is obtained at $m = 2$ case instead of the expected $m = 4$ case. Although the reason is not clear, it is obvious that this value is problematic, so it can be neglected.

In Table 3.25, HOMO and LUMO energy values and energy gap between HOMO-LUMO for Co_2 dimer are represented. The HFB method gives significantly smaller values for both multiplicity values and for both energy gap. It is meaningful since HFB is an only ex-

Table3.23: Total energies, E_m, in Hartrees, for Co_2 dimer for different multiplicities, m $(2S+1)$. The starred ones show the lowest energy.

method	$-E_1$	$-E_3$	$-E_5$	$-E_7$	$-E_9$	$-E_{11}$	$-E_{13}$	$-E_{15}$
B1LYP	289.9089	290.0088	290.0400	290.0675*	289.9906	289.8519	289.5032	289.2835
B3LYP	290.1572	290.2322	290.2855	290.2915*	290.1806	290.0641	289.7323	289.4179
B3P86	290.9203	290.9951	291.0649*	291.0548	290.9305	290.8402	290.5165	290.2057
B3PW91	290.2076	290.2888	290.3570*	290.3496	290.2707	290.1453	289.8255	289.5213
B971	290.0234	290.1342	290.1669*	290.1526	290.0646	289.8826	289.6515	289.3360
B972	290.4341	290.5023	290.5778*	290.5611	290.4392	290.2615	290.0387	289.7328
B98	290.0974	290.2246	290.2232	290.2320*	290.1458	289.9934	289.7323	289.4237
BHandH	288.9592	289.0931	289.0810	289.1573*	289.0719	288.8353	288.6190	288.4724
BHandHLYP	289.7437	289.8876	289.9151	289.9393*	289.8957	289.6122	289.3627	289.0768
HFB	288.7937	288.8510	288.8916	288.9062*	288.8208	288.7130	288.4981	288.2112
MPW1PW91	290.1317	290.2371	290.2684	290.2977*	290.2067	290.1059	289.7716	289.4738
O3LYP	290.5250	290.5775	290.6404*	290.6293	290.5318	290.3918	290.1405	289.7774
PBE1PBE	289.9921	290.0954	290.1489	290.1571*	290.0655	289.9613	289.7165	289.3340

Table3.24: Spectroscopic constants of the Co_2 dimer calculated for the multiplicity, m $(2S+1)$, at which the total energy is minimum. For notation used, see Table 3.20.

method	m	D_e	r_e	ω_e	q	μ
B1LYP	5	0.3685	2.5182	212.78	0.00000	0.0000
B3LYP	5	0.9957	2.4115	219.49	0.01815	0.1283
B3P86	5	1.3738	2.3978	236.80	0.00000	0.0000
B3PW91	5	2.0494	2.4109	232.33	0.00000	0.0000
B971	5	0.9233	2.4301	224.14	0.00000	0.0000
B972	5	2.4293	2.4262	225.71	0.00000	0.0000
B98	5	0.2612	2.0939	374.20	0.00000	0.0000
BHandH	5	-0.1486	2.4351	228.81	0.00000	0.0000
BHandHLYP	5	0.2753	2.5283	208.66	0.00000	0.0000
HFB	5	0.6974	2.1864	292.63	0.00000	0.0000
MPW1PW91	5	1.0276	2.4985	219.43	0.00000	0.0000
O3LYP	5	1.2879	2.4483	217.01	0.00000	0.0000
PBE1PBE	5	0.9169	2.4079	223.64	0.01815	0.1189
B1LYP	7	1.1169	2.4340	217.38	0.00000	0.0000
B3LYP	7	1.1590	2.4373	215.01	0.00000	0.0000
B3P86	7	1.1005	2.4110	224.78	0.00000	0.0000
B3PW91	7	1.8480	2.4229	221.80	0.00000	0.0000
B971	7	0.5316	2.4471	209.90	0.00000	0.0000
B972	7	1.9743	2.4202	213.41	0.00000	0.0000
B98	7	0.5012	2.4415	210.53	0.00000	0.0000
BHandH	7	1.9271	2.3370	264.00	0.00000	0.0000
BHandHLYP	7	0.9356	2.3950	240.17	0.00000	0.0000
HFB	7	1.0930	——	199.38	0.02873	0.0792
MPW1PW91	7	1.8258	2.4132	226.98	0.00000	0.0000
O3LYP	7	0.9870	2.4874	199.93	0.00000	0.0000
PBE1PBE	7	1.1391	2.4150	226.83	0.00000	0.0000

change method, no contribution from correlation. Both half and half functions, BHandH and BHandHLYP methods give greater values from other values. One more method, O3LYP disrupts the general consistency of results by smaller values. These results also in accordance with the SmCo dimer results. The results from other methods are close to each other; can be demostrated as $E_g(\alpha) = 3.10 \pm 0.19$ Hartrees and $E_g(\beta) = 2.10 \pm 0.30$ Hartrees for $m = 5$ and similarly $E_g(\alpha) = 3.32 \pm 0.18$ Hartrees and $E_g(\beta) = 2.63 \pm 0.26$ for $m = 7$.

3.2.3 Sm_2 Dimer Calculations

The third part of the dimer calculations consists of Sm_2 dimer energies and other characteristics. As mentioned before Sm is a massive atom with 62 electrons and this is the most problematic part of the dimer calculations since most of the energy calculations have not gave result. The present results are demonstrated in Table 3.26. According to the table, $m = 1$,

Table3.25: HOMO and LUMO energies (in Hartrees), and HOMO-LUMO gap (E_g) energies (in eV) of the Co_2 dimer, calculated for the multiplicity, m $(2S+1)$, at which the total energy is minimum.

method	m	HOMO(α)	LUMO(α)	$E_g(\alpha)$	HOMO(β)	LUMO(β)	$E_g(\beta)$
B1LYP	5	-0.20354	-0.08960	3.10046	-0.15723	-0.07948	2.11569
B3LYP	5	-0.20505	-0.09794	2.91461	-0.15276	-0.08643	1.80493
B3P86	5	-0.22666	-0.11276	3.09938	-0.18720	-0.09883	2.40467
B3PW91	5	-0.20526	-0.09175	3.08876	-0.16486	-0.07751	2.37691
B971	5	-0.20031	-0.08746	3.07080	-0.16641	-0.07989	2.35433
B972	5	-0.19875	-0.08366	3.13176	-0.16144	-0.07531	2.34372
B98	5	-0.20562	-0.08584	3.25938	-0.15496	-0.07571	2.15650
BHandH	5	-0.28473	-0.06748	5.91167	-0.17467	-0.08750	2.37202
BHandHLYP	5	-0.22139	-0.06049	4.37831	-0.20691	-0.05325	4.18130
HFB	5	-0.17026	-0.10092	1.88684	-0.10516	-0.08315	0.59892
MPW1PW91	5	-0.20677	-0.08795	3.23326	-0.15947	-0.07313	2.34943
O3LYP	5	-0.18640	-0.09524	2.48059	-0.13801	-0.08171	1.53200
PBE1PBE	5	-0.20676	-0.08556	3.29802	-0.15954	-0.07144	2.39732
B1LYP	7	-0.16814	-0.04240	3.42156	-0.19708	-0.09560	2.76141
B3LYP	7	-0.16941	-0.05145	3.20985	-0.20288	-0.11582	2.36902
B3P86	7	-0.19148	-0.07063	3.28850	-0.22738	-0.13706	2.45773
B3PW91	7	-0.17211	-0.05075	3.30237	-0.20390	-0.11376	2.45283
B971	7	-0.16112	-0.04564	3.14237	-0.19637	-0.10809	2.40222
B972	7	-0.15618	-0.04019	3.15625	-0.19708	-0.10704	2.45011
B98	7	-0.16475	-0.04631	3.22292	-0.19855	-0.10690	2.49392
BHandH	7	-0.18785	-0.02370	4.46675	-0.21208	-0.05592	4.24933
BHandHLYP	7	-0.19165	-0.02335	4.57968	-0.20498	-0.05968	3.95381
HFB	7	-0.13592	-0.05031	2.32957	-0.15880	-0.11311	1.24329
MPW1PW91	7	-0.17563	-0.04703	3.49938	-0.20391	-0.09802	2.88141
O3LYP	7	-0.15448	-0.04976	2.84958	-0.19382	-0.13289	1.65799
PBE1PBE	7	-0.17385	-0.04711	3.44877	-0.20319	-0.09783	2.86699

$m = 13$, and $m = 19$ are most probable multiplicity values, most of the calculation ended with an energy value. In the outermost shell of Sm atom has six unpaired electrons, so the expected multiplicity for Sm_2 dimer is 13. From Table 3.26 all the methods end up with expected value.

According to half-shell stability, $-E_{17}$ is the most probable result greater than the minimum energy, whereas most of the methods do not conclude calculations. Results for $-E_{19}$ are better than the expected $-E_{17}$.

The spectroscopic constants of Sm_2 dimer are summarized in Table 3.27. The binding energies alter in a wide range, from 0.0215 Hartrees to 0.9465 Hartrees. Table 3.24 which was

Table3.26: Total energies, E_m, in Hartrees, for a Sm_2 dimer for different multiplicities, m $(2S+1)$. The starred ones show the lowest energy. 'nc' indicates a 'not completed' calculation due to a non-convergent- or confused-SCF process.

method	$-E_1$	$-E_{11}$	$-E_{13}$	$-E_{15}$	$-E_{17}$	$-E_{19}$
B1LYP	162.0049	nc	162.4809*	nc	162.3261	161.7638
B3LYP	162.3152	nc	162.8333*	nc	nc	nc
B3P86	162.9753	nc	163.5781*	nc	nc	162.8820
B3PW91	162.3071	nc	162.9440*	nc	nc	162.2511
B971	162.2467	nc	162.7483*	162.6940	nc	161.9666
B972	162.3565	162.8510	162.9345*	nc	nc	162.1602
B98	162.2568	162.7206	162.7860*	nc	nc	162.0122
BHandH	160.0575	nc	161.0975*	nc	nc	160.3717
BHandHLYP	160.7964	nc	161.6445*	nc	161.4819	160.8953
HFB	nc	162.4818	162.5401*	nc	nc	nc
MPW1PW91	162.0955	162.6234	162.7453*	nc	nc	162.0657
O3LYP	162.5760	nc	163.2803*	nc	163.1469	162.5705
PBE1PBE	161.9428	nc	162.6501*	nc	nc	161.9049

arranged for Co_2, HFB method gives the minimum vibrational frequency and the maximum intermolecular distance remarkably different than all other methods. Except HFB, all other methods conclude the calculations with closer values for r_e and ω_e, which can be presented as 4.780 ± 0.108 Å 35.6 ± 3.3 cm^{-1} respectively. If HFB is included, the expression turns to $r_e = 4.88 \pm 0.203$ Å , where error duplicates.

Table 3.28 has been arranged for HOMO–LUMO energies and $E_g(\alpha)$ and $E_g(\beta)$ enegy gaps of Sm_2. It is clearly seen that again HFB gives the minimum result. Similar to the Co_2 calculations, half and half functional methods BHandH and BHandHLYP methods give significantly greater values than the other methods. Additionally, O3LYP also gives smaller values for $E_g(\alpha)$ and $E_g(\beta)$. The results of the other methods can be indicated as $E_g(\alpha) = 2.79 \pm 0.15$ Hartrees and $E_g(\beta) = 2.68 \pm 0.35$ Hartrees.

3.2.4 SCF Calculations

In the second part of dimer calculations we performed "single-point" (sp) self-consistent field calculations (SCF). In a sp calculation, GAUSSIAN 03 compels the dimer under question to converge as it is specified at the very beginning of the simulation, without changing the interatomic separation r. We carried out sp calculations for Co_2 dimer with multiplicity $m =$

Table3.27: Spectroscopic constants of the Sm_2 dimer calculated for the multiplicity, m $(2S+1)$, at which the total energy is minimum. For notation used, see Table 3.20.

method	m	D_e	r_e	ω_e	q	μ
B1LYP	13	0.1204	4.8416	33.4884	0.00000	0.0000
B3LYP	13	0.1460	4.8009	34.1305	0.00000	0.0000
B3P86	13	0.1905	4.6724	37.0425	0.00000	0.0000
B3PW91	13	0.6584	4.7043	37.3122	0.00000	0.0000
B971	13	0.9465	4.7183	37.7456	0.00000	0.0000
B972	13	0.2173	4.7396	36.8318	0.00000	0.0000
B98	13	0.6600	4.7398	36.7767	0.00000	0.0000
BHandH	13	0.4405	4.6959	36.8246	0.00189	0.0817
BHandHLYP	13	0.0215	4.8883	32.3220	0.00000	0.0000
HFB	13	0.0617	5.0780	27.6654	0.00000	0.0000
MPW1PW91	13	0.4742	4.6798	38.4687	0.00068	0.0278
O3LYP	13	0.9084	4.8032	36.9029	0.00245	0.0983
PBE1PBE	13	0.4327	4.6807	38.8403	0.00000	0.0000

5 and 7, for Sm_2 with $m = 13$, and for SmCo with $m = 10$; the multiplicity values here are the ones for which the energy minima are spotted.

