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# Theoretical study of diatomic molecules BN, SiN and LaH, electronic structure and spectroscopy

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# THÈSE

Pour obtenir le grade de  
**Docteur**

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**matériaux**

Présentée par **Salman Mahmoud**

## **TITRE DE LA THESE**

**Étude théorique des molécules diatomiques BN, SiN et  
LaH, structure électronique et spectroscopie**

**Theoretical study of diatomic molecules BN, SiN and  
LaH, electronic structure and spectroscopy**

**Soutenu le 5/12/2014 devant le jury composé de**

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## Abstract

In the present work a theoretical investigation of the lowest molecular states of BN, SiN and LaH molecule, in the representation  $^{2s+1}\Lambda^{(+/)}$ , has been performed via complete active space self-consistent field method (CASSCF) followed by multireference single and double configuration interaction method (MRSDCI). The Davidson correction noted as (MRSDCI+Q) was then invoked in order to account for unlinked quadruple clusters. The entire CASSCF configuration space was used as a reference in the MRCI calculation which has been performed via the computational chemistry program MOLPRO and by taking advantage of the graphical user interface Gabedit. Forty-two singlet, triplet, and quintet lowest electronic states in the  $^{2s+1}\Lambda^{(+/)}$  representation below  $95000\text{ cm}^{-1}$  have been investigated of the molecule BN. While twenty-eight electronic states in the representation  $^{2s+1}\Lambda^{(+/)}$  up to  $70000\text{ cm}^{-1}$  of the SiN molecule have been investigated. On the other hand the Twenty four low-lying electronic states of LaH in the representation  $^{2s+1}\Lambda^{(+/)}$  below  $35000\text{ cm}^{-1}$  have been studied by two different methods and by taking into consideration the spin orbit effect of the molecule LaH we give in the energy splitting of the eight electronic states. The potential energy curves (PECs) together with the harmonic frequency  $\omega_e$ , the equilibrium internuclear distance  $r_e$ , the rotational constants  $B_e$  and the electronic energy with respect to the ground state  $T_e$  have been calculated for the considered electronic states of BN, SiN and LaH molecule respectively. Using the canonical functions approach, the eigenvalues  $E_v$ , the rotational constants  $B_v$ , the centrifugal distortion

constants  $D_v$  and the abscissas of the turning points  $R_{min}$  and  $R_{max}$  have been calculated for electronic states up to the vibrational level  $v=51$  for LaH molecule. Eighteen and Nine electronic states have been investigated here for the first time for the molecules of BN and SiN respectively, while for LaH, news results are performed for twenty three electronic states of LaH molecule and the spin-orbit effect of LaH molecule is given here for the first time. A comparison with experimental and theoretical data for most of the calculated constants demonstrated a very good accuracy. Finally, we expect that the results of our work should invoke further experimental investigations for these molecules.

#### **Key Words**

Diatomic molecules, Ab initio Calculations, Multireference Configuration Interaction, Spectroscopic Constants, Fine Structure Constant, Electric Dipole Moment of the electron, Spin-orbit effects.

## Résumé

Une étude théorique *ab initio* des structures électroniques des molécules Diatomiques polaires BN, SiN et LaH dans la représentation  $^{2s+1}\Lambda^{(+/)}$  ont été effectués par la méthode du champ auto-cohérent de l'espace Actif complet (CASSCF), suivie par l'interaction de la configuration multiréférence (MRSDCI). La correction de Davidson, notée (MRSDCI+ Q), a ensuite été appliquée pour rendre compte de clusters ou agrégats quadruples non liés. L'ensemble de l'espace de configuration de CASSCF a été utilisé comme référence dans le calcul MRCI, qui a été effectués en utilisant le programme de calcul de chimie physique MOLPRO et en tirant parti de l'interface graphique Gabedit. Quarante-deux de plus bas états électroniques dans la représentation  $^{2s+1}\Lambda^{(+/)}$  au dessous de  $95000\text{ cm}^{-1}$  ont été étudiés de la molécule BN. Alors que vingt-huit états électroniques dans les représentations  $^{2s+1}\Lambda^{(+/)}$  jusqu'à  $70000\text{ cm}^{-1}$  de la molécule de SiN ont été étudiés. D'autre part, les vingt-quatre bas états électroniques de LaH dans les représentations  $^{2s+1}\Lambda^{(+/)}$  au dessous de  $35000\text{ cm}^{-1}$  ont été étudiées par deux méthodes différentes et en prenant en considération l'effet des spin-orbite de la molécule LaH et nous avons observé la division énergétique des huit états électroniques. Les courbes d'énergie potentielle ont été construites avec la fréquence co-harmonique  $\omega_e$ , la distance internucléaire de l'équilibre  $r_e$ , les constantes de rotation  $B_e$ . L'énergie électronique par rapport à l'état fondamentale  $T_e$  a été calculée pour les états électroniques considérés comme des BN, SiN et la molécule LaH respectivement. En utilisant l'approche des fonctions canoniques, les

valeurs propres  $E_v$ , les constantes rotationnelles  $B_v$ , la constante de distorsion centrifuge  $D_v$  et les abscisses des points de retournement  $R_{min}$  and  $R_{max}$  ont été calculés pour les états électroniques au niveau de vibration  $v=51$  pour LaH molécule.

Dix-huit et neuf états électroniques ont été étudiés pour la molécule BN et SiN respectivement, Pour LaH, vingt-trois états électroniques de la molécule LaH et l'effet de spin-orbite de molécule LaH sont donnés ici pour la première fois. La comparaison avec les données expérimentales et théoriques pour la plupart des constantes calculées démontre une très bonne précision. Enfin, ces résultats devraient ainsi mener à des études expérimentales plus poussées pour ces molécules.

### **Mots-Clés**

Diatomique molécules, Ab initio Calculations, Multireference Configuration Interaction, Constants Spectroscopique, Fine structure constant, Moment électriquedipolaire de l'électron, Spin Orbite-Effets.

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# Contents

<b>Abstract</b> .....	<b>I</b>
<b>Résumé</b> .....	<b>IV</b>
<b>Acknowledgements</b> .....	<b>VI</b>
<b>Contents</b> .....	<b>VIII</b>
<b>Introduction</b> .....	<b>12</b>
<b>References</b> .....	<b>16</b>
<b>Chapter one: Many Body problem</b> .....	<b>18</b>
1.1 Many Body Problems and Second Quantization.....	18
1.2 Fock space in Quantum theory.....	20
1.3 Operators in Second Quantization.....	21
1.3.1 Creation Operators.....	21
1.3.2 Annihilation Operators.....	22
1.4 Expressing of Quantum Mechanical Operators in second quantization.....	27
1.4.1 One Body operators.....	27
1.4.2 Two Body operators.....	29
1.5 Hamiltonian in second quantization.....	31
1.5.1 The Hamiltonian of a two body interaction.....	32
1.6 Spin in Second Quantization.....	35
1.6.1 Spin function.....	35

1.6.2 Spin Operators.....	36
1.7 Born Oppenheimer Approximations.....	38
1.8 Variation principle.....	43
1.9 Hartree fock theory .....	45
1.9.1 Hartree fock Approximations.....	46
1.9.2 Hartree fock wavefunction.....	46
1.10 Roothaan-Hall Equations.....	54
1.11 Restricted and unrestricted Hartree-Fock calculations.....	60
1.12 Configuration interaction.....	61
1.12.1 The CI Wave Functions.....	61
1.12.2 Optimization of the CI Wave Functions.....	62
1.13 Davidson correction.....	64
1.14 Basis set.....	65
1.15 Effective Core potentials (Pseudo-potentials).....	67
1.16 Correlation energy.....	67
1.17 Dynamic and non-dynamical correlation energy.....	69
1.18 Pseudo-potential and relativistic pseudo-potential.....	69
1.19 Complete Active Space Self Consistent Field (CASSCF).....	72
1.20 Multi-Configuration and Multi-Reference Methods.....	73
1.21 Multireference CI Wave Function MRSDCI.....	77
1.22 Spin-orbit Effects.....	77
1.23 Conclusion.....	82
<b>References</b> .....	83
<b>Chapter two: The Vibration-Rotation Calculation in a Diatomic Molecule</b> .....	87
2.1 Vibration-rotation canonical functions.....	87
2.2 The rotational Schrodinger equations.....	89
2.3 Analytic expressions of the rotation harmonics.....	92
2.3.1 Pure vibration ( $\Phi_0(x)$ ).....	92
2.3.2 Calculation of the rotational harmonics ( $\Phi_n(x)$ ).....	93
2.4 Numerical method.....	95
2.4.1 Calculation of the vibration wavefunction $\Phi_0(x)$ .....	95

---

2.4.2 Calculation of $\alpha_v(x)$ and $\beta_v(x)$ .....	95
2.4.3 Calculation of $\Phi'_0(x)$ .....	97
2.5 Diatomic centrifugal distortion constants (CDC).....	97
2.6 Conclusion.....	100
<b>References</b> .....	101
<b>Chapter three: Theoretical calculation of the low-lying electronic states of the molecule BN</b> .....	103
3.1 Introduction .....	103
3.2 Method of Calculations .....	105
3.3 Results and discussion.....	106
3.4 Dipole Moment.....	114
3.5 Conclusion.....	117
<b>References</b> .....	119
<b>Chapter four: Theoretical calculation of the electronic structure of the SiN molecule</b> .....	122
4.1 Introduction .....	122
4.2 Method of Calculations .....	122
4.3 Results and discussion.....	131
4.4 Conclusion.....	135
<b>References</b> .....	136
<b>Chapter five: Theoretical Calculation of the Low-Lying Electronic States of the Molecule LaH</b> .....	139
5.1 Introduction .....	139
5.2 Computational approach.....	140
5.3 Spin-Orbit effect.....	149
5.4 Vibration-rotation calculation.....	153
5.5 Conclusion.....	154
<b>References</b> .....	156

<b>Conclusion and Perspectives</b> .....	158
<b>Appendix I</b> .....	161
<b>Appendix II</b> .....	171
<b>Appendix III</b> .....	181
<b>Appendix IV</b> .....	199

## Introduction

The interest since past decade has been increasing in the theoretical and experimental study of the electronic structure of polar diatomic molecules, particularly due to their importance in chemistry [1], ultra cold interactions [2], astrophysics [3], quantum computing [4-6], precision measurements [7] and metallurgy [1]. The influence of quantum chemistry in all branches of chemistry becomes increasingly remarkable. Organic chemists use plenty quantum mechanics to estimate the relative stabilities of molecules, calculate the properties of reaction intermediates, analyze NMR and invest the mechanisms of chemical reactions spectra.

We report in this study the electronic properties and the spectroscopy of the low lying electronic states of several families of diatomic compounds, however, up to now theoretical and experimental studies of these molecules are much more limited.