To do so, we scanned the distance r between the two atoms of a dimer from 1.0 to 5.0 Å for Co_2 and SmCo, and from 2.0 to 7.0 Å for Sm_2. We carried out a total of 300 sp calculations for each cases considered. Figures 3.1–3.8 present the resulting outcomes for the most clear-looking r-intervals. The formation energy E_f of SmCo is calculated for B1LYP, say, as $E_f = -27.211\left(E_{10}^{SmCo} - E_7^{Sm} - E_4^{Co}\right)$ (eV) where E_7^{Sm} and E_4^{Co} values are from Tables 3.1 and 3.10, respectively, and E_{10}^{SmCo} values are the results of present sp-calculations.

Let us start with the SmCo scan results which shown in Figures 3.1 and 3.2, where we omitted the graph of HFB because it does not contain the electron correlation energy in its formulation. We see that all the results have some common features: most of the data points from the 300 sp calculations are organized in a plainly noticed order, leading to not-so-smooth and frequently broken plots. Nonetheless, we can safely say that all the graphs in these two figures are of the Lennard-Jones nature. Obviously, we do not speak, for any given method, of a consummate, faultless Lennard-Jones plot, since there happen to be many data points which are just out of the main plot.

It follows from Figures 3.1 and 3.2 that all the twelve methods resulted in almost the same equilibrium interatomic distance r_e around 3.0 Å. Noting that this value is just the aforesaid

Table3.28: HOMO and LUMO energies (in Hartrees), and HOMO-LUMO gap (E_g) energies (in eV) of the Sm_2 dimer, calculated for the multiplicity, m $(2S+1)$, at which the total energy is minimum.

method	m	HOMO(α)	LUMO(α)	$E_g(\alpha)$	HOMO(β)	LUMO(β)	$E_g(\beta)$
B1LYP	13	-0.10947	-0.00114	2.94781	-0.10027	0.01094	3.02618
B3LYP	13	-0.11148	-0.01194	2.70862	-0.10195	0.00055	2.78917
B3P86	13	-0.13263	-0.03559	2.64059	-0.12263	-0.02288	2.71434
B3PW91	13	-0.11404	-0.01658	2.65202	-0.10428	-0.00404	2.72767
B971	13	-0.10863	-0.00923	2.70481	-0.09866	0.00400	2.79352
B972	13	-0.10909	-0.00957	2.70808	-0.09935	0.00276	2.77855
B98	13	-0.11097	-0.00976	2.75406	-0.10112	0.00356	2.84849
BHandH	13	-0.12267	0.01919	3.86021	-0.11378	0.03194	3.96524
BHandHLYP	13	-0.12613	0.02056	3.99164	-0.11758	0.03338	4.10783
HFB	13	-0.07595	-0.04280	0.90206	-0.06459	0.01514	2.16956
MPW1PW91	13	-0.11559	-0.01237	2.80876	-0.10608	0.00060	2.90291
O3LYP	13	-0.09664	-0.01508	2.21936	-0.08795	-0.00248	2.32576
PBE1PBE	13	-0.11452	-0.01053	2.82971	-0.10478	0.00216	2.90999

one in Table 3.20, the features seen in these graphs are impressively beautiful. As to the corresponding formation energies E_f, except B98 and B971, they are in agreement to a great degree to the binding energy D_e values listed in Table 3.20.

We note before passing that two Becke functionals B98 and B971 have given rise almost to the same curve, for they both have the same D_e and r_e values for SmCo dimer. Their another peculiarity is that their curves cross the $E_f = 0$ line; if we are to speak of a proper Lennard-Jones curve for SmCo, this crossing should not have occurred.

A final point about the graphs in Figures 3.1 and 3.2 is that the plot of O3LYP contains actually more than one curve; if we had increased the data points in the sp calculations from 300 to 3000, say, we would clearly distinguish at least three distinct curves, all of them sharing the same equilibrium interatomic distance, r_e, value about 3.0 Å. The only difference among them would be their different D_e values. Actually this situation is common in all the curves seen in these two figures: although they are barely discernable, a careful eye can readily recognize the remnants of more than one curve in each of them.

We show in Figures 3.3 and 3.4 the curves which are the outcomes of sp-scan results for Co_2 dimer for multiplicity $m = 5$. Again we see that the data points are ordered in a noticeable order, resulting in occasionally broken curves. Obviously, the curves in these tables cannot be said to be of the Lennard-Jones nature. To compound the situation further, we see the

features exhibited in these graphs are not at all in agreement with those in Table 3.24 which are the results from optimization calculations. As we see in Table 3.24, the equilibrium interatomic distances were mostly about 2.40-2.50 Å. But in these curves, it is usually around 1.90-2.20 Å. Even worse, except B3P86, B3PW91, B972, MPW1PW91, and O3LYP, all the remaining seven functionals, the equilibrium point is above the $E_f = 0$ line, which is of course unacceptable, for it leads to a negative binding energy D_e! For the last, but not least, all the curves have parts again $E_f = 0$ line.

We see one more time that in the graphs of Co_2, which are the results of sp calculations; all the curves are composed of the remnants of several different curves. Take the B3LYP case in Figure 3.3 as an example. Its curve starts from right, say, continues to the left a while, then abruptly brakes and jumps to another part of curve, continues again a little, and again brakes suddenly jumping to the next one, and so on. Here the natural question is this: which features should be correct? Those seen in the curves of Figures 3.3 and 3.4 or those listed in Table 3.24. We believe that the results in Table 3.24 are the more acceptable ones because the r_e values there are somehow close to the experimental and the other theoretical literature values and, for the most, they are the results of optimization calculations.

Figures 3.5 and 3.6 present the sp-scan calculations results for again Co_2, but for $m = 7$ this time. All the comments we have made about the $m = 5$ case are seen to valid also here. Again we observe curves composed of several broken parts, with their minima above the $E_f = 0$ line (for B98, B971, and BHandHLYP). Again all of them have some part of their tails above the $E_f = 0$ line. More importantly, all the curves make their minimum around $r_e = 2$ Å, not at all in agreement with those listed in Table 3.24, which are around 2.3–2.5 Å. Nevertheless, the curves shown in Figures 3.5 and 3.6 are seem to have a better appearance, for they have better-ordered data points. Notice how B98 and B971 functionals have produced nearly flawless Lennord-Jones-like curves, though they have completely unacceptable D_e and r_e values.

All the curves exhibited in Figures 3.1–3.4 portend somehow the unceasing debate about the ground-state of Co_2 dimer: should its multiplicity be $m = 5$ or $m = 7$? Its correct answer seems still evasive. Each DFT functional produces its own result which is usually very different than that resulted from another functional. Only the r_e values are exempt from this fact for the time being. Finally in this section, in Figures 3.7 and 3.8 are the sp calculation results

for Sm_2 dimer. Curves bear features which are the reminiscent of a general Lennard-Jones curve. Although we see an overall order in these curves, we cannot speak of any smoothness. Nonetheless, the features observed here are much better than those for the Co_2 cases discussed above. In Sm_2 curves, at least the equilibrium interatomic distance r_e values are hinted to be close to those tabulated in Table 3.27. Even the situation for the binding energy D_e values are not bad at all; only the B3P86 and B972 (and maybe including O3LYP and BHandHLYP), cases in which the minima are above $E_f = 0$ line are unsatisfactory.

3.3 Trimers

The third part of the study consists of possible trimers of Co and Sm atoms. These are Co_3, Sm_3, $SmCo_2$, and Sm_3Co clusters. In accordance with dimer calculations, we can determine the calculate the minimum total energy with respect to multiplicity, the spectroscopic constants that are; binding energy D_e, equilibrium interatomic separation r_e, and fundamental frequency w_e, HOMO, LUMO, and HOMO-LUMO gap energy, dipole moment and excess charges on the atoms.

3.3.1 Co_3 Trimer Calculations

Before looking into the energy results for the Co_3 trimer, we should first note that two different multiplicity m values we may see. In the first case, if the multiplicity of the Co_2 dimer is really 5, this means that the Co_2 dimer has four unpaired electrons, then another three unpaired electrons will come from the third cobalt elements; this configuration gives us a total of seven unpaired electrons. As a result, we might expect a multiplicity value $m = 8$ for the Co_3 trimer. In the second case in which we may have a total of nine unpaired electrons in Co_3, three for each Co elements, then it is possible that the multiplicity of Co_3 would be $m = 10$. It is apparent from Table 3.29 that these expectations have materialized: Except for B3PW91, BHandHLYP, MPW1PW91, PBE1PBE, all the other nine methods have given the somewhat expected multiplicity value $m = 8$. The former four methods have resulted in $m = 10$ value. Are the minimum energy values E_8 and E_{10} so different from each other? As we see clearly from this table, the mentioned difference is so small, meaning that it is so difficult in reality to discern the real minimum configuration between them. Before passing, we might notice

that there is no distinct order or pattern among the energy values E_2 to E_{10}; after them they monotonically increase. Actually, the same situation can be seen in all the other atom, dimer, and trimer energy tables. What we want to say that it might be quite difficult to detect the real minimum energy configuration by looking only the first minimum, for this first minimum might only be a local minimum. Consequently, we humbly recommend a diligent researcher to scan all the possible multiplicity values, of course if he or she has no difficulty in allocating the time required.

Since it was not possible to determine absolutely the real multiplicity value for the Co_3 trimer, it seems appropriate to give all the geometric details, spectroscopic constants, charges, dipoles, and HOMO-LUMO energies for the Co_3 trimer separately for the $m = 8$ and 10 values. Table 3.30 tabulates the bond lengths, bond angles, and vibrational frequencies of the Co_3 trimer obtained for the 13 different DFT methods we employed.

For $m = 8$ in Table 3.30 (for the notation employed there, refer to Fig. 3.9), the first thing to note that all the methods have led to a linear geometric configuration (D_∞). Although the exact angle values are never exactly 180°, we can safely accept them to be so; the very small differences, including the MPW1PW91 case in which the discrepancy is a little bit larger, can be attributed to the initial random atomic configurations, to the accuracy of GAUSSIAN03 package, and to the performance of the computer we made use of. It is clear from the same table that there is a definite C_2 symmetry in the linear Co_3 trimers; that is, the R_{12} values are (nearly) equal to the R_{23} values. This is expected, because we are dealing with three identical and indistinguishable Co atoms, and there should be no way to label them. This, in turn, gives rise to the conclusion that the distance between the first and second atoms and that between the second and third atoms must be equal to each other, for a linear Co_3 trimer. It is seen from the same table that all the bond length R_{12} and R_{23} values for $m = 8$ are in a range of 2.28–2.44 Å. This consistency among the different 13 methods in giving nearly the same results is especially notable, hinting at the reliability of the methods, which are all the culmination of many researchers' unceasing quests for the ultimate perfect method.

As to the vibrational frequencies of the Co_3 dimer with $m = 8$, we see that the three fundamental frequencies are distinct from each other. We mean these values are not at all close to each other and that in a real spectroscopy measurement experiment, it is very likely to see three well-separated peaks for each of the fundamental frequencies listed in Table 3.30. Nu-

Table3.29: Total energies, E_m, in Hartrees, for Co_3 trimer for different multiplicities, $m\ (2S+1)$.

method	$-E_2$	$-E_4$	$-E_6$	$-E_8$	$-E_{10}$	$-E_{12}$	$-E_{14}$	$-E_{16}$	$-E_{18}$	$-E_{20}$
B1LYP	435.1196	435.0915	435.1257	435.1451*	435.1357	435.0579	434.9495	434.7862	434.5371	434.2429
B3LYP	435.4596	435.4332	435.4669	435.4848*	435.4746	435.3863	435.2762	435.1070	434.8597	434.5579
B3P86	436.6143	436.5396	436.6197	436.6328*	436.6327	436.5465	436.4376	436.2773	436.0272	435.7453
B3PW91	435.5515	435.5233	435.5568	435.5704	435.5729*	435.4912	435.3880	435.2332	434.9882	434.7123
B971	435.2110	435.2543	435.2670	435.2831*	435.2701	435.1670	435.0578	434.8792	434.6062	434.3244
B972	435.8247	435.8147	435.8847	435.8980*	435.8820	435.7768	435.6474	435.4793	435.2081	434.9253
B98	435.3438	435.3415	435.3832	435.4003*	435.3882	435.2871	435.1962	435.0062	434.7339	434.4550
BHandH	433.7472	433.7257	433.7616	433.7849*	433.7837	433.7073	433.6367	433.4232	433.2363	432.9933
BHandHLYP	434.7492	434.8915	434.9262	434.9537	434.9565*	434.9048	434.8032	nc	434.4003	434.1592
HFB	433.3568	433.3578	433.3486	433.3815*	433.3814	433.3085	433.2067	433.0915	432.8984	432.6275
MPW1PW91	435.4724	435.4425	435.4765	435.4900	435.4944*	435.4196	435.3224	435.1232	434.9353	434.6537
O3LYP	435.9738	435.9123	435.9841	435.9972*	435.9868	435.8934	435.7569	435.6035	435.3816	435.0761
PBE1PBE	435.2616	435.2271	435.2665	435.2810	435.2841*	435.2086	435.0997	434.9579	434.7239	434.4430

Table3.30: Bond lengths R_{12} and R_{23} (Å), bond angle θ_{123} (deg), and vibrational frequencies ω_n (cm^{-1}) of Co_3 trimer. For the notation used, see Fig. 3.9.

method	m	R_{12}	R_{23}	θ_{123}	ω_1	ω_2	ω_3
B1LYP	8	2.3383	2.3383	179.9977	57.9769	165.2187	273.1134
B3LYP	8	2.3054	2.3054	179.9875	40.3645	168.1510	282.4238
B3P86	8	2.2804	2.2803	179.9540	36.6931	170.6370	287.0438
B3PW91	8	2.3013	2.2930	179.5183	68.0735	171.4295	288.1704
B971	8	2.3291	2.3284	179.9959	67.8216	164.7834	277.5973
B972	8	2.2958	2.2958	179.9965	47.7114	166.3232	276.8408
B98	8	2.3307	2.3305	179.9822	77.3060	168.5791	284.1932
BHandH	8	2.3346	2.3346	179.9963	76.4149	159.2871	273.1480
BHandHLYP	8	2.4423	2.4428	179.9971	66.3563	142.6938	245.1946
HFB	8	2.3170	2.3167	179.9897	63.2225	157.6999	232.7209
MPW1PW91	8	2.3164	2.3235	179.1373	68.4773	166.5265	281.8294
O3LYP	8	2.2769	2.2769	179.8262	52.9335	164.3737	263.5213
PBE1PBE	8	2.3211	2.3214	179.9848	58.7694	169.3582	280.1786
B1LYP	10	2.4931	2.4931	60.2067	161.6978	163.3248	217.0806
B3LYP	10	2.4701	2.4701	60.4498	161.8123	162.8664	218.8316
B3P86	10	2.4008	2.4961	58.6009	166.5900	182.7480	233.8198
B3PW91	10	2.4150	2.5096	58.6799	166.0688	179.6791	229.8943
B971	10	2.5424	2.4762	59.1337	162.6439	171.0763	213.8466
B972	10	2.5201	2.4335	58.8170	161.4558	173.0234	216.3178
B98	10	2.4858	2.4858	60.8054	158.7981	167.4695	211.4643
BHandH	10	2.5399	2.5399	60.3833	141.6028	167.9064	175.9585
BHandHLYP	10	2.9937	2.9994	59.7120	69.0480	92.2697	95.1655
HFB	10	2.6259	2.4800	58.0495	134.6271	146.6539	187.9772
MPW1PW91	10	2.4276	2.5127	58.8097	165.9933	179.6142	229.2789
O3LYP	10	2.3551	2.5231	57.6225	156.5483	171.2290	219.1099
PBE1PBE	10	2.4258	2.5109	58.8808	167.9620	180.6394	229.9148

merically, these three frequency values are roughly centered around 65, 165, and 280 cm^{-1}. Now we have come to the $m = 10$ case. It follows from the second part of Table 3.30 that, the minimum energy configuration for this case are all equilateral triangles, though nearly all of them are distorted. This distortion is the biggest in O3LYP and the smallest B1LYP and these are the reasons why the R_{12} and R_{23} values are so apart for O3LYP and equal to each other for B1LYP. Except for BHandHLYP, the bond lengths of the equilateral structures are in the range of 2.36–2.63 Å. The corresponding value for BHandHLYP is about 3.00 Å, which we believe is not reliable. We remember from Table 3.24 that BHandHLYP method gave us a 2.395-Å the bond length for the Co_2 dimer. It seems unrealistic that in forming a Co_3 trimer from a Co_2 dimer by adding a third Co atom would increase this 2.395-Å value to 3.00-Å, for this would be a huge leap in the atomic scale. A close look at the corresponding vibrational frequency values reveals the same oddness for BHandHLYP method; its results are remarkably smaller than those of other methods. By the way, a similar situation in concerning these

frequency values are noticed for BHandH and HFB methods; for the latter this should be seen normal if we remember that HFB does not include the crucially important electron correlation phenomenology in its formulation. (Note that the frequency values of HFB are not drastically different from others.) We do not manage to ascribe *properly* the strangeness witnessed in BHandH case to a logical reason for the time being, for this requires a profound analysis into the internal details of the BHandH method's formulation, which is out of scope of this master thesis. Apart from the mentioned three methods, the numerical frequency values of the other ten methods are centered around 160, 170, and 220 cm^{-1}, with the former two being somehow close to each other.

We give in Table 3.31 the calculated excess charge on the atoms of the Co_3 trimer and the closely related dipole moment values for again the $m = 8$ and 10 cases. It is seen a net charge separation for all the results listed in this table. In the geometrically linear $m = 8$ case, the symmetry dictates a zero net dipole moment, as is clearly seen in the last column: we have two dipoles, opposite to each other, one say, to the left and the other to the right, possessing nearly the same magnitude, leading to a zero dipole moment. Again the non-zero but very small μ values are acceptable within the accuracy of the results. Referring to Table 3.30, we see that all the non-zero μ values belong to the non-perfect linear geometries. It is plain from the same table that $2|q_1| = 2|q_3| = q_2$, of course, this is unsurprising. Numerically, the charge values are in a wide range such that $0.14|e| < q_2 < 0.29|e|$.

In the $m = 10$ cases, which are geometrically equilateral triangles, we observe *symmetric* charge separations in all the cases considered, but not so much clearly as in the case of the linear $m = 8$ geometries mentioned above. We note that the magnitudes of these charge values are so small if we compare them with those for the $m = 8$ cases. There might be two explanations here. Firstly, we may suppose that there is no charge separation at all in the ingredients Co atoms of the trimer, so that there is no net resulting dipole moment. This also explains the feature seen in the $m = 10$ portion of Table 3.31: the more distorted triangle, the bigger total dipole moment value it has. Secondly, there *is* really a charge separation among Co atoms, which are listed in the same table, so that we have some amount of total dipole moments, though they are very small. Therefore, the numeric μ values are distributed in a broad range: 0.0051 D for B98 and 0.1728 D for HFB. Not surprisingly, here again HFB determines, probably incidentally, the extremum value for the μ value.

Table3.31: Calculated excess charge (in units of electron charge) on atoms and dipole moments (in Debye) of Co_3 trimer.

method	m	q_1	q_2	q_3	μ
B1LYP	8	-0.144537	0.289072	-0.144534	0.0001
B3LYP	8	-0.121604	0.243213	-0.121609	0.0001
B3P86	8	-0.119827	0.239652	-0.119826	0.0003
B3PW91	8	-0.094048	0.187872	-0.093824	0.0137
B971	8	-0.120109	0.240230	-0.120121	0.0016
B972	8	-0.091263	0.182526	-0.091263	0.0000
B98	8	-0.114555	0.229116	-0.114561	0.0004
BHandH	8	-0.135364	0.270729	-0.135364	0.0000
BHandHLYP	8	-0.135942	0.271805	-0.135863	0.0010
HFB	8	-0.068695	0.137315	-0.068619	0.0005
MPW1PW91	8	-0.079160	0.158003	-0.078843	0.0145
O3LYP	8	-0.099895	0.199796	-0.099901	0.0009
PBE1PBE	8	-0.116921	0.233828	-0.116907	0.0007
B1LYP	10	0.013894	-0.027789	0.013895	0.0788
B3LYP	10	0.010801	-0.021603	0.010801	0.0525
B3P86	10	0.009223	-0.017803	0.008580	0.1361
B3PW91	10	0.008662	-0.017616	0.008954	0.1328
B971	10	0.002091	-0.003327	0.001236	0.0839
B972	10	0.000675	-0.001468	0.000793	0.1134
B98	10	0.009839	-0.019678	0.009839	0.0051
BHandH	10	-0.001741	0.003482	-0.001741	0.0143
BHandHLYP	10	-0.002614	0.005284	-0.002670	0.0519
HFB	10	0.013931	-0.027650	0.013719	0.1728
MPW1PW91	10	0.004903	-0.009380	0.004477	0.1152
O3LYP	10	0.022138	-0.044295	0.022157	0.1101
PBE1PBE	10	0.005352	-0.011242	0.005890	0.1140

The HOMO and LUMO energies and HOMO-LUMO energy gaps E_g for Co_3 dimer are tabulated in Table 3.32. It can be easily noticed that the trend in other HOMO-LUMO tables does not change in this table; meaning that HFB and O3LYP again give the minimum values among all results, additionally BHandH and BHandHLYP give notably greater values than others. Except these methods, the results of other nine methods can be described as in a good manner. For $m = 8$ case, the results of latter group can be expressed as $E_g(\alpha) = 3.22 \pm 0.12$ Hartrees and $E_g(\beta) = 2.72 \pm 0.23$ Hartrees. These ranges are a bit larger for $m = 10$; $E_g(\alpha) = 2.91 \pm 0.13$ Hartrees and $E_g(\beta) = 3.24 \pm 0.33$ Hartrees. At the end of Co_3 trimer calculations, we can conclude that the results of $m = 8$ case seem more acceptable than the results of $m = 10$. The unexpected or doubtful situations that are mentioned above are generally about the multiplicity value 10, especially for values exhibited in Table 3.30.

Table3.32: HOMO and LUMO energies (in Hartrees), and HOMO-LUMO gap (E_g) energies (in eV) of the Co_3 trimer, calculated for the multiplicity, m $(2S+1)$, at which the total energy is minimum.

method	m	HOMO(α)	LUMO(α)	$E_g(\alpha)$	HOMO(β)	LUMO(β)	$E_g(\beta)$
B1LYP	8	-0.19403	-0.07465	3.24849	-0.18281	-0.08683	2.61175
B3LYP	8	-0.19695	-0.08307	3.09883	-0.18662	-0.09491	2.49556
B3P86	8	-0.21808	-0.10037	3.20305	-0.20541	-0.11420	2.48195
B3PW91	8	-0.19681	-0.08015	3.17448	-0.18388	-0.09092	2.52957
B971	8	-0.19014	-0.07569	3.11434	-0.18223	-0.08994	2.51134
B972	8	-0.18888	-0.07189	3.18346	-0.18294	-0.09016	2.52467
B98	8	-0.19232	-0.07613	3.16169	-0.18384	-0.08596	2.66345
BHandH	8	-0.20682	-0.04572	4.38375	-0.19754	-0.03962	4.29722
BHandHLYP	8	-0.20295	-0.04950	4.17559	-0.19371	-0.04293	4.10293
HFB	8	-0.16259	-0.08170	2.20113	-0.13958	-0.09685	1.16274
MPW1PW91	8	-0.19740	-0.07466	3.33993	-0.18488	-0.07642	2.95135
O3LYP	8	-0.18043	-0.07800	2.78726	-0.17037	-0.10302	1.83269
PBE1PBE	8	-0.19759	-0.07512	3.33258	-0.18444	-0.08792	2.62644
B1LYP	10	-0.17084	-0.05896	3.04441	-0.21324	-0.09033	3.34455
B3LYP	10	-0.17257	-0.06886	2.82209	-0.21865	-0.10809	3.00849
B3P86	10	-0.19342	-0.09114	2.78318	-0.24005	-0.12377	3.16414
B3PW91	10	-0.17392	-0.07094	2.80223	-0.21628	-0.10050	3.15053
B971	10	-0.16570	-0.06300	2.79461	-0.21104	-0.10395	2.91407
B972	10	-0.16259	-0.05983	2.79624	-0.21726	-0.10560	3.03842
B98	10	-0.17050	-0.06436	2.88822	-0.21449	-0.10226	3.05393
BHandH	10	-0.20163	-0.04480	4.26756	-0.21568	-0.04341	4.68770
BHandHLYP	10	-0.22233	-0.04411	4.84961	-0.20843	-0.04138	4.54566
HFB	10	-0.13907	-0.06770	1.94208	-0.14890	-0.10631	1.15893
MPW1PW91	10	-0.17780	-0.06633	3.03325	-0.21766	-0.08626	3.57558
O3LYP	10	-0.15564	-0.06754	2.39732	-0.19639	-0.11801	2.13283
PBE1PBE	10	-0.17642	-0.06643	2.99298	-0.21711	-0.08574	3.57476

3.3.2 Sm_3 Trimer Calculations

Only $m = 19$ and $m = 21$ calculations give results, even no results for MPW1PW91, BHandH, and BHandHLYP methods. Inspite of too few data there is not an accuracy about minimum energy multiplicity. HFB and O3LYP indicate the minimum energy at $m = 19$, other seven methods at $m = 21$. Since Sm atom has six unpaired electrons, the expected multiplicity value is 19, whereas most of the methods failed to conclude the calculation at this multiplicity. Table 3.33 demonstrates the all attained results of minimum energy values of Sm_3. The starred values in the energy tables indicate the minimum energy values through this study, however in the previous table except O3LYP, all methods give only one result, so

these minimum values are not reliable to accept them exact minimum points. By comparing to the previous total energy tables, it is clearly seen that Sm_3 trimer calculations are the most difficult and challenging ones, since even Sm atom is an extensive one with 62 electrons, three Sm atoms not easy to handle.