By the reaction of boron atoms with  $N_2$  or  $NH_3$  at high temperatures, boron nitride BN, which is a ceramic material, can be formed [8]. This material is of substantial chemical and industrial importance [9]; the solid BN is isoelectronic to carbon and exists in several allotropic forms including the graphite-like  $\alpha$ -BN and the diamond-like  $\beta$ -BN as well as in different morphologies (nanotubes [10-11], nanosheets [12], nanocapsules [13], films etc). The BN films can grow by either

the chemical vapor deposition (CVD) or the physical vapor deposition (PVD) techniques. The accurate determination of the ground electronic state of molecule BN has been historically a very difficult task.

The remarkable interest of silicon nitride reside in many properties such as strength, hardness, chemical inertness, good resistance to corrosion, high thermal stability, and good dielectric properties [14-15]. And the transition metal monohydrides and monohalides have been extensively studied over several decades because they are of considerable interest in various fields such as astrophysics, catalytic chemistry, high-temperature chemistry and surface material [16–18]

In chapter 1 of this PhD thesis, we present a brief overview for the theoretical backgrounds of the computational methods used in the present work. The theoretical backgrounds for the electronic structure calculations in the Hartree-Fock method, followed by Complete Active Space Calculations and Multireference Configuration Interaction methods are written within the formalism of second quantization. A brief discussion for the theoretical background of spin orbit relativistic interactions in diatomic molecules has been also included within the context of the first chapter.

In chapter 2, we present the canonical function's approach for solving the vibrational and rotational Schrödinger equation in a diatomic molecule. This has allowed us to compute the vibrational energy structures and rotational constants for the ground and excited electronic states of each molecule.

In chapter 3, we list the results of our calculations for the electronic structures, without spin orbit effects, of BN diatomic molecules. In the present

work Forty-two singlet, triplet, and quintet lowest electronic states in the  $^{2s+1}\Lambda^{(\pm)}$  representation below  $95000\text{ cm}^{-1}$  have been investigated of the molecule BN. Potential energy curves were constructed and spectroscopic constants were computed. And to be more accurate, the spectroscopic constants are obtained by three different methods. Various other physical properties were also computed such as the permanent electric dipole moment.

In chapter 4, we reported the results of our calculations for the electronic structures of SiN diatomic molecules, without spin orbit effects. In our present work Twenty eight electronic states in the representation  $^{2s+1}\Lambda^{(+/-)}$  up to  $70000\text{ cm}^{-1}$  of the SiN molecule have been investigated. Potential energy curves were constructed and spectroscopic constants were computed. Various other physical properties were also computed such as the permanent electric dipole moment.

In chapter 5, we list the results of our calculations for the electronic structures, with and without spin orbit effects, of LaH diatomic molecules. In the present work Twenty four low-lying electronic states of LaH in the representation  $^{2s+1}\Lambda^{(+/-)}$  below  $35000\text{ cm}^{-1}$  have been studied by two different method. Potential energy curves were constructed and spectroscopic constants were computed. Various other physical properties were also computed such as the permanent electric dipole moment.

Throughout this thesis, we try to validate our theoretical results by comparing the calculated values of the present work to the experimental and theoretical values in literature. The comparison between the values of the present work to the experimental and theoretical results shows a very good agreement. The

small percentage relative error reported in our calculations for all of the molecular constants reflects the nearly exact representation of the true physical system by the wave functions used in our calculations. The extensive results in the Present work on the electronic structures with relativistic spin orbit effects of the molecules LaH are presented here for the first time in literature. Finally, we expect that the results of our work should invoke further experimental investigations for these molecules.

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# Many Body Problems

Computational physics is a valuable tool that helps people understand problems with the use of a computer and allows one to investigate the molecular structure and properties of atoms, molecules and solids. One of these techniques is the *ab initio* calculations, which means in Latin “from the beginning”. This name is given to computations that are based on solving the Schrödinger equation for any molecule. Once this equation is solved, a variety of chemical and physical properties can be determined, derived directly from theoretical principles with no inclusion of experimental data [1- 3].

In this chapter, our goal is to show the development of approximations which are more accurate than the independent particle model and can take account of electron correlation effects. Hartree-Fock theory followed by the methods of Complete Active Space Self Consistent Field (CASSCF) and Multi-reference Configuration Interaction (MRCI) play a principle role in the development of approximate treatments of correlation effects. A key feature of these calculations is the use of the method of second quantization. We therefore start by introducing the second quantization formalism in quantum mechanics.

## 1.1 Many Body Problems and Second Quantization

Second quantization is a formalism that forms an essential ingredient used to describe and treating the quantum many-body systems. In the second quantization

formalism, the number of the particles is not fixed and the information of the single particle bases are integrated in the operators unlike the first quantization formalism, the wave function has fixed number of the particles, and is c-number which is operated by other operators like Hamiltonian. In this approach, the quantum many-body states are represented in the Fock state basis, which are constructed by filling up each single-particle state with a certain number of identical particles. The second quantization formalism introduces the creation and annihilation operators to construct and handle the Fock states, providing useful tools to the study of the quantum many-body theory.

In this chapter, the main goal is to show how we describe the electronic Hamiltonian, other quantum-mechanical operators, spin, and state vectors in second-quantization language. We also show how we use the tools of second quantization to describe many approximation techniques (e.g., Hartree-Fock, configuration interaction (CI), multi-configuration self-consistent field (MCSCF)) which are currently in wide use within the quantum chemistry community. The need for such approximation methods is, of course, motivated by our inability to exactly solve electronic structure problems for more than one electron. First let us observe that the Schrödinger equation can be easily written for an atom or, more particularly, for a molecule of arbitrary complexity. The difficulty is usually said to lie not in writing down the appropriate Eigenvalue problem but in the development of accurate approximations to the solutions of this molecular Schrödinger equation. However, the Schrödinger equation for a system of arbitrary complexity has another problem associated with it, namely, it applies to a fixed number of particles. In other words the Schrödinger equation applies to systems in which the number of particles is conserved. However, in many physical processes the number of particles is not conserved and particles can be created or destroyed. Then there

arises the need for a new approach in quantum mechanics, namely the second quantization approach, which allows for the creation and destruction of particles.

## 1.2 Fock space in quantum theory

Fock space is an abstract linear vector space where each determinant is represented by an occupation number (ON) vector  $|K\rangle$

$$|K\rangle = |k_1, k_2, \dots, k_M\rangle \quad (1.1)$$

where

$$k_p = \begin{cases} 1 & \phi_p \text{ occupied} \\ 0 & \phi_p \text{ not occupied} \end{cases} \quad (1.2)$$

For an orthonormal set of spin orbitals the inner product between two ON vectors  $|K\rangle$  and  $|m\rangle$  which have the same number of electrons is

$$\langle k|m\rangle = \delta_{k,m} = \prod_{p=1}^M \delta_{k_p m_p} \quad (1.3)$$

And for the states with different number of electrons

$$\langle k|m\rangle = 0 \quad (1.4)$$

$F(M, 0)$  is the subspace which consists of occupied number vectors with no electrons; it contains a single vector which is called the true vacuum state

$$|vac\rangle = |0_1, 0_2, \dots, 0_M\rangle \quad (1.5)$$

the vacuum state is normalized to unity

$$\langle vac|vac\rangle = 1 \quad (1.6)$$

## 1.3 Operators in Second Quantization

### 1.3.1 Creation Operators

The second quantization method involves the use of so-called creation and annihilation operators. These operators respectively create and annihilate particles in specified single-particle states. The basic object of second quantization is the creation operator acting on some state, this operator adds a particle to the system in the state  $\alpha$ . let  $|\psi\rangle$  be an arbitrary Slater determinants with N-particles, so let us define the creation operator  $a_i^\dagger$  by its action on this arbitrary state

$$a_i^\dagger |\chi_1, \chi_2, \dots, \chi_N\rangle = |\chi_i, \chi_1, \chi_2, \dots, \chi_N\rangle \quad (1.7)$$

clearly that  $a_\alpha^\dagger$  maps the N-particle state with proper symmetry  $|\chi_1, \chi_2, \dots, \chi_N\rangle$  to N+1 particle state  $|\chi_i, \chi_1, \chi_2, \dots, \chi_N\rangle$ . The order in which two creation operators can act to a determinant is crucial. Let us show

$$a_i^\dagger a_j^\dagger |\chi_1, \chi_2, \dots, \chi_N\rangle = a_i^\dagger |\chi_j, \chi_1, \chi_2, \dots, \chi_N\rangle = |\chi_i, \chi_j, \chi_1, \chi_2, \dots, \chi_N\rangle \quad (1.8)$$

on the other hand

$$\begin{aligned} a_j^\dagger a_i^\dagger |\chi_1, \chi_2, \dots, \chi_N\rangle &= a_j^\dagger |\chi_i, \chi_1, \chi_2, \dots, \chi_N\rangle = |\chi_j, \chi_i, \chi_1, \chi_2, \dots, \chi_N\rangle \\ &= -|\chi_i, \chi_j, \chi_1, \chi_2, \dots, \chi_N\rangle \end{aligned} \quad (1.9)$$

where using the antisymmetry property of Slater determinants. Adding Eqs. (1.8) and (1.9), we have

$$a_i^\dagger a_j^\dagger + a_j^\dagger a_i^\dagger |\chi_1, \chi_2, \dots, \chi_N\rangle = 0 \quad (1.10)$$

where we have  $|\chi_1, \chi_2, \dots, \chi_N\rangle$  is an arbitrary determinant, we can discover the operator relation

$$a_i^\dagger a_j^\dagger + a_j^\dagger a_i^\dagger = 0 = \{a_i^\dagger, a_j^\dagger\} \quad (1.11)$$

since,

$$a_i^\dagger a_j^\dagger = -a_j^\dagger a_i^\dagger \quad (1.12)$$

so we can change the order of two creation operators provided and we change the sign. If we have ( $i=j$ ), then we have

$$a_i^\dagger a_i^\dagger = -a_i^\dagger a_i^\dagger = 0 \quad (1.13)$$

This equation states that we cannot create two electrons in the same spin orbital (Pauli principle). Thus

$$a_i^\dagger a_i^\dagger |\chi_1, \chi_2, \dots, \chi_N\rangle = a_i^\dagger |\chi_i, \chi_1, \chi_2, \dots, \chi_N\rangle = |\chi_i, \chi_i, \chi_1, \chi_2, \dots, \chi_N\rangle = 0$$

more generally,

$$a_i^\dagger |\chi_1, \chi_2, \dots, \chi_N\rangle = 0 \quad \text{if } i \in \{1, 2, \dots, N\} \quad (1.14)$$

This equation states that we cannot create an electron in spin orbital if one already exists.

### 1.3.2 Annihilation Operators

The Hermitian conjugate of the creation operator is given by  $a_i = (a_i^\dagger)^\dagger$  which is called an annihilation operator. Suppose  $|\chi_{N+1}\rangle$  is a state with  $N+1$  particles, then we have

$$a_i |\chi_i, \chi_1, \chi_2, \dots, \chi_N\rangle = |\chi_1, \chi_2, \dots, \chi_N\rangle \quad (1.15)$$

The annihilation operator annihilates or destroys a particle from the system, which can only act in a determinant if the spin orbital is immediately to the left. Why is the annihilation operator defined as the adjoint of creation operators? Let us consider the determinant

$$|\Psi\rangle = |\chi_i, \chi_j\rangle = 0 \quad (1.16)$$

clearly that

$$|\Psi\rangle = a_i^\dagger |\chi_j\rangle = 0 \quad (1.17)$$

The adjoint of this equation is

$$\langle\Psi| = \langle\chi_j| (a_i^\dagger)^\dagger = \langle\chi_j| a_i \quad (1.18)$$

Multiplying Eq. (1.18) to the right by  $|\Psi\rangle$ , we have

$$\langle\Psi|\Psi\rangle = \langle\chi_j| a_i |\Psi\rangle$$

since  $\langle\Psi|\Psi\rangle = 1 = \langle\chi_j|\chi_j\rangle$  therefore our formalism is consistent when

$$a_i |\Psi\rangle \equiv a_i |\chi_i, \chi_j\rangle = |\Psi\rangle \quad (1.19)$$

From Eq. (1.18) we can conclude that the annihilation operator  $a_i$  act like a creation operator if it operates on a determinant to the left. Similarly,  $a_i^\dagger$  act like an annihilation operator if it operates to the left.

To obtain the anticommutation relation satisfied by annihilation operator we have

$$a_j a_i + a_i a_j = 0 = \{a_j, a_i\} \quad (1.20)$$

since

$$a_j a_i = -a_i a_j \quad (1.21)$$

so we can change the order of two annihilation operators by changing the sign, if  $i=j$ , then we obtain

$$a_i a_i = -a_i a_i = 0 \quad (1.22)$$

therefore we cannot remove an electron from a spin orbital, if it is not already exist

$$a_i |\chi_1, \chi_2, \dots, \chi_N\rangle = 0 \quad \text{if } i \notin \{1, 2, \dots, N\} \quad (1.23)$$

In order to interchange creation and annihilation operator, consider the operator  $(a_i a_i^\dagger + a_i^\dagger a_i)$  acting on an arbitrary determinant  $|\chi_1, \chi_2, \dots, \chi_N\rangle$ , if spin an orbital  $\chi_i$  is not occupied in this determinant, we have

$$\begin{aligned} (a_i a_i^\dagger + a_i^\dagger a_i) |\chi_1, \chi_2, \dots, \chi_N\rangle \\ = a_i a_i^\dagger |\chi_1, \chi_2, \dots, \chi_N\rangle \\ = a_i |\chi_i, \chi_1, \chi_2, \dots, \chi_N\rangle = |\chi_1, \chi_2, \dots, \chi_N\rangle \end{aligned} \quad (1.24)$$

On other hand if the spin orbital  $\chi_i$  is occupied in this determinant, on can find

$$\begin{aligned} (a_i a_i^\dagger + a_i^\dagger a_i) |\chi_1, \chi_2, \chi_i, \dots, \chi_N\rangle &= a_i^\dagger a_i |\chi_1, \chi_2, \chi_i, \dots, \chi_N\rangle \\ &= -a_i^\dagger a_i |\chi_i, \chi_1, \chi_2, \dots, \chi_N\rangle \end{aligned}$$

$$\begin{aligned}
&= -a_i^\dagger |\chi_1, \chi_2, \dots, \chi_N\rangle \\
&= -|\chi_i, \chi_1, \chi_2, \dots, \chi_N\rangle \\
&= |\chi_1, \chi_2, \chi_i \dots, \chi_N\rangle
\end{aligned} \tag{1.25}$$

Since we obtain the same determinant in both cases, therefore we conclude the operator relation

$$a_i a_i^\dagger + a_i^\dagger a_i = 1 = \{a_i, a_i^\dagger\} \tag{1.26}$$

Finally consider  $(a_j^\dagger a_i + a_i a_j^\dagger)|\chi_1, \chi_2, \dots, \chi_N\rangle$  when  $i \neq j$ , this expression can be nonzero only if the spin orbital  $\chi_i$  appears and the spin orbital  $\chi_j$  does not appear in the determinant. We obtain zero as a result of the antisymmetry property of determinants.

$$\begin{aligned}
&(a_i a_j^\dagger + a_j^\dagger a_i)|\chi_1, \chi_2, \chi_i \dots, \chi_N\rangle \\
&= -(a_i a_j^\dagger + a_j^\dagger a_i)|\chi_i, \chi_1, \chi_2, \dots, \chi_N\rangle \\
&= -a_i |\chi_j, \chi_i, \chi_1, \chi_2, \dots, \chi_N\rangle - a_j^\dagger |\chi_1, \chi_2, \dots, \chi_N\rangle \\
&= a_i |\chi_i, \chi_j, \chi_1, \chi_2, \dots, \chi_N\rangle - |\chi_j, \chi_1, \chi_2, \dots, \chi_N\rangle \\
&= |\chi_j, \chi_1, \chi_2, \dots, \chi_N\rangle - |\chi_j, \chi_1, \chi_2, \dots, \chi_N\rangle = 0
\end{aligned} \tag{1.27}$$

thus we have

$$a_i a_j^\dagger + a_j^\dagger a_i = 0 = \{a_i, a_j^\dagger\} \quad i \neq j \tag{1.28}$$

Therefore from the Eqs. (1.28) and (1.26), the anticommutation relation between a creation and an annihilation operator is

$$a_i a_j^\dagger + a_j^\dagger a_i = \delta_{ij} = \{a_i, a_j^\dagger\} \quad (1.29)$$

All property of Slater determinant is combined in the anticommutation relations between two creation operators Eq. (1.10), between two annihilation operators Eq. (1.20), and a creation and an annihilation operator Eq. (1.29).

Sometimes we need in quantum mechanics a transformation between position space  $(x, y, z)$  and momentum space  $(p_x, p_y, p_z)$  which is done by the Fourier transform

$$|\vec{p}\rangle = \int d^d x |\vec{x}\rangle \langle \vec{x} | \vec{p} \rangle = \int d^d x |\vec{x}\rangle e^{i\vec{p}\cdot\vec{x}} \quad (1.30)$$

and, conversely

$$|\vec{x}\rangle = \int \frac{d^d p}{(2\pi)^d} |\vec{p}\rangle e^{-i\vec{p}\cdot\vec{x}} \quad (1.31)$$

then, the operators themselves obey

$$\begin{aligned} a^\dagger(\vec{p}) &= \int d^d x a^\dagger(\vec{x}) e^{i\vec{p}\cdot\vec{x}}, & a^\dagger(\vec{x}) &= \int \frac{d^d p}{(2\pi)^d} a^\dagger(\vec{p}) e^{-i\vec{p}\cdot\vec{x}} \\ a(\vec{p}) &= \int d^d x a(\vec{x}) e^{-i\vec{p}\cdot\vec{x}}, & a(\vec{x}) &= \int \frac{d^d p}{(2\pi)^d} a(\vec{p}) e^{i\vec{p}\cdot\vec{x}} \end{aligned}$$

## 1.4 Expressing of Quantum Mechanical Operators in second quantization

Expectation values of operators correspond to physical observables and should be therefore independent of the representation given to the states and operators. We need to know how first quantized operators can be translated into their second quantized version. In second quantization all operators can be expressed in terms of the fundamental creation and annihilation operators defined in the previous section. An operator in the Fock space can be thus constructed in second quantization by requiring its matrix elements between ON vectors to be equal to the corresponding matrix elements between Slater determinants of the first quantization operator. The operators can be categorized according to how many particles they act on; there are one-body operator which can be written as a sum of terms, each of which only involve the coordinates of a single particle and two body operators, which can be written as a some of terms, each of which only involve the coordinates of a single particle.

### 1.4.1 one-body operators

Let us start with the so-called one-particle operators  $F$ , in first quantization one electron operators (kinetic energy) are written as

$$F = \sum_{s=1}^N f(\chi_i) \tag{1.32}$$

where the sums run over all particles in the system and is  $f_i$  an operator acting on the  $i$ -th particle. The kinetic energy, total momentum, etc. are example of such operators. For now, we will focus to give its expression in terms of creation and

annihilation operators. Let us suppose that  $|\Psi_0\rangle, |\Psi_1\rangle, \dots$  constitute a complete, orthonormal set of single particle states. It is obvious that in this basis the total quantity  $F$  can be calculated by summing over all states and counting how many particles occupy them, we can express the operator  $F$  in terms of creation  $a_i^\dagger$  and annihilation operators  $a_i$

$$F = \sum_{ij} f_{ij} a_i^\dagger a_j \quad (1.33)$$

where, the operators  $a_i^\dagger a_j$  shift a single electron from the orbital  $|\Psi_j\rangle$ , into orbital  $|\Psi_i\rangle$ . Eventually, the summation in Eq. (1.33) runs over all pairs of occupied spin orbitals. The term  $f_{ij}$  in second quantization could be linked to the first quantization operator by the relation

$$f_{ij} = \langle \Psi_i | f | \Psi_j \rangle \quad (1.34)$$

The second quantization has many advantages, one of them is that it treats systems with different numbers of particles on an equal footing. This is a particularly convenient when one dealing with infinite systems such as solids.

To show how the equivalence second quantization with our previous development, based on Slater determinant, let us using second quantization to calculate the energy of ground state,  $|\Psi_0\rangle = |\chi_1, \chi_2, \chi_3, \dots, \chi_a, \chi_b \dots, \chi_N\rangle$ , therefore

$$\langle \Psi_0 | F | \Psi_0 \rangle = \sum_{ij} f_{ij} \langle \Psi_0 | a_i^\dagger a_j | \Psi_0 \rangle \quad (1.35)$$

Since  $a_j$  and  $a_i^\dagger$  trying to eliminate an electron ( $a_j$  to the right and  $a_i^\dagger$  to the left) the indices must belong to the set  $\{a,b,\dots\}$  and therefore

$$\langle \Psi_0 | F | \Psi_0 \rangle = \sum_{ab} f_{ab} \langle \Psi_0 | a_a^\dagger a_b | \Psi_0 \rangle \quad (1.36)$$

using the equation  $a_a^\dagger a_b = \delta_{ab} - a_b a_a^\dagger$

then we have

$$\langle \Psi_0 | a_a^\dagger a_b | \Psi_0 \rangle = \delta_{ab} \langle \Psi_0 | \Psi_0 \rangle - \langle \Psi_0 | a_b a_a^\dagger | \Psi_0 \rangle \quad (1.37)$$

the second term equal to zero, since  $a_a^\dagger$  try to create an electron that already exist in  $|\Psi_0\rangle$ . Since  $\langle \Psi_0 | \Psi_0 \rangle = 1$ , finally we obtain

$$\langle \Psi_0 | F | \Psi_0 \rangle = \sum_{ab} f_{ab} \delta_{ab} = \sum_{ab} f_{ab} \quad (1.38)$$

in equivalence with the first quantization.