Table3.33: Total energies, E_m, in Hartrees, for Sm_3 trimer for different multiplicities, m $(2S + 1)$. The starred ones show the lowest energy. 'nc' indicates a 'not completed' calculation due to a non-convergent- or confused-SCF process.

method	$-E_{19}$	$-E_{21}$
B1LYP	nc	243.7079*
B3LYP	nc	244.2362*
B3P86	nc	245.3442*
B3PW91	nc	244.3930*
B971	nc	244.0959*
B972	nc	244.3823*
B98	nc	244.1446*
BHandH	nc	nc
BHandHLYP	nc	nc
HFB	243.8163*	nc
MPW1PW91	nc	nc
O3LYP	244.9254*	244.8975
PBE1PBE	nc	243.9542*

The spectroscopic constants of Sm_3 trimer are demonstrated in Table 3.34, which are optimized interatomic separations, bond angle, and vibrational frequencies. Because of the lack of information about Sm_3 trimer, we prefer to give all attained results. The corresponding calculations of expected multiplicity value for Sm_3 conclude only for HFB and O3LYP methods. Although their bond lengths are very close each other around 4.7 Å, bond angles are 60.1 and 126.7 °, different from each other. The vibrational frequencies of this trimer are given nearly the same by HFB method, but no significant relation for O3LYP. The information about $m = 19$ case for Sm_3 is not enough to discuss on it. If we continue from the second part of the same table, where $m = 21$ cases are demonstrated, we can see that only method that breaks the general tendency is B972. Except B972, other methods give separation values R_{12} and R_{23} are in the range of 4.19 - 4.30 Å. The bond angle changes from 111 ° to 118 ° and we cannot talk about symmetry for the geometrical structure of Sm_3 trimers. The only thing, remarkable about frequencies is that at least two of them are comperatively close two each other and the remaining one is smaller than these two. These three frequency values are

roughly centered around 12, 53, and 57 cm^{-1}.

Table3.34: Bond lengths R_{12} and R_{23} (Å), bond angle θ_{123} (deg), and vibrational frequencies ω_n (cm^{-1}) of Sm_3 trimer.For the notation used, see Fig. 3.9.

method	m	R_{12}	R_{23}	θ_{123}	ω_1	ω_2	ω_3
HFB	19	4.7886	4.7956	60.0690	33.1440	33.6374	34.4114
O3LYP	19	4.7378	4.7272	126.7256	5.7828	32.3123	45.3594
B1LYP	21	4.2668	4.2696	113.7498	11.4360	49.9752	57.3797
B3LYP	21	4.2477	4.2490	111.8027	15.3370	51.9261	57.9838
B3P86	21	4.2110	4.1936	113.6510	9.3339	54.7454	59.5442
B3PW91	21	4.2336	4.2522	117.6514	12.5195	53.5626	57.8730
B971	21	4.2662	4.2396	117.7272	13.9140	55.8347	59.1260
B972	21	3.8016	3.9382	69.9648	31.4646	44.3272	70.8001
B98	21	4.2689	4.2319	118.4543	12.3124	54.1845	57.7793
BHandH	21	–	–	–	–	–	–
BHandHLYP	21	–	–	–	–	–	–
HFB	21	–	–	–	–	–	–
MPW1PW91	21	–	–	–	–	–	–
O3LYP	21	4.2917	4.3024	115.4995	14.1583	49.7005	56.4101
PBE1PBE	21	4.2255	4.2512	117.9038	14.3396	53.7545	59.2637

According to Table 3.35, there is no symmetry between the charges of the Sm_3 trimer. The dipole moment values for $m = 19$ are not notable, however for $m = 21$ they seem accurate and close to the 1.6 Debye with the exception of B972 methods which gives 1.3 Debye approximately.

It is interesting to note in HOMO–LUMO table of Sm_3 (Table 3.36) that for $m = 19$ case only methods HFB and O3LYP give results which method were gain a fame by generating exceptional situations. It can be more meaningful to talk about only $m = 21$ case for this table. The methods BHandH, BHandHLYP, HFB, and MPW1PW91 have not been completed the calculations as seen in table. O3LYP gives the minimum value for $E_g(\alpha)$ as 0.90 Hartrees where the others are averaged around 1.30 Hartrees. There is an exceptional case for B972 also, for the fist time in HOMO–LUMO tables, it gives $E_g(\beta)$ value minimum as 0.84 Hartrees where the other values are around 1.50 Hartrees.

Table3.35: Calculated excess charge (in units of electron charge) on atoms and dipole moments (in Debye) of Sm_3 trimer.

method	m	q_1	q_2	q_3	μ
HFB	19	-0.000199	0.000331	-0.000132	0.0015
O3LYP	19	-0.004715	0.005272	-0.000558	0.1981
B1LYP	21	-0.039669	0.077510	-0.037841	1.6431
B3LYP	21	-0.037984	0.077902	-0.039918	1.5683
B3P86	21	-0.040334	0.086364	-0.046030	1.6384
B3PW91	21	-0.046829	0.087904	-0.041075	1.6758
B971	21	-0.024885	0.057284	-0.032400	1.6228
B972	21	-0.041501	0.144653	-0.103152	1.3033
B98	21	-0.027456	0.063010	-0.035554	1.5795
BHandH	21	–	–	–	–
BHandHLYP	21	–	–	–	–
HFB	21	–	–	–	–
MPW1PW91	21	–	–	–	–
O3LYP	21	-0.039062	0.077230	-0.038168	1.6493
PBE1PBE	21	-0.044694	0.081461	-0.036767	1.7668

3.3.3 $SmCo_2$ Trimer Calculations

The total energy and corresponding multiplicity values of $SmCo_2$ are demonstrated in Table 3.37. By a short glimpse, an interesting situation take attention, that is the discrimination of the corresponding multiplicity values for minimum energy. There are two values, $m = 3$ and $m = 11$ and for the first time given multiplicities are not consecutive values. As mentioned before, Sm atom has 6 unpaired electrons and Co atom has 3, so to experience the $m = 3$ case three of these atom has to be tied as remaining only two unpaired electrons, this situation seems not so feasible. Unfortunatelly, nearly half of our methods give this nonsense value for multiplicity, which are B3LYP, B3P86, B3PW91, B972, BHandH, HFB, and O3LYP. Besides, the results of $m = 11$ case are plausible as will be discussed in a short time. Another interesting thing is that the difference between energies are very small for all possible multiplicity values. For example, all energy values from $-E_1$ to $-E_19$ fluctuate between the values 370.9404-371.3720 Hartrees for B1LYP, the difference is 0.4316 Hartrees and another example PBE1PBE values from 371.0343 to 371.5420 Hartrees, the difference is 0.5077 Hartrees. If we closely look to Table 3.37 to catch any pattern among energy values, the only thing we will obtain is a clutter.

In Table 3.38 and Table 3.39, the spectroscopic constants of $SmCo_2$ are displayed for both

Table3.36: HOMO and LUMO energies (in Hartrees), and HOMO-LUMO gap (E_g) energies (in eV) of the Sm_3 trimer, calculated for the multiplicity, m $(2S+1)$, at which the total energy is minimum.

method	m	HOMO(α)	LUMO(α)	$E_g(\alpha)$	HOMO(β)	LUMO(β)	$E_g(\beta)$
HFB	19	-0.07445	-0.03798	0.99240	-0.06394	0.00297	1.82071
O3LYP	19	-0.08784	-0.02207	1.78969	-0.07916	-0.01133	1.84575
B1LYP	21	-0.04760	0.00447	1.41690	-0.09871	-0.04145	1.55812
B3LYP	21	-0.04947	-0.00501	1.20982	-0.10075	-0.04911	1.40520
B3P86	21	-0.07490	-0.03013	1.21825	-0.12144	-0.06662	1.49173
B3PW91	21	-0.05624	-0.01152	1.21689	-0.10319	-0.04778	1.50778
B971	21	-0.05095	-0.00279	1.31050	-0.10044	-0.05010	1.36982
B972	21	-0.06333	-0.01399	1.34261	-0.08840	-0.05746	0.84192
B98	21	-0.05260	-0.00322	1.34370	-0.10164	-0.04920	1.42696
BHandH	21	–	–	–	–	–	–
BHandHLYP	21	–	–	–	–	–	–
HFB	21	–	–	–	–	–	–
MPW1PW91	21	–	–	–	–	–	–
O3LYP	21	-0.04128	-0.00819	0.90042	-0.08514	-0.04290	1.14941
PBE1PBE	21	-0.05806	-0.00559	1.42778	-0.10415	-0.04371	1.64466

$m = 3$ and $m = 11$ cases. The $m = 3$ case, only the seven methods are take into account, which gives the minimum energies at this value for the reasons mentioned above. Despite all disalignments, bond lengths R_{12} and R_{23} are in accordance with each other. The two values are already equal to each other for all methods and varies in a range 2.93-3.04 Å can be regarded as close to each other among all methods. Except BHandH and B3LYP methods, they show nearly linear geometric configurations, even B3P86 and B3PW91 gives 180°. O3LYP method disturbs the general accuracy of vibrational frequency by giving three frequency values around 109, 119, and 146 cm^{-1}. Other methods seen as coherent with the frequency values around 23, 116, and 150 cm^{-1}. The charge seperation and dipole moment values, which can be checked from Table 3.39, are compatible with the results of Table 3.38. It has to be point out at that the unfeasible situation about $m = 3$ multiplicity value of $SmCo_2$ is making compact bonds with this linearly geometric structure.

The results of more acceptable multiplicity $m = 11$ from the same tables indicates two different structure, one is very close to linear geometric configurations and the other gives bond angle around 163°. The latter group consists of B1LYP, B3LYP, B3P86, B3PW91, B971, and B98. Although there is a significant discrimination about bond angle among the methods, other all constants, bond lengths, vibrational frequencies, and excess charges are in almost perfect agreement. The bond lengths might be described as $R_i = 2.98 \pm 0.06$ Å and vibrational frequencies are very close to average values 23, 113, and 147 cm^{-1}. In addition

Table3.37: Total energies, E_m, in Hartrees, for $SmCo_2$ trimer for different multiplicities, m $(2S+1)$.

method	$-E_1$	$-E_3$	$-E_5$	$-E_7$	$-E_9$	$-E_{11}$	$-E_{13}$	$-E_{15}$	$-E_{17}$	$-E_{19}$
B1LYP	370.9404	371.3683	371.2813	371.3110	371.3404	371.3720*	371.3630	371.3094	371.2319	371.0836
B3LYP	371.3499	371.7761*	371.7239	371.7503	371.7435	371.7748	371.7667	371.7103	371.6241	371.4695
B3P86	372.4809	372.9115*	372.8918	372.8843	372.8536	372.9094	372.9061	372.8507	372.7723	372.6373
B3PW91	371.4313	371.8854*	371.8652	371.8076	371.8325	371.8832	371.8802	371.8279	371.7552	371.6144
B971	371.1997	371.5868	371.5587	371.5740	371.5557	371.5934*	371.5784	371.5089	371.4350	371.2719
B972	371.6799	372.0979*	372.0664	372.0777	372.0660	372.0976	372.0812	372.0187	371.8881	371.7558
B98	371.2790	371.6831	371.6630	371.6715	371.6438	371.6913*	371.6762	371.6087	371.5373	371.3780
BHandH	369.0493	369.7590*	369.7386	369.6944	369.6715	369.7573	369.7536	369.7200	369.6666	369.5323
BHandHLYP	370.4053	370.8037	370.6520	370.7347	370.7585	370.8192*	370.8075	370.7501	370.6895	370.5791
HFB	nc	370.2119*	370.1849	370.2081	370.1715	370.2064	370.2085	370.1714	370.0983	369.9873
MPW1PW91	371.2493	371.7319	371.6793	371.7115	371.7013	371.7332*	371.7309	371.6512	371.6176	371.4784
O3LYP	371.8877	372.3369*	372.3126	372.2690	372.2878	372.3338	372.3273	372.2664	372.1758	372.0207
PBE1PBE	371.0343	371.5413	371.4987	371.5193	371.5081	371.5420*	371.5399	371.3687	371.4264	371.2839

charges match the equality $2|q_1| = 2|q_3| = q_2$ perfectly, even their numerical values are so close to each other, might be averaged at $0.6|e|$ for $|q_1|$ and so $|q_3|$. The discrimination is also observed in dipole moment values, as expected; the structures close to linear geometry give μ nearly zero and the others give aproximately $1.5|e|$. Only PBE1PBE is an exception here, with the value $0.6|e|$.