## 1.4.2 two-body operators

On the other hand, now we discuss the representation in second quantization for two electron operators such as the electron-electron repulsion and the electron-electron spin orbit operators. In first quantization these operators were written as

$$G = \sum_{i \neq j} g_{ij} (\chi_i, \chi_j) \quad (1.39)$$

While the second quantization representation of this operator can then be written as

$$G = \frac{1}{2} \sum_{ijkl} g_{ijkl} a_i^\dagger a_j^\dagger a_l a_k \quad (1.40)$$

for the sum of two electron operators, we obtain

$$\langle \Psi_0 | G | \Psi_0 \rangle = \frac{1}{2} \sum_{ijkl} g_{ijkl} \langle \Psi_0 | a_i^\dagger a_j^\dagger a_l a_k | \Psi_0 \rangle \quad (1.41)$$

As the one particle operator the indices  $i, j, k, l$  must be belong to  $\{a, b, \dots\}$

$$\langle \Psi_0 | G | \Psi_0 \rangle = \frac{1}{2} \sum_{abcd} g_{abcd} \langle \Psi_0 | a_a^\dagger a_b^\dagger a_c a_d | \Psi_0 \rangle \quad (1.42)$$

Our strategy is to move the creation operator to the right until they operate in  $|\Psi_0\rangle$ ,

$$\begin{aligned} \langle \Psi_0 | a_a^\dagger a_b^\dagger a_c a_d | \Psi_0 \rangle &= \delta_{bd} \langle \Psi_0 | a_a^\dagger a_c | \Psi_0 \rangle - \langle \Psi_0 | a_a^\dagger a_d a_b^\dagger a_c | \Psi_0 \rangle \\ &= \delta_{bd} \delta_{ac} \langle \Psi_0 | \Psi_0 \rangle - \delta_{bd} \langle \Psi_0 | a_c a_a^\dagger | \Psi_0 \rangle - \delta_{bc} \langle \Psi_0 | a_a^\dagger a_d | \Psi_0 \rangle \\ &\quad + \langle \Psi_0 | a_a^\dagger a_d a_c a_b^\dagger | \Psi_0 \rangle \\ &= \delta_{bd} \delta_{ac} - \delta_{bc} \delta_{ad} \langle \Psi_0 | \Psi_0 \rangle + \delta_{bc} \langle \Psi_0 | a_d a_a^\dagger | \Psi_0 \rangle \\ &= \delta_{bd} \delta_{ac} - \delta_{bc} \delta_{ad} \end{aligned} \quad (1.43)$$

therefore we get

$$\langle \Psi_0 | G | \Psi_0 \rangle = \frac{1}{2} \sum_{ab} g_{aabb} - g_{abba} \quad (1.44)$$

This is in agreement with the result obtained by first quantization for the two electrons operators.

First quantization	Second quantization
<ul style="list-style-type: none"> <li>One-electron operator: <math>F = \sum_{s=1}^N f(\chi_i)</math></li> </ul>	<ul style="list-style-type: none"> <li>One-electron operator: <math>F = \sum_{ij} f_{ij} a_i^\dagger a_j</math></li> </ul>
<ul style="list-style-type: none"> <li>Two-electron operator: <math>G = \sum_{i \neq j} g_{ij} (\chi_i, \chi_j)</math></li> </ul>	<ul style="list-style-type: none"> <li>Two-electron operator: <math>G = \frac{1}{2} \sum_{ijkl} g_{ijkl} a_i^\dagger a_j^\dagger a_l a_k</math></li> </ul>
<ul style="list-style-type: none"> <li>Operators are independent of the spin-orbital basis</li> </ul>	<ul style="list-style-type: none"> <li>Operators depend on the spin-orbital basis</li> </ul>

• Operators depend on the number of electrons	• Operators are independent of electrons
• Operators are exact	• Projected operators

Table 1.1: Comparison between first and second quantization representations.

## 1.5 Hamiltonian in second quantization

To describe the electronic structure of any system we should start always by presenting the corresponding Hamiltonian, in this sense, it is important to get familiar with the form that some basic Hamiltonians adopt in second quantization. Combining the results of previous section, we may now construct the full second quantization representation of the electronic Hamiltonian operator. The molecular Hamiltonian is represented as a sum of one- and two-electron terms

$$H = H_0 + H' + h_{nuc} \quad (1.45)$$

where

$$H_0 = \sum_{i=1}^N h(\chi_i) \quad (1.46)$$

$$H' = \frac{1}{2} \sum_{i \neq j}^N \sum_j^N g(\chi_i, \chi_j) \quad (1.47)$$

Now we will rewrite this Hamiltonian in terms of creation and annihilation operator. Then the single-particle operator  $H_0$  can be expressed with the help of  $a_i^\dagger$  and  $a_j$  as:

$$H_0 = \sum_{ij} \langle \Psi_i | h | \Psi_j \rangle a_i^\dagger a_j = \sum_{ij} h_{ij} a_i^\dagger a_j \quad (1.48)$$

and

$$h_{ij} = \langle \Psi_i | h | \Psi_j \rangle = \int \Psi_i^*(x) h(x) \Psi_j(x) dx \quad (1.49)$$

The operator for the electron-electron interaction  $H'$  acquires the form

$$H' = \frac{1}{2} \sum_{ijkl} g_{ijkl} a_i^\dagger a_j^\dagger a_l a_k \quad (1.50)$$

therefore the many-body Hamiltonian in second quantization is represented by a polynomial in the operators  $a_i^\dagger$  and  $a_j$  which has the form

$$H = \sum_{ij} h_{ij} a_i^\dagger a_j + \frac{1}{2} \sum_{ijkl} g_{ijkl} a_i^\dagger a_j^\dagger a_l a_k + h_{nuc} \quad (1.51)$$

where in atomic unites

$$h_{ij} = \int \Psi_i^*(x) \left( -\frac{1}{2} \nabla^2 - \sum_l \frac{Z_l}{r_l} \right) \Psi_j(x) dx \quad (1.52)$$

$$g_{ijkl} = \iint \frac{\Psi_i^*(x_1) \Psi_k^*(x_2) \Psi_j(x_1) \Psi_l(x_2) dx_1 dx_2}{r_{12}} \quad (1.53)$$

and

$$h_{nuc} = \frac{1}{2} \sum_{i \neq j} \frac{Z_i Z_j}{R_{ij}} \quad (1.54)$$

Here the  $Z_l$ 's represent the nuclear charges;  $r_1$ ,  $r_{12}$ , and  $R_{ij}$  represent the electron-nuclear, the electron-electron, and the internuclear separations. This Hamiltonian contains the full set of electronic interactions in a given basis and is independent of the electronic state studied.

### 1.5.1 The Hamiltonian of a Two Body Interaction

The electron Hamiltonian of a two body interaction can be written as a summation of one and two electron operators. The crucial point is that we can think about both the motion in the external potential  $U(\chi)$ , as well as the interaction potential term, in terms of the density operator. Therefore we can write H as

$$H = \sum_{i=1}^2 \frac{\vec{p}_i^2}{2m} + U(\vec{x} - \vec{y}) \quad (1.55)$$

where the two-particles Hamiltonian is of the form

$$H = \frac{1}{2} \sum_{k_1 k_2 k_3 k_4} U_{k_1 k_2 k_3 k_4} a_{k_1}^\dagger a_{k_2}^\dagger a_{k_3} a_{k_4} = \frac{1}{2} \sum_{k_1 k_2 k_3 k_4} \langle K_1 K_2 | U^{(2)} | K_3 K_4 \rangle a_{k_1}^\dagger a_{k_2}^\dagger a_{k_3} a_{k_4} \quad (1.56)$$

the eigenstates of a plane wave is of the form

$$\Psi_n(r) = \frac{1}{\sqrt{V}} \exp(iK_n r). \quad k_n = \frac{2\pi}{L} n. \quad n = (n_1, n_2, n_3) \quad (1.57)$$

with  $V=L^3$  and  $n_{1,2,3}$  are integer. Then using Eq.(1.57), the matrix element in Eq.(1.56) can be evaluated and has the form.

$$\langle K_1 K_2 | U^{(2)} | K_3 K_4 \rangle = \iint \frac{1}{V^2} e^{-iK_{1x} - iK_{2y} + iK_{3x} + iK_{4y}} U(x - y) d^3x d^3y \quad (1.58)$$

This expression can be simplified and evaluated by choosing ( $a = x - y$ ) as an integration variable instead of  $y$  after which the integral in Eq.(1.58) as

$$\begin{aligned} & \left( \int e^{i(K_4 - K_2)a} U(a) d^3a \right) \times \left( \int e^{-iK_{1x} - iK_{2x} + iK_{3x} + iK_{4x}} d^3r \right) \\ & = \tilde{U}(K_2 - K_4) \delta_{K_1 + K_2 = K_3 + K_4} \end{aligned} \quad (1.59)$$

where  $\tilde{U}(K) = \int e^{-iKr} U(r) d^3r$ , is the Fourier transform of the interaction potential.

$$\delta_{K_1 + K_2 = K_3 + K_4} = \begin{cases} V, & K_1 + K_2 = K_3 + K_4 \\ 0, & K_1 + K_2 \neq K_3 + K_4 \end{cases} \quad (1.60)$$

Finally, we conclude that the Two-Body Hamiltonian takes the form

$$H = \frac{1}{2} \sum_{K_1+K_2=K_3+K_4} \tilde{U}(K_2 - K_4) a_{k_1}^\dagger a_{k_2}^\dagger a_{k_3} a_{k_4} \quad (1.61)$$

The sum is taken over all integers parameterizing the plane wave states Eq.(1.57) subject to the constraint  $\vec{K}_1 + \vec{K}_2 = \vec{K}_3 + \vec{K}_4$  this constraint, arises due to translational invariance of the system. This physically expresses the conservation of momentum in two particles scattering. This means that if two particles interact the total momentum of the system cannot change. Actually, this is the Coulomb interaction occurring between two electrons with  $U(k)$  representing the Coulomb two electron operator. The whole process could be visualized with the aid of the Feynman diagram shown in Figure 1.1.

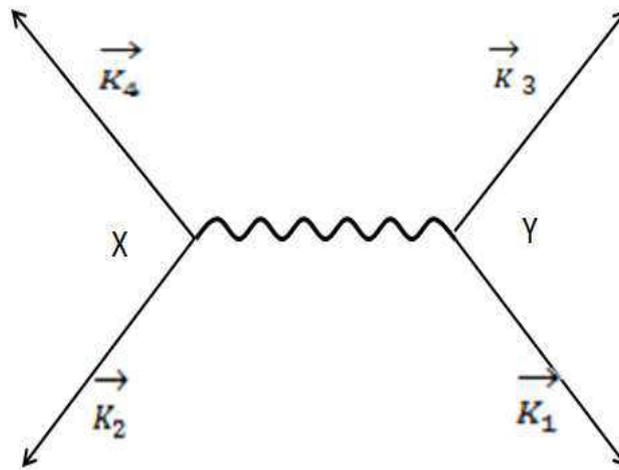


Fig 1.1. The two body interaction

## 1.6 Spin in Second quantization

### 1.6.1 Spin Functions

To completely describe an electron, it is necessary to specify its spin. To do this, we introduce two spin functions  $\alpha(\omega)$  and  $\beta(\omega)$  corresponding to spin up and spin down respectively. The spin coordinate takes on only two values representing the two allowed values of the projected spin angular momentum of the electron  $m_s = 1/2$  and  $m_s = -1/2$ . The spin space is accordingly spanned by two functions, which are taken to be the Eigenfunctions  $\alpha(1/2)$  and  $\beta(-1/2)$  of the projected spin angular momentum operator  $S_z$  where these functions are orthonormal

$$\langle \alpha | \alpha \rangle = \langle \beta | \beta \rangle = 1 .$$

$$\langle \alpha | \beta \rangle = \langle \beta | \alpha \rangle = 0 .$$

$$S_z^c \alpha \left( \frac{1}{2} \right) = \frac{1}{2} \alpha \left( \frac{1}{2} \right), \quad S_z^c \beta \left( -\frac{1}{2} \right) = -\frac{1}{2} \beta \left( -\frac{1}{2} \right). \quad (1.62)$$

These spin functions are usually Eigenfunctions of the total spin angular momentum operator  $S^2$

$$(S^c)^2 \alpha(m_s) = s(s+1) \alpha(m_s) = \frac{3}{4} \alpha(m_s). \quad (1.63)$$

These spin Eigenfunctions form an orthonormal set, which is in accordance with the general theory of angular momentum in quantum mechanics. To describe a system consists of N-electrons, it is more convenient to write the electronic wave function  $\psi$  as a product of an orbital part and a spin part. Where spin orbital are written as

$$\phi_{p\sigma}(r, m_s) = \phi_p(r) \sigma(m_s) \quad (1.64)$$

Therefore the creation and annihilation operators  $a_{p\sigma}^+$  and  $a_{q\tau}$  are defined to act on an electron with orbital functions  $\Phi_p, \Phi_q$  and spin eigenfunctions  $\sigma$  and  $\tau$ .

## 1.6.2 Spin operators

In section (1.4) we describe the one and two electron operators neglecting the effect of electronic spin. This is an important physical property that must be included in the definition of one and two electron operators. From Eq. (1.4) the one electron operators has the form

$$F = \sum_{s=1}^N f(r_i) \quad (1.65)$$

this can be written in the spin-orbital basis as

$$F = \sum_{p\sigma} \sum_{q\tau} f_{p\sigma,q\tau} a_{p\sigma}^+ a_{q\tau}. \quad (1.66)$$

The integrals vanish for opposite spins

$$\begin{aligned} f_{p\sigma,q\tau} &= \int \phi_p^*(r) \sigma^*(m_s) f^c(r) \phi_q(r) \sigma(m_s) dr dm_s. \\ &= \delta_{\sigma\tau} \int \phi_p^*(r) f^c(r) \phi_q(r) dr = f_{pq} \delta_{\sigma\tau}. \end{aligned} \quad (1.67)$$

with

$$f_{pq} = \int \phi_p^*(r) f^c(r) \phi_q(r) dr \quad (1.68)$$

Therefore the one electron operator in the second quantization for the spin free has the form

$$f = \sum_{pq} f_{pq} E_{pq} \quad (1.69)$$

where the singlet excitation operator is given by

$$E_{pq} = a_{p\sigma}^\dagger a_{q\sigma} + a_{p\tau}^\dagger a_{q\tau} \quad (1.70)$$

similar to one electron, the two electron operators can be written as

$$g = \frac{1}{2} \sum_{p\sigma q\tau r\mu sv} g_{pq,q\tau,r\mu,sv} a_{p\sigma}^\dagger a_{r\mu}^\dagger a_{sv} a_{q\tau}. \quad (1.71)$$

The orthogonality of the spin functions make most of the terms in the two electron operator vanish

$$g_{pq,q\tau,r\mu,sv} = g_{pqrs} \delta_{\sigma\tau} \delta_{\mu\nu} \quad (1.72)$$

where  $g_{pqrs}$  are the two-electron integrals in ordinary space and the second quantization representation of a two electron operator with the inclusion of spin give

$$\begin{aligned} g &= \frac{1}{2} \sum_{pqrs} g_{pqrs} \sum_{\sigma\tau} a_{p\sigma}^\dagger a_{r\tau}^\dagger a_{s\tau} a_{q\sigma} = -\frac{1}{2} \sum_{pqrs} g_{pqrs} \sum_{\sigma\tau} a_{p\sigma}^\dagger a_{r\tau}^\dagger a_{q\sigma} a_{s\tau} \\ &= -\frac{1}{2} \sum_{pqrs} g_{pqrs} \left( \sum_{\sigma\tau} a_{p\sigma}^\dagger (-a_{q\sigma} a_{r\tau}^\dagger + \delta_{qr} \delta_{\sigma\tau}) a_{s\tau} \right) \\ &= \frac{1}{2} \sum_{pqrs} g_{pqrs} \left( \sum_{\sigma\tau} a_{p\sigma}^\dagger a_{q\sigma} a_{r\tau}^\dagger a_{s\tau} - \delta_{qr} \delta_{\sigma\tau} a_{p\sigma}^\dagger a_{s\tau} \right) \\ &= \frac{1}{2} \sum_{pqrs} g_{pqrs} (E_{pq} E_{rs} - \delta_{qr} E_{ps}), \end{aligned} \quad (1.73)$$

with the two electron excitation operator

$$e_{pqrs} = E_{pq} E_{rs} - \delta_{qr} E_{ps} = \sum_{\sigma\tau} a_{p\sigma}^\dagger a_{r\tau}^\dagger a_{s\tau} a_{q\sigma}. \quad (1.74)$$

therefore the second quantization representation of the nonrelativistic molecular electronic Hamiltonian in the spin-orbital basis is given by

$$H = \sum_{pq} h_{pq} E_{pq} + \frac{1}{2} \sum_{pqrs} g_{pqrs} e_{pqrs} + h_{nuc} \quad (1.75)$$

This expression of the molecular Hamiltonian given in Eq. (1.75) is different from the spin free Hamiltonian operator given in Eq. (1.51) by its dependence on the single and double excitation operators ( $E_{sq}$ ,  $e_{pqrs}$ ), which is in turn depending on the spin through the operators  $a_{p\sigma}^\dagger a_{q\sigma}$  and  $a_{r\tau}^\dagger a_{s\tau}$  appearing in Eqs. (1.70) and (1.74).

## 1.7 The Born Oppenheimer approximation

The electronic structure and the properties of any molecule, in any of its available stationary states may be determined in principle by the solution of Schrödinger's time-independent equation [3] which is a complicated many-body problem. This complicity can be reducing considerably by applying some physical considerations. For a system of N electrons moving in the potential field due to the nuclei, this equation takes the form

$$H\Psi = E\Psi \quad (1.76)$$

where  $\Psi$  is the molecular wavefunction, E is the energy of the system and H is the Hamiltonian operator which has the form

$$\begin{aligned}
H = & - \sum_{i=1}^N \frac{1}{2} \nabla_i^2 - \sum_{A=1}^M \frac{1}{2M_A} \nabla_A^2 - \sum_{i=1}^N \sum_{A=1}^M \frac{Z_A}{r_{iA}} + \sum_{i=1}^N \sum_{j>i}^N \frac{1}{r_{ij}} \\
& + \sum_{A=1}^M \sum_{B>A}^M \frac{Z_A Z_B}{R_{AB}}
\end{aligned} \tag{1.77}$$

this equation becomes

$$\begin{aligned}
& \left( - \sum_{i=1}^N \frac{1}{2} \nabla_i^2 - \sum_{A=1}^M \frac{1}{2M_A} \nabla_A^2 - \sum_{i=1}^N \sum_{A=1}^M \frac{Z_A}{r_{iA}} + \sum_{i=1}^N \sum_{j>i}^N \frac{1}{r_{ij}} + \sum_{A=1}^M \sum_{B>A}^M \frac{Z_A Z_B}{R_{AB}} \right) \Psi \\
& = E\Psi
\end{aligned} \tag{1.78}$$

where  $M_A$  is the ratio of the mass of nucleus A to the mass of an electron,  $Z_A$  is the atomic number of nucleus A, and  $r_{iA}$  is the distance of the electron from the nucleus A. The first and the second terms are respectively for the calculation of the kinetic energies of the electrons, and the nuclei. The third term represents the attraction between electrons and nuclei, the fourth and fifth terms represent the repulsive forces between electrons and between nuclei, respectively.

Since nuclei are much heavier than electrons, their velocities are much smaller. Born and Oppenheimer in 1927 [4] takes note of the great difference between the masses of the electrons and those of the nuclei, hence, to a good approximation, one can consider the electrons in a molecule to be moving in the field of fixed nuclei [5, 6]. Mathematically, this approximation states that Schrödinger equation can be separated into one part which describes the electronic wave function for a fixed nuclear geometry, and another part which describes the nuclear wave function where the energy from the electronic wave function plays the role of potential energy. Then the Hamiltonian takes the form.

$$H = H_{elec} + H_{nucl} \quad (1.79)$$

where  $H_{nucl}$  and  $H_{elec}$  are respectively the nuclear and electronic Hamiltonians. In order to separate Eq.(1.78) we use a trial wavefunction  $\Psi$  of the form:

$$\Psi(r_i, R_A) = \psi(r_i, R_A)\phi(R_A) \quad (1.80)$$

where the first factor represents the electronic motions with fixed nuclear coordinates and the second factor represents the nuclear motions themselves. Substituting Eq. (1.80) into Eq. (1.78) and after some mathematical manipulation we get

$$\begin{aligned} & \phi \left( - \sum_{i=1}^N \frac{1}{2} \nabla_i^2 - \sum_{i=1}^N \sum_{A=1}^M \frac{Z_A}{r_{iA}} + \sum_{i=1}^N \sum_{j>i}^N \frac{1}{r_{ij}} \right) \psi \\ & + \psi \left( - \sum_{A=1}^M \frac{1}{2M_A} \nabla_A^2 + \sum_{A=1}^M \sum_{B>A}^M \frac{Z_A Z_B}{R_{AB}} \right) \phi \\ & - \sum_{A=1}^M \frac{1}{M_A} (\nabla_A \psi) \nabla_A \phi - \sum_{A=1}^M \frac{1}{2M_A} \phi \nabla_A^2 \psi = E \psi \phi \end{aligned} \quad (1.81)$$