Table3.38: Bond lengths R_{12} and R_{23} (Å), bond angle θ_{123} (deg), and vibrational frequencies ω_n (cm^{-1}) of $SmCo_2$ trimer. For the notation used, see Fig. 3.9.

method	m	R_{12}	R_{23}	θ_{123}	ω_1	ω_2	ω_3
B3LYP	3	2.9331	2.9331	161.1631	17.5528	116.3024	149.7179
B3P86	3	2.9266	2.9266	180.0000	20.4975	118.8106	155.7995
B3PW91	3	2.9452	2.9452	180.0000	23.0975	116.8782	153.0267
B972	3	2.9434	2.9434	179.9705	16.7771	112.6143	147.2985
BHandH	3	2.9317	2.9317	148.4707	31.3149	118.1967	147.4468
HFB	3	3.0368	3.0382	179.8909	32.3718	107.4464	139.8954
O3LYP	3	2.9686	2.9670	174.2533	108.7929	118.5958	146.2946
B1LYP	11	2.9752	2.9752	162.9116	18.4599	113.6248	146.5105
B3LYP	11	2.9542	2.9542	162.1995	18.9965	115.8427	149.5719
B3P86	11	2.9186	2.9186	163.5896	20.4025	118.6954	154.0548
B3PW91	11	2.9392	2.9392	165.4604	17.6081	116.3699	151.2471
B971	11	2.9653	2.9653	163.0069	24.5386	113.9750	147.7167
B972	11	2.9645	2.9646	179.9848	32.7519	112.9972	147.8264
B98	11	2.9660	2.9660	163.2708	24.4891	113.5142	147.0553
BHandH	11	2.9454	2.9454	180.0000	13.8876	111.8542	147.2085
BHandHLYP	11	3.0413	3.0413	179.9766	19.4891	106.3679	138.8708
HFB	11	3.0283	3.0324	179.9553	17.3908	108.9150	141.1502
MPW1PW91	11	2.9515	2.9516	179.9731	31.4940	114.1198	149.7423
O3LYP	11	2.9779	2.9779	179.9968	28.9573	110.6921	144.6396
PBE1PBE	11	2.9521	2.9521	180.0000	35.5184	113.7510	149.1385

The general tendency about HOMO–LUMO tables has not been broken for $SmCo_2$ trimer which tabulated in Table 3.40. That means HBF and O3LYP give smaller vaues for $E_g(\alpha)$ and $E_g(\beta)$ and half and half methods BHandH and BHandHLYP methods give greater values in comparison to other methods. To examplify this, we can notify the results for $m = 11$ case of HFB method as $E_g(\alpha) = 1.69$ Hartrees and $E_g(\beta) = 0.91$ Hartrees and for BHandH method as $E_g(\alpha) = 3.98$ Hartrees and $E_g(\beta) = 3.83$ Hartrees. Other methods are average around $E_g(\alpha) = 2.90$ Hartrees and $E_g(\beta) = 2.75$ Hartrees.

Table3.39: Calculated excess charge (in units of electron charge) on atoms and dipole moments (in Debye) of $SmCo_2$ trimer.

method	m	q_1	q_2	q_3	μ
B3LYP	3	-0.589815	1.179631	-0.589815	1.8171
B3P86	3	-0.595703	1.191407	-0.595703	0.0000
B3PW91	3	-0.598929	1.197858	-0.598929	0.0000
B972	3	-0.599011	1.198022	-0.599011	0.0029
BHandH	3	-0.594011	1.188022	-0.594011	2.8019
HFB	3	-0.570854	1.141626	-0.570772	0.0111
O3LYP	3	-0.594475	1.187688	-0.593214	0.5286
B1LYP	11	-0.601043	1.202085	-0.601042	1.6473
B3LYP	11	-0.598515	1.197035	-0.598519	1.7165
B3P86	11	-0.602447	1.204895	-0.602448	1.5750
B3PW91	11	-0.606147	1.212293	-0.606147	1.3890
B971	11	-0.598255	1.196510	-0.598255	1.5898
B972	11	-0.611554	1.223105	-0.611551	0.0015
B98	11	-0.602870	1.205739	-0.602870	1.5761
BHandH	11	-0.600931	1.201863	-0.600931	0.0000
BHandHLYP	11	-0.611686	1.223373	-0.611686	0.0023
HFB	11	-0.592752	1.185177	-0.592425	0.0116
MPW1PW91	11	-0.608873	1.217731	-0.608859	0.0027
O3LYP	11	-0.608725	1.217449	-0.608724	0.0003
PBE1PBE	11	-0.603623	1.207247	-0.603623	0.5558

3.3.4 Sm_2Co Trimer Calculations

The last part of this study is allocated to the Sm_2Co trimer calculations. In Table 3.41, total energy values are given and seen that minimum energies are given at two different multiplicity values $m = 12$ and $m = 16$, intensively at latter one. B3P86, B3PW91, O3LYP, and PBE1PBE give minimum at $m = 12$, however the values are very close to each other, even the difference are about 0.0024 Hartrees of the first three and 0.0003 Hartrees for the last one. There cannot be catched any pattern, energy values are fluctuated for all possible multiplicity values, and additionally too many missing data which make evaluation harder. The missing results are not surprising for us since this trimer includes two Sm atoms. Even the dimer of Sm atom failed to give enery values completely, can be seen in Table 3.26.

Because of two values of multiplicity, we arrange the following tables as including the both of them. As we start from $m = 12$ case, all results seen in accordance with each other. All the bond angles are around 74 $^\circ$ and the vibrational frequency values can be averaged around 56, 77, and 112cm^{-1} . For $m = 16$, situation is not that simple, even three groups of angle, means that of geometrical structure. The first group consist of B3P86, B3PW91, B971, O3LYP, and

Table3.40: HOMO and LUMO energies (in Hartrees), and HOMO-LUMO gap (E_g) energies (in eV) of the $SmCo_2$ trimer, calculated for the multiplicity, m $(2S+1)$, at which the total energy is minimum.

method	m	HOMO(α)	LUMO(α)	$E_g(\alpha)$	HOMO(β)	LUMO(β)	$E_g(\beta)$
B3LYP	3	-0.15811	-0.06810	2.44930	-0.16732	-0.06344	2.82672
B3P86	3	-0.17819	-0.08053	2.65746	-0.18914	-0.07622	3.07271
B3PW91	3	-0.15750	-0.05796	2.70862	-0.16859	-0.05425	3.11135
B972	3	-0.15508	-0.05484	2.72767	-0.15999	-0.05246	2.92604
BHandH	3	-0.17482	-0.03257	3.87082	-0.18101	-0.03165	4.06429
HFB	3	-0.09318	-0.06240	0.83757	-0.13313	-0.05303	2.17963
O3LYP	3	-0.14157	-0.06182	2.17011	-0.15096	-0.05884	2.50671
B1LYP	11	-0.16764	-0.06195	2.87597	-0.15470	-0.05368	2.74889
B3LYP	11	-0.17009	-0.07061	2.70699	-0.15669	-0.06231	2.56821
B3P86	11	-0.19115	-0.08261	2.95352	-0.17504	-0.07499	2.72250
B3PW91	11	-0.17049	-0.06064	2.98917	-0.15427	-0.05290	2.75842
B971	11	-0.16556	-0.06471	2.74427	-0.15318	-0.05454	2.68413
B972	11	-0.16363	-0.05861	2.85774	-0.15215	-0.04852	2.81992
B98	11	-0.16801	-0.06453	2.81583	-0.15462	-0.05405	2.73665
BHandH	11	-0.18413	-0.03791	3.97885	-0.17098	-0.03033	3.82728
BHandHLYP	11	-0.18326	-0.03974	3.90538	-0.17066	-0.03244	3.76116
HFB	11	-0.13255	-0.07053	1.68765	-0.08983	-0.05650	0.90696
MPW1PW91	11	-0.17268	-0.05603	3.17421	-0.15648	-0.04783	2.95652
O3LYP	11	-0.15313	-0.06524	2.39161	-0.13865	-0.05657	2.23351
PBE1PBE	11	-0.17191	-0.05858	3.08387	-0.15638	-0.04978	2.90073

PBE1PBE methods corresponding angles are approximately 74 $^\circ$, reflects isosceles triangle geometric structure with equal R_{12} and R_{23} values. The corresponding frequency values are averaged around 62, 73, and 104 cm^{-1}. BHandH and MPW1PW91 constitute the second group that the corresponding angles are around 94 and 92 $^\circ$ and the bond lengths are equal to each other for each method. The geometric structure seems to be close to isosceles right triangle. There is not a similarity between the frequency values ω_n for these two methods. The last group consists of six methods, B1LYP, B3LYP, B972, B98, BHandHLYP, and HFB, whose angle can be average around 177 $^\circ$ seems close the linear structure but can not be acceptable as so. The bond lengths are equal to each other similar to the other groups. the values of HFB is a bit smaller than others, so except it frequency values of other methods are around 27, 56, and 100 cm^{-1}.

There is no need to say much about excess charge and dipole moments of Sm_2Co trimer. All charge values seems symmetric for $m = 12$, so they can fulfill the mentioned equality $2|q_1| = 2|q_3| = q_2$. Although this is not the case for $m = 12$, their dipole moments are in accordance with each other. There are two groups for dipole moments at multiplicity value 16. One of them average about 3.80 Hartrees and the other group is about 0.17 Hartrees. This

Table3.41: Total energies, E_m, in Hartrees, for Sm_2Co trimer for different multiplicities, m $(2S+1)$.

method	$-E_2$	$-E_4$	$-E_6$	$-E_8$	$-E_{10}$	$-E_{12}$	$-E_{14}$	$-E_{16}$	$-E_{18}$	$-E_{20}$	$-E_{22}$	$-E_{24}$
B1LYP	nc	nc	307.3820	307.3734	307.5552	307.5601	307.5523	307.5624*	307.5323	307.4605	307.3784	307.0865
B3LYP	nc	307.7121	307.9101	307.9813	308.0214	308.0275	308.0043	308.0281*	307.9994	307.9300	307.8385	307.5513
B3P86	308.8220	309.1482	309.0449	nc	nc	309.1517*	309.1374	309.1493	309.0756	309.0660	308.9809	308.7021
B3PW91	307.7418	307.9437	nc	308.1239	nc	308.1614*	308.1476	308.1590	308.1380	308.0806	nc	307.7271
B971	nc	307.4331	307.7423	307.8121	307.8582	307.8624	307.8394	307.8648*	nc	307.7706	307.6494	307.3577
B972	308.0024	307.8218	nc	308.2037	308.2475	308.2530	308.2433	308.2547*	308.2249	308.1544	308.0260	307.7352
B98	nc	nc	307.8209	307.8919	307.9350	307.9401	307.9176	307.9420*	307.9149	307.8336	307.7259	307.4439
BHandH	nc	nc	nc	305.4312	305.6189	305.7035	305.6746	305.7107*	305.6688	305.6405	305.5412	305.3087
BHandHLYP	nc	nc	306.4881	306.4552	306.6448	306.6041	306.6453	306.6562*	306.5205	306.5799	306.4869	306.2436
HFB	307.0138	306.8543	306.9288	306.9803	307.0095	307.0157	307.0051	307.0163*	306.9895	nc	nc	nc
MPW1PW91	nc	307.7370	307.8477	nc	307.9257	nc	307.9279	307.9381*	nc	307.8640	307.7892	307.5190
O3LYP	308.6259	308.3850	308.5235	308.5933	308.6275	308.6350*	308.6196	308.6327	308.6116	308.5434	308.4483	308.1325
PBE1PBE	nc	307.4739	307.6745	307.7317	307.7556	307.7695*	307.7558	307.7692	307.7286	307.6919	307.6012	307.3458

Table3.42: Bond lengths R_{12} and R_{23} (Å), bond angle θ_{123} (deg), and vibrational frequencies ω_n (cm^{-1}) of Sm_2Co trimer. For the notation used, see Fig. 3.9.

method	m	R_{12}	R_{23}	θ_{123}	ω_1	ω_2	ω_3
B3P86	12	3.0963	3.0994	74.5181	60.1835	78.8503	117.1174
B3PW91	12	3.1245	3.1245	74.3311	52.9945	77.9446	113.8776
O3LYP	12	3.1705	3.1696	74.3520	59.0937	74.5383	106.2918
PBE1PBE	12	3.1119	3.2255	74.4213	54.6425	78.5844	111.8161
B1LYP	16	3.2014	3.2014	178.4943	27.4209	56.1642	100.9899
B3LYP	16	3.1809	3.1808	178.4454	28.0331	57.5204	102.3097
B3P86	16	3.1634	3.1634	74.2914	62.1771	75.4311	111.4082
B3PW91	16	3.1844	3.1844	74.4633	59.3317	74.1704	106.6047
B971	16	3.2368	3.2368	73.6098	67.9045	73.6846	103.9630
B972	16	3.1973	3.1973	177.1633	26.0410	56.4952	100.9982
B98	16	3.1957	3.1957	174.3087	26.7266	58.2751	106.2278
BHandH	16	3.0301	3.0301	94.0566	34.7092	69.8729	110.8845
BHandHLYP	16	3.2544	3.2544	179.0175	24.9222	52.3997	98.5364
HFB	16	3.3108	3.3108	175.1862	20.9194	52.1416	81.7126
MPW1PW91	16	3.0778	3.0778	92.0486	27.1021	39.5214	112.6796
O3LYP	16	3.2529	3.2529	73.9851	66.4491	71.6462	98.0373
PBE1PBE	16	3.1925	3.1925	73.8788	58.8473	75.3725	106.0738

discrimination is about the geometry of the trimers, can be observed clearly when the methods are compared with the angle discrimination of Table 3.42.