The last line on the left hand side of Eq. (1.78) is a perturbation term, which is smaller than the first term by a factor of  $(m_e/M_A)$  so we can neglect it. Hence Eq. (1.81) becomes:

$$\begin{aligned}
 & \phi \left( - \sum_{i=1}^N \frac{1}{2} \nabla_i^2 - \sum_{i=1}^N \sum_{A=1}^M \frac{Z_A}{r_{iA}} + \sum_{i=1}^N \sum_{j>i}^N \frac{1}{r_{ij}} \right) \psi \\
 & + \psi \left( - \sum_{A=1}^M \frac{1}{2M_A} \nabla_A^2 + \sum_{A=1}^M \sum_{B>A}^M \frac{Z_A Z_B}{R_{AB}} \right) \phi = E \psi \phi
 \end{aligned} \tag{1.82}$$

this can be written in the following form:

$$\begin{aligned}
 & \phi \left( - \sum_{i=1}^N \frac{1}{2} \nabla_i^2 - \sum_{i=1}^N \sum_{A=1}^M \frac{Z_A}{r_{iA}} + \sum_{i=1}^N \sum_{j>i}^N \frac{1}{r_{ij}} \right) \psi \\
 & = -\psi \left( - \sum_{A=1}^M \frac{1}{2M_A} \nabla_A^2 + \sum_{A=1}^M \sum_{B>A}^M \frac{Z_A Z_B}{R_{AB}} \right) \phi + E \psi \phi
 \end{aligned} \tag{1.83}$$

Dividing Eq. (1.83) by  $\psi\phi$  we get

$$\begin{aligned}
 & \frac{\left( - \sum_{i=1}^N \frac{1}{2} \nabla_i^2 - \sum_{i=1}^N \sum_{A=1}^M \frac{Z_A}{r_{iA}} + \sum_{i=1}^N \sum_{j>i}^N \frac{1}{r_{ij}} \right) \psi}{\psi} \\
 & = \frac{- \left( - \sum_{A=1}^M \frac{1}{2M_A} \nabla_A^2 + \sum_{A=1}^M \sum_{B>A}^M \frac{Z_A Z_B}{R_{AB}} \right) \phi}{\phi} + E
 \end{aligned} \tag{1.84}$$

Both sides of Eq. (1.84) should be equal to a constant, say  $E_e$ , so it becomes:

$$\left\{ \begin{aligned}
 & \frac{\left( - \sum_{i=1}^N \frac{1}{2} \nabla_i^2 - \sum_{i=1}^N \sum_{A=1}^M \frac{Z_A}{r_{iA}} + \sum_{i=1}^N \sum_{j>i}^N \frac{1}{r_{ij}} \right) \psi}{\psi} = E_e \\
 & \frac{- \left( - \sum_{A=1}^M \frac{1}{2M_A} \nabla_A^2 + \sum_{A=1}^M \sum_{B>A}^M \frac{Z_A Z_B}{R_{AB}} \right) \phi}{\phi} + E = E_e
 \end{aligned} \right. \tag{1.85}$$

The first line in Eq. (1.85) represents the electronic Schrödinger equation which can be written as:

$$\left( -\sum_{i=1}^N \frac{1}{2} \nabla_i^2 - \sum_{i=1}^N \sum_{A=1}^M \frac{Z_A}{r_{iA}} + \sum_{i=1}^N \sum_{j>i}^N \frac{1}{r_{ij}} \right) \psi = E_e \psi \quad (1.86)$$

The solution of Eq.(1.86) is the electronic wave function

$$\psi = \psi(r_i, R_A) \quad (1.87)$$

Eq. (1.87) describes the motion of the electrons and explicitly depends on the electronic coordinates but depends parametrically on the nuclear coordinates. The electronic energy is of the form

$$E_{elec} = E_{elec}(R_A) \quad (1.88)$$

After calculating the electronic energy eigenvalues ( $E_{elec}$ ), we should include the constant nuclear repulsion term in the expression of the total molecular energy  $E_{tot}$

$$E_{tot} = E_{elec} + \sum_{A=1}^M \sum_{B>A}^M \frac{Z_A Z_B}{R_{AB}} \quad (1.89)$$

In order to describe the nuclear vibrations and rotations, we should solve the nuclear Schrödinger equation (Eq.(1.85)) which can be written as

$$\left( -\sum_{A=1}^M \frac{1}{2M_A} \nabla_A^2 + E_t(R_A) \right) \phi = E \phi \quad (1.90)$$

where, the solutions of this equation give the eigenfunctions and eigenvalues of the vibrational and rotational energy levels of a molecule. This will be described in details in next chapter.

## 1.8 Variation Principle

For a very narrow class of systems the Schrödinger equation can be solved exactly. In cases where the exact solution cannot be achieved, the wavefunction may be approximated by a form that is easier to handle mathematically. In this section we will discuss an important theorem, called the variation principle which is a method enables us to make estimates of energy levels using trial as guessed wave functions. The better the guessed trial state is the better the approximation.

The variation principle states that the expectation value of the energy  $E_T$  calculated with an arbitrary (valid) normalized wave function  $\Psi_T$  is an upper bound for the exact energy  $E_0$  of the ground state of the system

$$E_T = \langle \Psi_T | H | \Psi_T \rangle \geq E_0 \quad (1.91)$$

where  $E_0$  is the ground state energy. Eq.(1.91) holds  $E_T = E_0$  only when the wave function  $\Psi_T$  is identical to the true exact wave function of the system. One can show that the energy  $E_T$  is always greater than or equal to  $E_0$ . This means that the best choice of  $\Psi_T$  is the one which minimizes  $E_T$ . This is the main idea behind the variation theorem in which we take a normalized trial wave function that depends on certain parameter that can be varied until the energy expectation value reaches a minimum.

The process of energy minimization can be greatly simplified if we write the wave function as a linear combination of trial basis functions [7]. Consider a normalized trial function  $\Psi_T$  and expand it in basis vectors

$$\Psi_T = \sum_n c_n \Psi_n \quad (1.92)$$

where  $c_n$  are the expansion coefficients and  $\Psi_n$  an Eigen state of  $H$ . Substituting Eq.(1.92) into Eq.(1.91) we obtain

$$E_T = \langle \Psi_T | H | \Psi_T \rangle = \sum_{nm} c_n c_m \langle \Psi_n | H | \Psi_m \rangle = \sum_{nm} c_n c_m H_{nm} \quad (1.93)$$

To reach the minimization of energy in Eq.(1.93), we should finding the optimum set of coefficients  $c_n$ , therefore

$$\frac{\partial E_T}{\partial c_i} = \frac{\partial}{\partial c_i} \langle \Psi_T | H | \Psi_T \rangle = 0 \quad i = 1, 2, \dots, N \quad (1.94)$$

We may enforce the normalization condition, then the process of minimizing a set of parameters subject to a constraint this is a constrained optimization and can be handled by means of Lagrange multipliers [8].

$$l(c_i, E_T) = \sum_{nm} c_n c_m H_{nm} - E (\sum_n c_n^2 - 1) \quad (1.95)$$

then we explicitly minimize the Lagrangian

$$\frac{\partial l}{\partial c_i} = 0 \quad (1.96)$$

Then

$$\frac{\partial l}{\partial c_i} = \sum_m c_m H_{im} + \sum_n c_n H_{in} - 2ES_{nm} c_i = 0 \quad (1.97)$$

Finally, we can write the secular equation in matrix notation, as

$$Hc = ESC \quad (1.98)$$

where H and S are the matrix representations of the Hamiltonian and the overlap operator and their elements are defined by

$$H_{nm} = \langle \Psi_n | \hat{H} | \Psi_m \rangle \quad (1.99)$$

$$S_{nm} = \langle \Psi_n | \Psi_m \rangle \quad (1.100)$$

## 1.9 Hartree–Fock theory

The main goal is to solve the Schrödinger equation which cannot be completely solved for molecules without approximations. The Hartree–Fock (HF) method [10, 11] is a technique of approximation for the determination of the wave function and the energy which is the one simplest approximate theory to solve the many-body Hamiltonian. It was developed to solve the electronic time-independent Schrödinger equation after invoking the Born-Oppenheimer approximation. The problem arises from the fact that the Schrödinger equation for molecules with more than one electron cannot be solved exactly due to the presence of the electron-electron repulsion term. In the previous section we discussed the variational theorem which states that the energy calculated from the equation  $E = \langle \psi | H | \psi \rangle$  must be greater or equal to the true ground-state energy of the molecule. In

practice, always we use an approximation to the true wave function of the system, thus the variationally calculated molecular energy will always be greater than the true energy. Since Hartree-Fock is a variational method, the true energy always lies below any calculated energy by this method.

### 1.9.1 The Hartree–Fock approximation

The Hartree-Fock approximation seeks to approximately solve the electronic Schrödinger equation, and it assumes that the wave function can be approximated by a single Slater determinant made up of one spin orbital per electron and the energy is optimized with respect to variations of these spin orbitals. The electronic Schrödinger equation can be written much more simply by using the atomic units, therefore Eq.(1.83) becomes

$$\left( -\sum_{i=1}^N \frac{1}{2} \nabla_i^2 - \sum_{i=1}^N \sum_{A=1}^2 \frac{Z_A}{|r_i - R_A|} + \sum_{i=1}^N \sum_{j>i}^N \frac{1}{|r_i - r_j|} \right) \psi = E_e \psi \quad (1.101)$$

This equation cannot be solved exactly due to the presence of the electron-electron repulsion term. This makes it impossible to separate the Schrödinger equation for a diatomic molecule into N one-electron equations which could be solved exactly.

### 1.9.2 Hartree fock wavefunction

The simplest wavefunction which can be used to describe the ground state can be written of the form

$$|\Psi_{HF}\rangle = \prod_i^N a_i^\dagger |0\rangle \quad (1.102)$$

this wavefunction can be written in a simple form

$$\begin{aligned} \Psi_0(\chi_1, \chi_2 \dots \chi_N) \\ = (N!)^{-1/2} \det|\varphi_1(\chi_1)\varphi_2(\chi_2) \dots \varphi_N(\chi_N)| \end{aligned} \quad (1.103)$$

where  $\varphi_1(\chi_1), \varphi_2(\chi_2) \dots, \varphi_N(\chi_N)$  are the occupied best spin orbitals. The best spin orbitals to use are the solutions of the one-electron Schrödinger equation

$$F\varphi = \varepsilon\varphi \quad (1.104)$$

where  $F$  is the Hamiltonian describing the kinetic energy and potential energy of a single electron and  $\varepsilon$  is the energy of the spin orbital. The potential energy in  $F$  comes from the electrostatic field provided by the nuclei on a single electron and the electron-electron repulsion which comes from a single electron and an average electrostatic field due to all the other electrons *i.e.* in this equation a single electron is moving in the field of the nuclei and the average field due to all the other electrons. This is known as Hartree-Fock approximation and Eq.(1.104) is known as the Hartree-Fock equation [11, 12]. To derive this equation we assume a wavefunction of the form

$$\begin{aligned} \Psi(\chi_1, \chi_2, \dots, \chi_N) \\ = (N!)^{-1/2} \det|\varphi_1(\chi_1) \varphi_2(\chi_2) \dots \varphi_N(\chi_N)| \end{aligned} \quad (1.105)$$

the energy of this wavefunction is given by

$$E_e = \frac{\langle \Psi | H | \Psi \rangle}{\langle \Psi | \Psi \rangle} \quad (1.106)$$

Since  $\Psi(\chi)$  is a normalized wavefunction therefore the denominator of equation (1.106) is equal to 1. Hence equation (1.106) becomes

$$E_e = \langle \Psi | H | \Psi \rangle \quad (1.107)$$

where H is the full electronic Hamiltonian and it is given by

$$H = \sum_{i=1}^N h(i) + \frac{1}{2} \sum_{i=1}^N \sum_{j=1}^N \frac{1}{|r_i - r_j|} \quad (1.108)$$

the first term represents the kinetic and potential energies of a single electron and the second term represents the electron-electron repulsion. Substituting Eq.(1.108) in Eq.(1.107) and after some mathematical manipulation we get

$$E_e = \langle \Psi | \sum_{i=1}^N h(i) | \Psi \rangle + \frac{1}{2} \langle \Psi | \sum_{i=1}^N \sum_{j=1}^N \frac{1}{|r_i - r_j|} | \Psi \rangle \quad (1.109)$$

After expanding the sum of h and substituting Eq.(1.105) into the first part of Eq.(1.109) and by taking into consideration the orthonormality of the spin orbitals we can write

$$\langle \Psi | \sum_{i=1}^N h(i) | \Psi \rangle = \sum_{i=1}^N \langle \varphi_i | h | \varphi_i \rangle \quad (1.110)$$

The second sum in the second term of Eq.(1.109) is over all  $\frac{1}{2}n(n-1)$  unique pairs of electrons. Each term in the sum gives the same result because the electrons are indistinguishable. So after substituting Eq.(1.105) in the second term of Eq.(1.109) and after some mathematical manipulation we obtain

$$\frac{1}{2} \langle \Psi | \sum_{i=1}^N \sum_{j=1}^N \frac{1}{|r_i - r_j|} | \Psi \rangle = \frac{1}{2} \sum_{i=1}^N \sum_{j=1}^N \langle \varphi_j | J_i - K_i | \varphi_j \rangle \quad (1.111)$$

where  $J_i$  and  $K_i$  are the coulomb and exchange operators respectively and they are defined as

$$\begin{cases} J_i | \varphi_j(\chi_1) \rangle = \langle \varphi_i(\chi_2) | \frac{1}{|r_1 - r_2|} | \varphi_i(\chi_2) \rangle | \varphi_j(\chi_1) \rangle \\ \text{and} \\ K_i | \varphi_j(\chi_1) \rangle = \langle \varphi_i(\chi_2) | \frac{1}{|r_1 - r_2|} | \varphi_j(\chi_2) \rangle | \varphi_i(\chi_1) \rangle \end{cases} \quad (1.112)$$

The Coulomb operator represents the electrostatic repulsion between electrons and the exchange operator is a kind of correction to  $J$  because electrons in different orbitals having same spin avoid each other more than just because of Columbic interaction. After substituting Eqs.(1.110) and (1.111) into Eq.(1.109) and substituting the obtained equation in

$$E_t = E_e + \frac{Z_1 Z_2}{4\pi\epsilon_0 |R_1 - R_2|} \quad (1.113)$$

we get

$$E_t = \sum_{i=1}^N \langle \varphi_i | h | \varphi_i \rangle + \frac{1}{2} \sum_{i=1}^N \sum_{j=1}^N \langle \varphi_j | J_i - K_i | \varphi_j \rangle + \frac{Z_1 Z_2}{|R_1 - R_2|} \quad (1.114)$$

where, the last term is the internuclear repulsion term in atomic units. The best spin orbitals used to construct equation (1.103) are those giving a minimum energy. Hence, we should minimize  $E_t$  with respect to the spin orbitals in a way that the spin orbitals remain orthonormal. This is a constrained optimization and can be handled by means of Lagrange multipliers [8]. The condition is that a small change

in the orbitals should not change the Lagrange function, *i.e.* the Lagrange function is stationary with respect to an orbital variation. So we write

$$L = E_t - \sum_{i=1}^N \sum_{j=1}^N \lambda_{ij} (\langle \varphi_i | \varphi_j \rangle - \delta_{ij}) \quad (1.115)$$

Equation (1.115) is the Lagrange function. The variation of this function is given by

$$\delta L = \delta E - \sum_{i=1}^N \sum_{j=1}^N \lambda_{ij} (\langle \delta \varphi_i | \varphi_j \rangle + \langle \varphi_i | \delta \varphi_j \rangle) = 0 \quad (1.116)$$

and the variation of the energy is given by

$$\begin{aligned} \delta E = & \sum_{i=1}^N (\langle \delta \varphi_i | h | \varphi_i \rangle + \langle \varphi_i | h | \delta \varphi_i \rangle) \\ & + \frac{1}{2} \sum_{i=1}^N \sum_{j=1}^N (\langle \delta \varphi_i | J_j - K_j | \varphi_i \rangle + \langle \varphi_i | J_j - K_j | \delta \varphi_i \rangle + \langle \delta \varphi_j | J_i - K_i | \varphi_j \rangle \\ & + \langle \varphi_j | J_i - K_i | \delta \varphi_j \rangle) \end{aligned} \quad (1.117)$$

Since the sums in equation (1.117) are for all  $i$  and  $j$  therefore the third and fifth terms are identical and the fourth and sixth terms are also identical. So they may be collected to cancel the factor of  $\frac{1}{2}$  and after some mathematical manipulation Eq.(1.117) becomes

$$\delta E = \sum_{i=1}^N (\langle \delta \varphi_i | F | \varphi_i \rangle + \langle \varphi_i | F | \delta \varphi_i \rangle) \quad (1.118)$$

where  $F$  is the Fock operator and it is given by

$$F = h + \sum_{j=1}^N (J_j - K_j) \quad (1.119)$$

The Fock operator may be regarded as the effective Hamiltonian for a single electron moving in the field of the nuclei (contained in  $h$ ) together with an effective “coulomb-exchange” field representing the presence of the other electrons. Substituting Eq.(1.118) into Eq.(1.116) and making use of the fact that  $\langle \varphi | \delta \varphi \rangle = \langle \delta \varphi | \varphi \rangle^*$  and  $\langle \varphi | F | \delta \varphi \rangle = \langle \delta \varphi | F | \varphi \rangle^*$  we get

$$\begin{aligned} \delta L = & \left( \sum_{i=1}^N \langle \delta \varphi_i | F | \varphi_i \rangle - \sum_{i=1}^N \sum_{j=1}^N \lambda_{ij} \langle \delta \varphi_i | \varphi_j \rangle \right) \\ & + \left( \sum_{i=1}^N \langle \delta \varphi_i | F | \varphi_i \rangle^* - \sum_{i=1}^N \sum_{j=1}^N \lambda_{ij} \langle \delta \varphi_j | \varphi_i \rangle^* \right) \\ = & 0 \end{aligned} \quad (1.120)$$

The variation of either  $\langle \delta \varphi |$  or  $\langle \delta \varphi |^*$  should make  $\delta L = 0$  therefore we can write

$$\left\{ \begin{aligned} \sum_{i=1}^N \langle \delta \varphi_i | f | \varphi_i \rangle - \sum_{i=1}^N \sum_{j=1}^N \lambda_{ij} \langle \delta \varphi_i | \varphi_j \rangle &= 0 \\ \text{and} \\ \sum_{i=1}^N \langle \delta \varphi_i | f | \varphi_i \rangle^* - \sum_{i=1}^N \sum_{j=1}^N \lambda_{ij} \langle \delta \varphi_j | \varphi_i \rangle^* &= 0 \end{aligned} \right. \quad (1.121)$$

Taking the complex conjugate of the lower line in Eq.(1.121) and subtracting it from the upper line in equation (1.121) we get

$$\sum_{i=1}^N \sum_{j=1}^N (\lambda_{ij} - \lambda_{ij}^*) \langle \delta \varphi_i | \varphi_j \rangle = 0 \quad (1.122)$$

Equation (1.122) means that the Lagrange multipliers are elements of a Hermitian matrix ( $\lambda_{ij} = \lambda_{ij}^*$ ). After some mathematical manipulation, we can write the upper

line of Eq. (1.121) as a scalar product of  $\delta\Psi_i$  and a function that must evidently vanish, so we can write this function as

$$F\varphi_i = \sum_{j=1}^N \lambda_{ij} \varphi_j \quad (1.123)$$

Eq.(1.123) can be represented by a system as follows

$$\begin{aligned} F\varphi_1 &= [\lambda_{11}\varphi_1 + \lambda_{12}\varphi_2 + \cdots + \lambda_{1N}\varphi_N] & i = 1 \\ F\varphi_2 &= [\lambda_{21}\varphi_1 + \lambda_{22}\varphi_2 + \cdots + \lambda_{2N}\varphi_N] & i = 2 \\ &\vdots & \vdots & \vdots & \vdots & \vdots \\ F\varphi_N &= [\lambda_{N1}\varphi_1 + \lambda_{N2}\varphi_2 + \cdots + \lambda_{NN}\varphi_N] & i = N \end{aligned}$$

and

$$F\varphi = \lambda\varphi \quad (1.124)$$

Equation (1.124) is not the standard form of Eq.(1.104) because  $\lambda$  is not a diagonal matrix. Since  $\lambda$  is a Hermitian matrix, therefore we can transform it to a diagonal matrix  $\varepsilon$  by unitary transformation [13]. Using this transformation, Eq.(1.124) becomes

$$F\varphi' = \varepsilon\varphi' \quad (1.125)$$

Omitting the primes on  $\varphi$  Eq.(1.125) becomes

$$F\varphi = \varepsilon\varphi \quad (1.126)$$

equation (1.126) now has the standard form of Eq.(1.104). In other words, every spin orbital satisfies:

$$F\varphi_i = \varepsilon_i\varphi_i \quad (1.127)$$

where  $F$  is the Fock operator of the electron occupied in spin orbital  $\varphi_i$  and  $\varepsilon_i$  is the energy of spin orbital  $\varphi_i$ . So, we need to minimize the Hartree-Fock wave function. Therefore to arrive at the optimal determinant that may be found by solving a set of

effective one electron Schrödinger equations, called the Hartree-Fock equations and their associated Hamiltonian operator, which is called the Fock operator  $F$

$$F = h + \sum_{i=1}^N (J_i - K_i) \quad (1.128)$$

$$\begin{cases} J_i |\varphi_j(r_1)\rangle = \langle \varphi_i(r_2) | \frac{1}{|r_1-r_2|} | \varphi_i(r_2)\rangle | \varphi_j(r_1)\rangle \\ \text{and} \\ K_i |\varphi_j(r_1)\rangle = \langle \varphi_i(r_2) | \frac{1}{|r_1-r_2|} | \varphi_j(r_2)\rangle | \varphi_i(r_1)\rangle \end{cases} \quad (1.129)$$

where,  $J_i$  is the Coulomb operator which represents the electrostatic repulsion between electrons and  $K_i$  which is called the exchange term which is a correction to the two Coulomb interactions that arises from the antisymmetry of the wave function. In other words, after some mathematical manipulation The Hartree-Fock eigenvalue equation can be written

$$F|\Psi_i\rangle = \varepsilon_i|\Psi_i\rangle \quad (1.130)$$

where,  $F$  is the Fock operator of the electron occupied in spin orbital  $\Psi_i$  and  $\varepsilon_i$  is the energy of spin orbital  $\Psi_i$ .