From Table 3.44 we can investigate the HOMO–LUMO energies and energy gaps of Sm_2Co trimer for multiplicity values 12 and 16. There are four methods given for $m = 12$ case which are B3P86, B3PW91, O3LYP, and PBE1PBE. The O3LYP known by giving smaller energy gap values from previous similar discussions, here is the same situation however the difference is not so remarkable. For $m = 16$ case BHandH and BHandHLYP give greater values and HFB again gives the smaller values as expected, however for the time being O3LYP does not show significant difference from other methods. B3LYP, B972, and B98 also give smaller values, close to O3LYP, can be defined as around 1.85 Hartrees for $E_g(\alpha)$, where the average of the other methods is 2.18 Hartrees. A similar incident exist for $E_g(\beta)$, HFB significantly small, O3LYP and B971 also smaller but the difference is not so exact. BHandH and BHandHLYP demonstrate greater values as usual. The average of the remaining methods is 1.56 Hartrees.

Table3.43: Calculated excess charge (in units of electron charge) on atoms and dipole moments (in Debye) of Sm_2Co trimer.

method	m	q_1	q_2	q_3	μ
B3P86	12	0.403150	-0.804128	0.400978	3.7349
B3PW91	12	0.393664	-0.787327	0.393664	3.7048
O3LYP	12	0.406509	-0.805947	0.399437	3.8616
PBE1PBE	12	0.429600	-0.786355	0.356755	3.8478
B1LYP	16	0.446890	-0.893781	0.446891	0.0870
B3LYP	16	0.448514	-0.897070	0.448556	0.0885
B3P86	16	0.390296	-0.780592	0.390296	3.8876
B3PW91	16	0.384138	-0.768275	0.384138	3.8481
B971	16	0.384868	-0.769736	0.384868	3.8910
B972	16	0.427848	-0.855696	0.427848	0.1795
B98	16	0.439240	-0.878480	0.439240	0.3130
BHandH	16	0.455413	-0.910825	0.455413	3.5345
BHandHLYP	16	0.441154	-0.882307	0.441154	0.0636
HFB	16	0.429272	-0.858540	0.429268	0.2944
MPW1PW91	16	0.422975	-0.845954	0.422979	3.4561
O3LYP	16	0.382235	-0.764471	0.382236	3.8888
PBE1PBE	16	0.389958	-0.779916	0.389957	3.9040

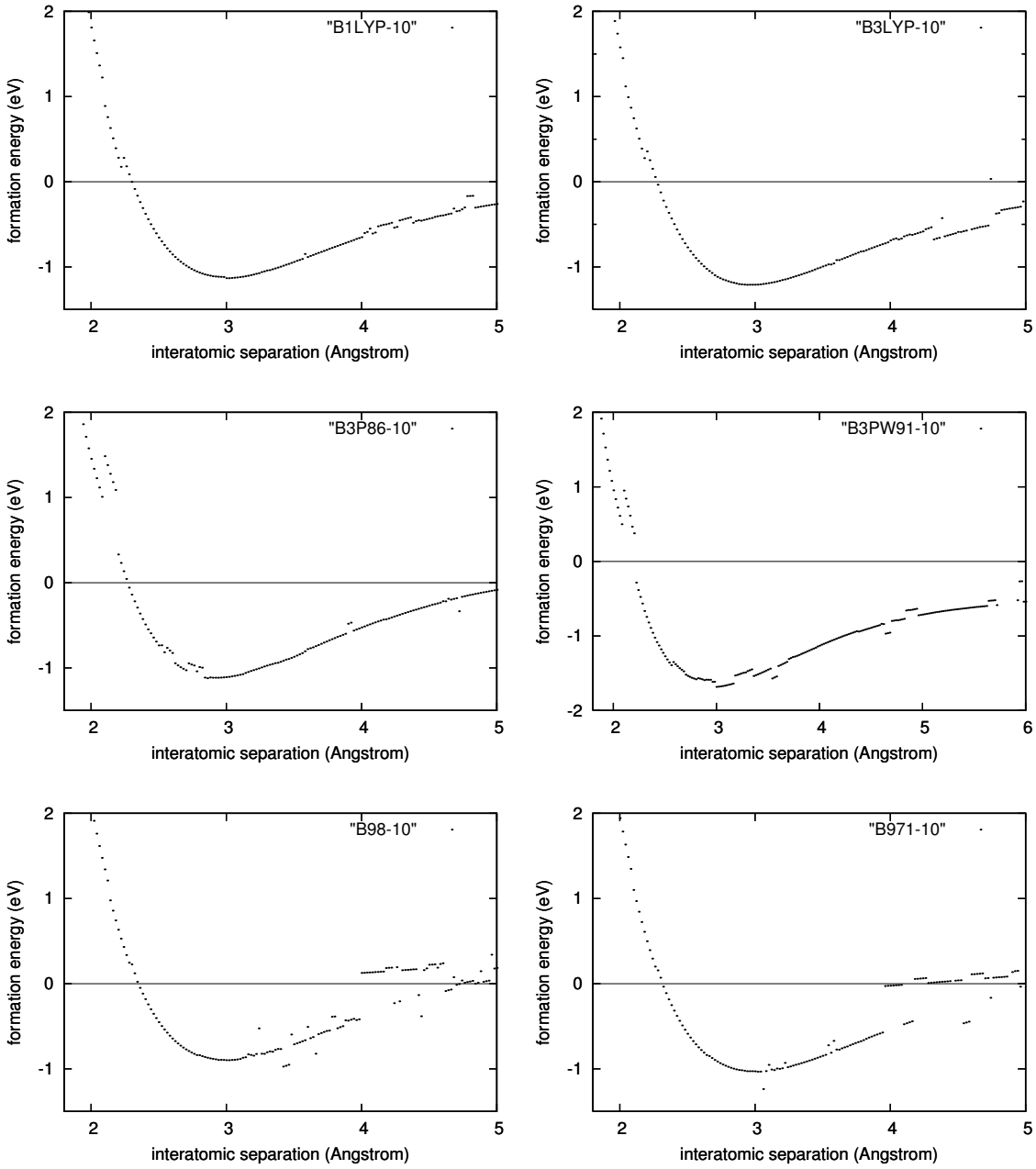

Figure 3.1: Nominal Lennard-Jones curves, describing the nature of the interaction between Sm and Co atoms, for the 12 methods in Tables or in which the total energy values are minimum for the multiplicity $m = 10$.

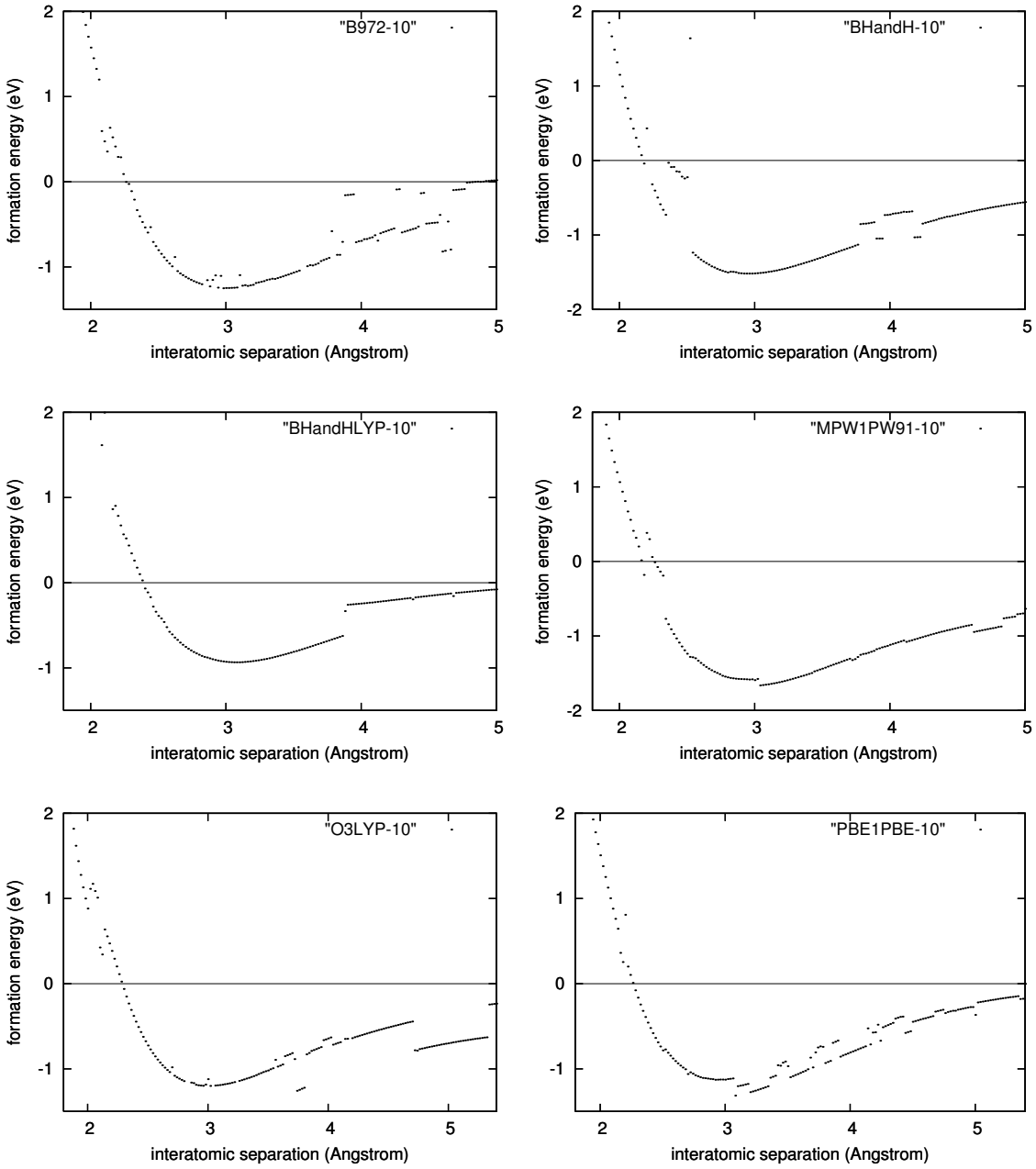

Figure 3.2: Nominal Lennard-Jones curves, describing the nature of the interaction between Sm and Co atoms, for the 12 methods in Tables or in which the total energy values are minimum for the multiplicity $m = 10$ (Cont).

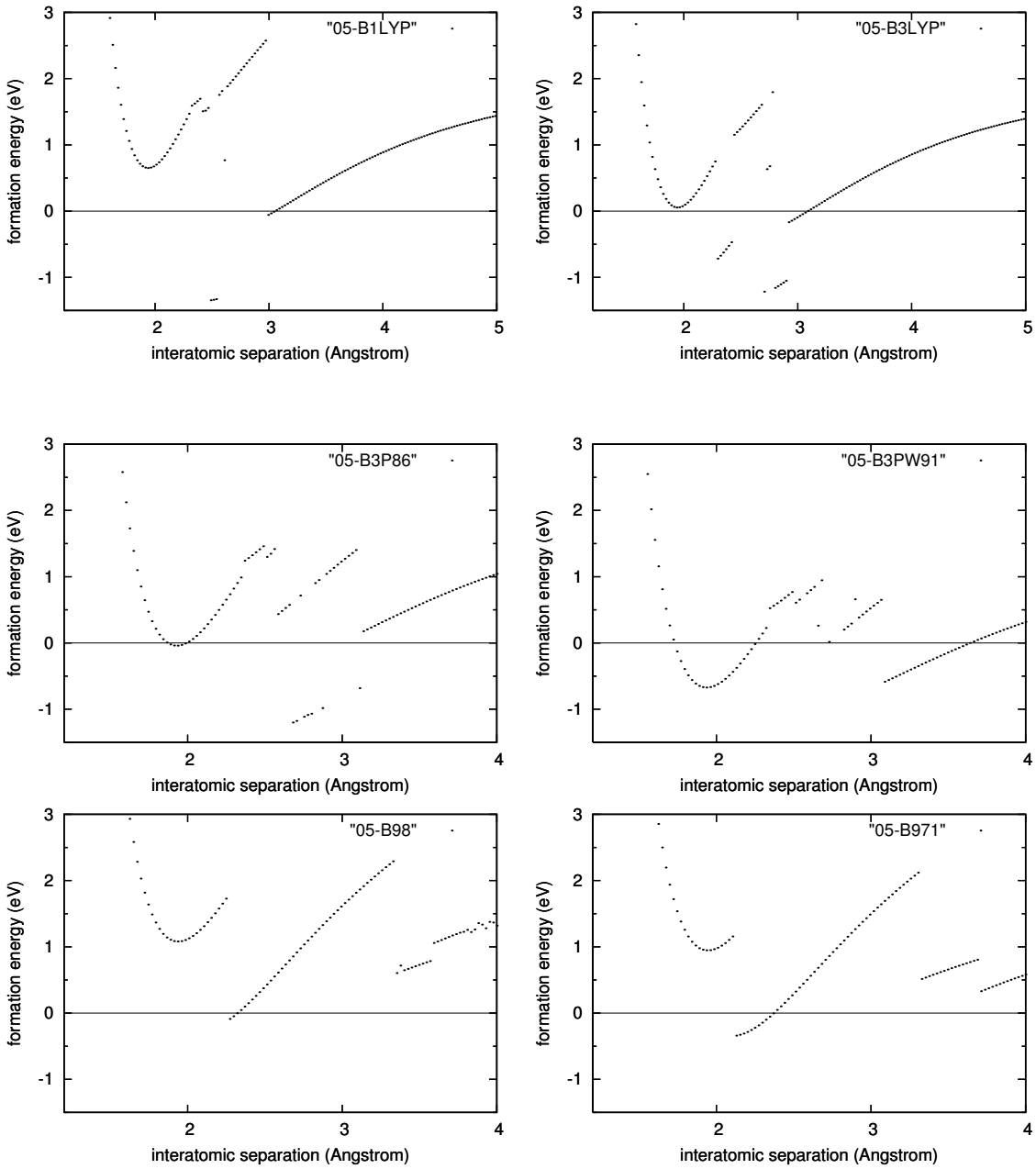

Figure 3.3: Nominal Lennard-Jones curves for Co_2 dimer with respect to DFT methods for $m = 7$.

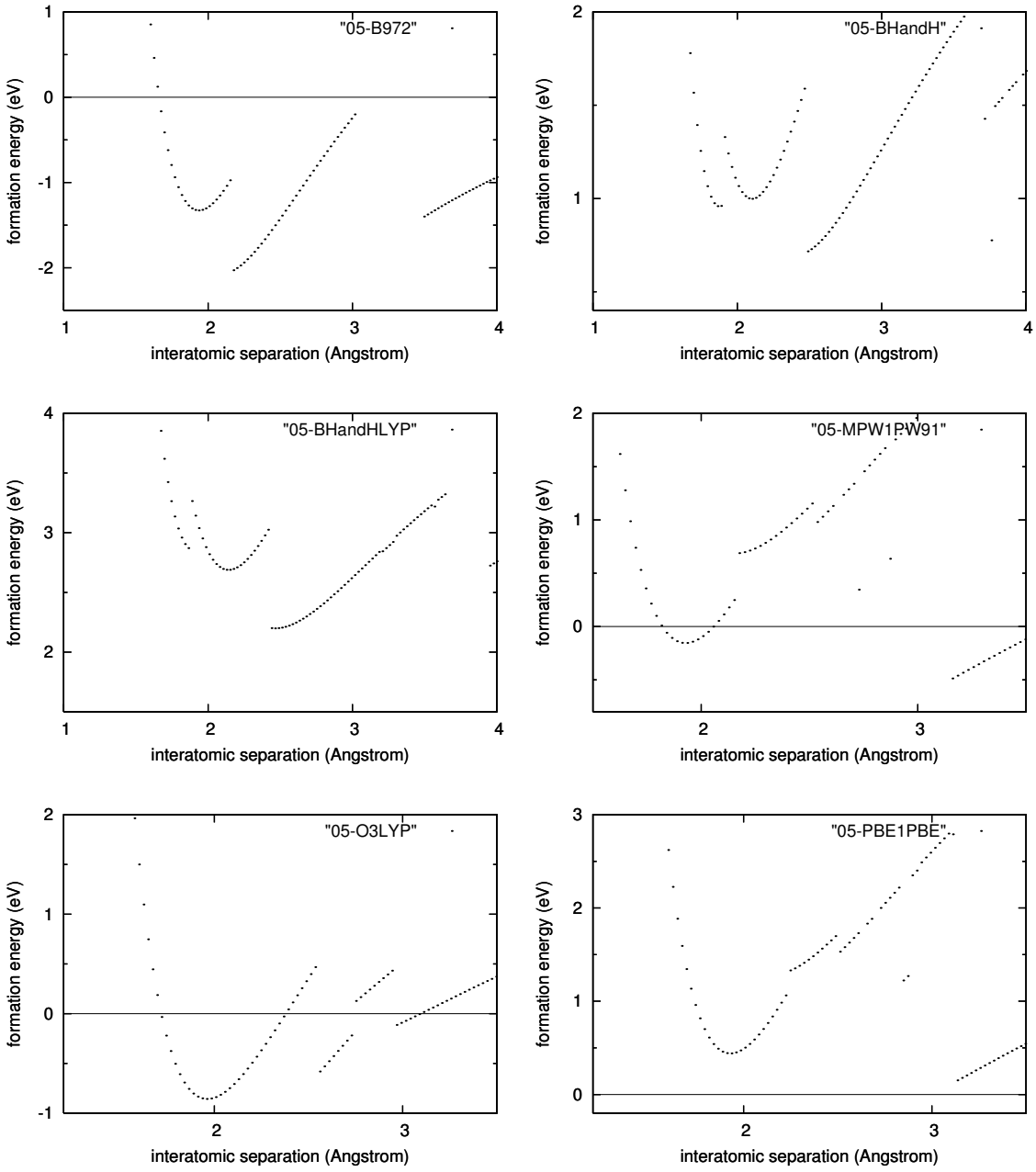

Figure 3.4: Nominal Lennard-Jones curves for Co_2 dimer with respect to DFT methods for $m = 7$.(Cont.)

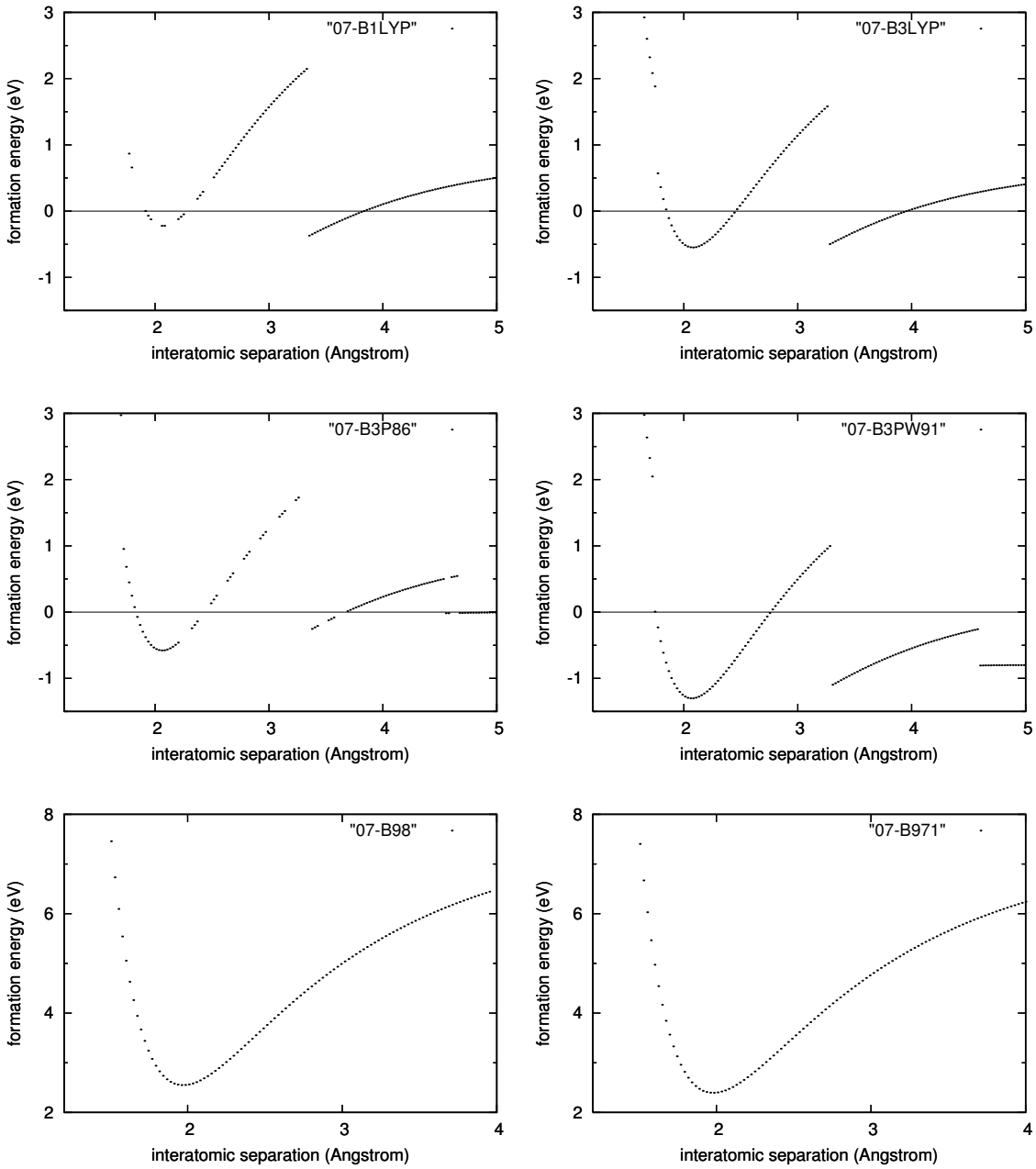

Figure 3.5: Nominal Lennard-Jones curves for Co_2 dimer with respect to DFT methods for $m = 7$.

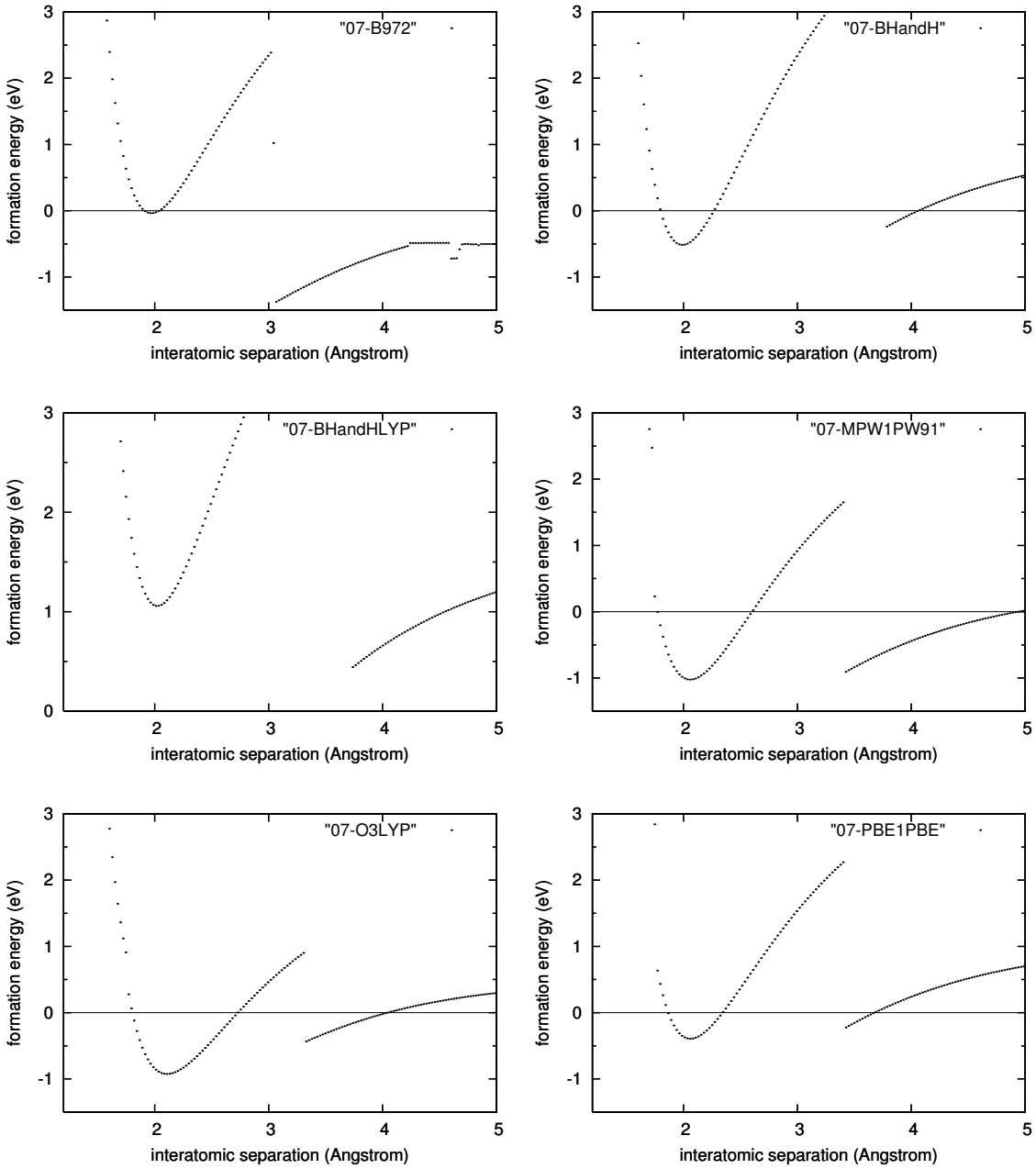

Figure 3.6: Nominal Lennard-Jones curves for Co_2 dimer with respect to DFT methods for $m = 7$.(Cont.)

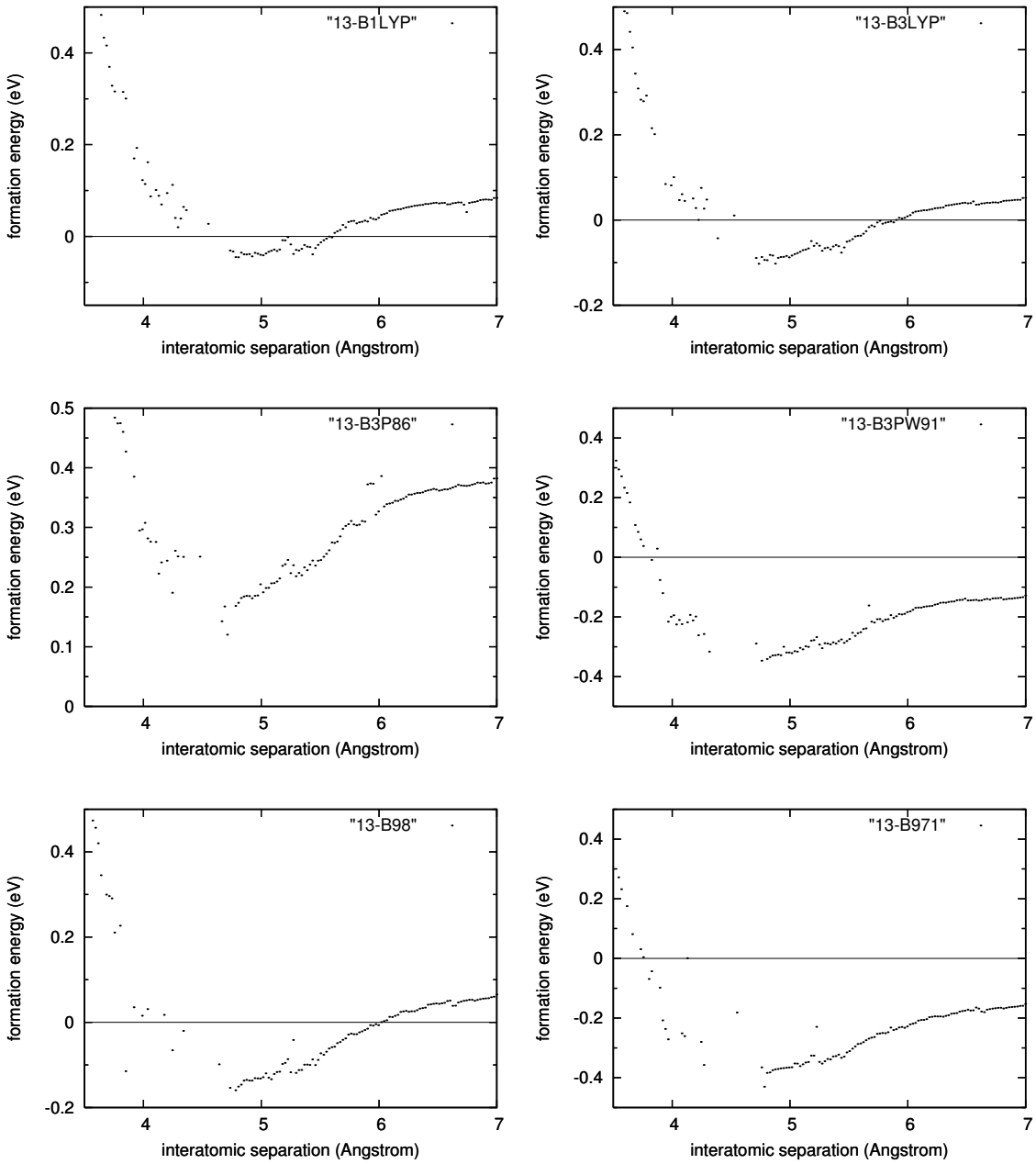

Figure 3.7: Nominal Lennard-Jones curves for Sm_2 dimer with respect to DFT methods.

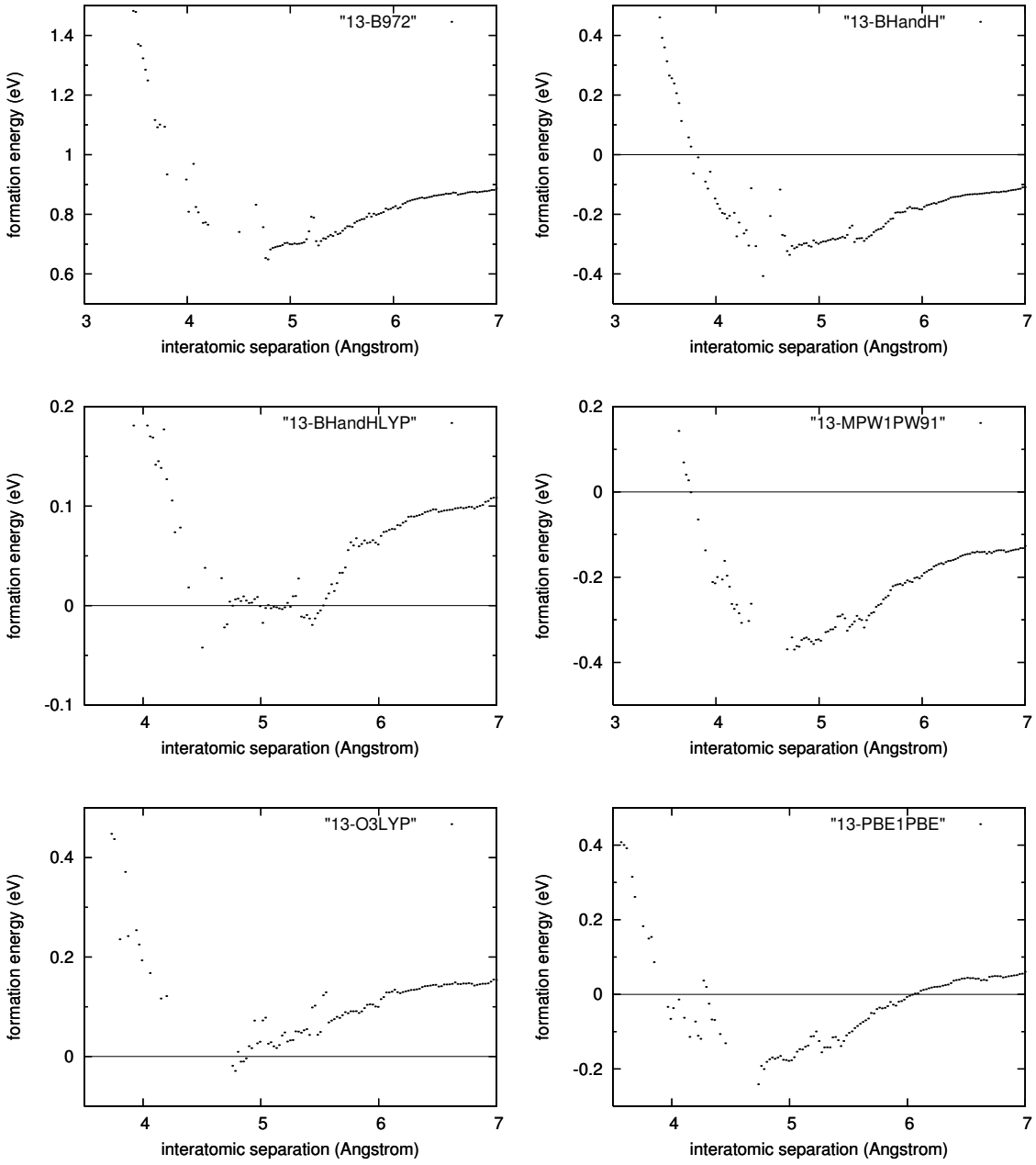

Figure 3.8: Nominal Lennard-Jones curves for Sm_2 dimer with respect to DFT methods.(Cont.)

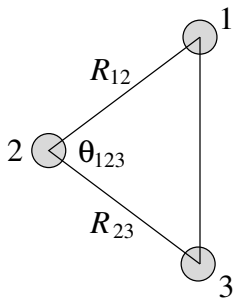

Figure 3.9: Trimer Angle

Table3.44: HOMO and LUMO energies (in Hartrees), and HOMO-LUMO gap (E_g) energies (in eV) of the Sm_2Co trimer, calculated for the multiplicity, m $(2S+1)$, at which the total energy is minimum.

method	m	HOMO(α)	LUMO(α)	$E_g(\alpha)$	HOMO(β)	LUMO(β)	$E_g(\beta)$
B3P86	12	-0.13578	-0.05568	2.17963	-0.12802	-0.07806	1.35948
B3PW91	12	-0.11612	-0.03589	2.18317	-0.10857	-0.05753	1.38887
O3LYP	12	-0.09799	-0.03146	1.81037	-0.09176	-0.05411	1.02451
PBE1PBE	12	-0.11804	-0.03480	2.26508	-0.11043	-0.05564	1.49091
B1LYP	16	-0.09642	-0.01973	2.08684	-0.10866	-0.04019	1.86316
B3LYP	16	-0.09837	-0.03002	1.85990	-0.11056	-0.04886	1.67894
B3P86	16	-0.13590	-0.05779	2.12548	-0.12584	-0.07777	1.30805
B3PW91	16	-0.11669	-0.03745	2.15623	-0.10624	-0.05702	1.33934
B971	16	-0.10942	-0.03317	2.07487	-0.10576	-0.06681	1.05988
B972	16	-0.09557	-0.02716	1.86153	-0.11128	-0.04953	1.68030
B98	16	-0.09843	-0.02881	1.89446	-0.11260	-0.04939	1.72003
BHandH	16	-0.13011	-0.00969	3.27679	-0.11506	-0.03015	2.31052
BHandHLYP	16	-0.11381	-0.00180	3.14591	-0.12582	-0.02118	2.84740
HFB	16	-0.06861	-0.04180	0.72954	-0.06281	-0.03200	0.83838
MPW1PW91	16	-0.12123	-0.03623	2.31297	-0.10574	-0.05338	1.42479
O3LYP	16	-0.09969	-0.03198	1.84248	-0.09120	-0.05468	0.99376
PBE1PBE	16	-0.11789	-0.03247	2.32440	-0.10807	-0.05373	1.47867

CHAPTER 4

CONCLUSION

In the present study, structural and electronic properties of Sm-Co cluster systems are studied theoretically. We deal with the microclusters of samarium and cobalt in all combinations Sm_mCo_n up to $(m+n=3)$. We performed the density functional theory (DFT) calculations.

This work consists of three main parts. In the first part of our study, we investigated structural and electronic properties of Sm and Co atoms and their ions, by indicating self consistent energies for all possible values of the multiplicity. Also their ionization energies and electron affinities are searched for possible ions. In the second part SmCo, Co_2, and Sm_2 dimers are investigated according to self consistent energy. In addition, we presented binding energy D_e, bond lengths, r_e, the fundamental frequency w_e, charge q, dipole moment μ, the calculated HOMO (highest occupied molecular orbital), LUMO (lowest unoccupied molecular orbital), and HOMO–LUMO gap energies of dimers. The third part of the calculations cover the structural and electronic properties of Co_3, Sm_3, $SmCo_2$, and Sm_2Co trimers. We investigated the minimum energy configurations of the trimers (bond lengths and bond angle, as well as their fundamental frequencies w_n). For all the microclusters considered, we presented the possible dissociation channels and the corresponding dissociation energies, the calculated HOMO, LUMO, and HOMO–LUMO gap energies. We also gave the calculated dipole moments and excess charges on the atoms of the trimers.

Within the scope of this study, we met in the literature of microclusters there are limited experimental and theoretical studies focused on Sm_mCo_n alloys. To our best knowledge, there is no study other than Co_2 for the rest of the clusters mentioned above. Therefore, exploring the uncertain geometrical and electronic properties of the remaining microclusters has been constituted the aim of present study.

In this study we presented our theoretical computational outcomes on the structural and energetic features Sm_mCo_n microclusters via DFT techniques. We believe that the structural features obtained in this treatise are reasonable and reliable. The present study can be seen a preliminary work for higher order microcluster of transition metal–rare earth alloys.

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