## 1.10 Roothaan-Hall equations

In this section, we are concerned with procedures for calculating restricted Hartree-Fock wavefunctions [14, 15] and especially we consider here only the closed shell calculations. The restricted spin orbitals have the same spatial function for spin up and down. Therefore, our molecular states are allowed to have only an even number ( $N$ ) of electrons with all electrons paired such that ( $n=N/2$ ) spatial orbitals are doubly occupied. Now we want to convert Eq.(1.126) to a spatial eigenvalue equation where each of the occupied spatial orbitals is doubly occupied, this equation can be written as

$$F(\chi_1)\varphi_i(\chi_1) = \varepsilon_i\varphi_i(\chi_1) \quad (1.131)$$

According to equation

$$\begin{cases} \varphi(\chi) = \psi(r)\alpha(\omega) \\ \text{and} \\ \overline{\varphi}(\chi) = \psi(r)\beta(\omega) \end{cases} \quad (1.132)$$

$\varphi_i(\chi_1)$  Have either  $\alpha$  or  $\beta$  spin function. Assuming that it has  $\alpha$  spin function, Eq.(1.131) can be written as

$$F(\chi_1)\psi_j(r_1)\alpha(\omega_1) = \varepsilon_j\psi_j(r_1)\alpha(\omega_1) \quad (1.133)$$

where  $\varepsilon_j$ , is the energy of the spatial orbital  $\psi_j$  which is identical with  $\varepsilon_i$ . Multiplying both sides of Eq.(1.133) by  $\alpha^*(\omega_1)$  and integrating over spin gives

$$\left[ \int \alpha^*(\omega_1)F(\chi_1)\alpha(\omega_1)d\omega_1 \right] \psi_j(r_1) = \varepsilon_j\psi_j(r_1) \quad (1.134)$$

the lower line of Eq.(1.129) can be written as

$$K_i |\varphi_j(\chi_1)\rangle = \left\langle \varphi_i(\chi_2) \left| \frac{1}{|r_1 - r_2|} P_{12} \right| \varphi_i(\chi_2) \right\rangle |\varphi_j(\chi_1)\rangle \quad (1.135)$$

where,  $P_{12}$  is an operator which, operating to the right, interchanges electron 1 and electron 2. Now substituting the upper line of Eqs.(1.129) and (1.135) into Eq.(1.128) and after some mathematical manipulation we get

$$F(\chi_1) = h(r_1) + \sum_{c=1}^N \varphi_c^*(\chi_2) \frac{1}{|r_1 - r_2|} (1 - P_{12}) \varphi_c(\chi_2) d\chi_2 \quad (1.136)$$

Therefore, Eq.(1.134) becomes:

$$\begin{aligned} & \left[ \int \alpha^*(\omega_1) F(\chi_1) \alpha(\omega_1) d\omega_1 \right] \\ &= \left[ \int \alpha^*(\omega_1) h(r_1) \alpha(\omega_1) d(\omega_1) \right] \psi_j(r_1) \\ &+ \left[ \sum_{c=1}^N \iint \alpha^*(\omega_1) \varphi_c^*(\chi_2) \frac{1}{|r_1 - r_2|} (1 \right. \\ &\quad \left. - P_{12}) \varphi_c(\chi_2) \alpha(\omega_1) d(\omega_1) d\chi_2 \right] \psi_j(r_1) = \varepsilon_j \psi_j(r_1) \end{aligned} \quad (1.137)$$

Let  $F(r_1) = \int \alpha^*(\omega_1) F(\chi_1) \alpha(\omega_1) d\omega_1$  be the closed shell Fock operator. Hence, Eq.(1.137) becomes:

$$\begin{aligned} F(r_1) \psi_j(r_1) &= h(r_1) \psi_j(r_1) \\ &+ \sum_{c=1}^N \iint \alpha^*(\omega_1) \varphi_c^*(\chi_2) \frac{1}{|r_1 - r_2|} \varphi_c(\chi_2) \alpha(\omega_1) \psi_j(r_1) d\omega_1 d\chi_2 \\ &- \sum_{c=1}^N \iint \alpha^*(\omega_1) \varphi_c^*(\chi_2) \frac{1}{|r_1 - r_2|} \varphi_c(\chi_1) \alpha(\omega_2) \psi_j(r_2) d\omega_1 d\chi_2 \\ &= \varepsilon_j \psi_j(r_1) \end{aligned} \quad (1.138)$$

where we have performed the integration over  $d\omega_1$  in the expression involving  $h(r_1)$  and used  $P_{12}$  to generate the explicit exchange form. In a closed shell, the sum over occupied spin orbitals includes an equal sum over those with  $\alpha$  spin function and those with  $\beta$  spin function. Therefore, Eq. (1.138) becomes

$$\begin{aligned}
& F(r_1)\psi_j(r_1) \\
&= h(r_1)\psi_j(r_1) \\
&+ \sum_{c=1}^{N/2} \iiint \alpha^*(\omega_1)\psi_c^*(r_2)\alpha^*(\omega_2) \frac{1}{|r_1 - r_2|} \psi_c(r_2)\alpha(\omega_2)\alpha(\omega_1)\psi_j(r_1)d\omega_1d\omega_2dr_2 \\
&+ \sum_{c=1}^{N/2} \iiint \alpha^*(\omega_1)\psi_c^*(r_2)\beta^*(\omega_2) \frac{1}{|r_1 - r_2|} \psi_c(r_2)\beta(\omega_2)\alpha(\omega_1)\psi_j(r_1)d\omega_1d\omega_2dr_2 \\
&- \sum_{c=1}^{N/2} \iiint \alpha^*(\omega_1)\psi_c^*(r_2)\alpha^*(\omega_2) \frac{1}{|r_1 - r_2|} \psi_c(r_1)\alpha(\omega_1)\alpha(\omega_2)\psi_j(r_2)d\omega_1d\omega_2dr_2 \\
&- \sum_{c=1}^{N/2} \iiint \alpha^*(\omega_1)\psi_c^*(r_2)\beta^*(\omega_2) \frac{1}{|r_1 - r_2|} \psi_c(r_1)\beta(\omega_1)\alpha(\omega_2)\psi_j(r_2)d\omega_1d\omega_2dr_2 \\
&= \varepsilon_j \psi_j(r_1) \tag{1.139}
\end{aligned}$$

Now we can perform the integrations over  $d\omega_1$  and  $d\omega_2$ . The last term in Eq. (1.139) disappears because of spin orthogonality. After little algebra Eq. (1.139) becomes

$$\begin{aligned}
F(r_1)\psi_j(r_1) &= h(r_1)\psi_j(r_1) + \left[ 2 \sum_{c=1}^{N/2} \int \psi_c^*(r_2) \frac{1}{|r_1 - r_2|} \psi_c(r_2) dr_2 \right] \psi_j(r_1) \\
&\quad - \left[ \sum_{c=1}^{N/2} \int \psi_c^*(r_2) \frac{1}{|r_1 - r_2|} \psi_j(r_2) dr_2 \right] \psi_c(r_1) = \varepsilon_j \psi_j(r_1) \quad (1.140)
\end{aligned}$$

the closed shell coulomb and exchange operators are

$$\begin{cases}
J_c(r_1)\psi_j(r_1) = \left[ \int \psi_c^*(r_2) \frac{1}{|r_1 - r_2|} \psi_c(r_2) dr_2 \right] \psi_j(r_1) \\
\text{and} \\
K_c(r_1)\psi_j(r_1) = \left[ \int \psi_c^*(r_2) \frac{1}{|r_1 - r_2|} \psi_j(r_2) dr_2 \right] \psi_c(r_1)
\end{cases} \quad (1.141)$$

Hence, the closed shell Fock operator has the form

$$F(r_1) = h(r_1) + \sum_{c=1}^{N/2} [2J_c(r_1) - K_c(r_1)] \quad (1.142)$$

In this section we present the Roothaan-Hall formulation of the Hartree-Fock theory, in which the molecular orbitals (MOs) are expanded in a set of atomic orbitals (AOs) whose expansion coefficients are used as the variational parameters [16, 17]. Therefore, the closed shell spatial Hartree-Fock equation is given by

$$F|\Psi_j\rangle = \varepsilon_j |\Psi_j\rangle \quad (1.143)$$

In other words, every spatial orbital satisfies

$$F(r_1)\Psi_j(r_1) = \varepsilon_j \Psi_j(r_1) \quad (1.144)$$

where,  $\varepsilon_j$  is the energy of spatial orbital  $\Psi_j$ . Eq. (1.144) is an eigenvalue equation where each spatial orbital  $\Psi_j$  is doubly occupied. Eq. (1.144) can be solved numerically, commonly, for atoms. No practical procedures are presently available,



Basis function  $\theta_2$  gives:

$$\begin{cases} \sum_{s=1}^M c_{s1} F_{2s} = \varepsilon_1 \sum_{s=1}^M c_{s1} S_{2s} \\ \vdots \\ \sum_{s=1}^M c_{sM} F_{2s} = \varepsilon_M \sum_{s=1}^M c_{sM} S_{2s} \end{cases} \quad (1.147 - 2)$$

Finally, basis function  $\theta_M$  gives:

$$\begin{cases} \sum_{s=1}^M c_{s1} F_{Ms} = \varepsilon_1 \sum_{s=1}^M c_{s1} S_{Ms} \\ \vdots \\ \sum_{s=1}^M c_{sM} F_{Ms} = \varepsilon_M \sum_{s=1}^M c_{sM} S_{Ms} \end{cases} \quad (1.147 - M)$$

Where  $F_{rs}$  and  $S_{rs}$  are the elements of the Fock and overlap matrices respectively and they are given by:

$$\begin{cases} F_{rs} = \int \theta_r^* F \theta_s dv \\ \text{and} \\ S_{rs} = \int \theta_r^* \theta_s dv \end{cases} \quad (1.148)$$

In the M sets of equations (1.147-1) to (1.148-M) each set itself contains M equations, for a total of  $M \times M$  equations. These equations are the Roothaan-Hall equations. Roothaan-Hall equations are usually written as:

$$\sum_{s=1}^M F_{rs} c_{sj} = \sum_{s=1}^M S_{rs} c_{sj} \varepsilon_j \quad (1.149)$$

Where  $r=1, 2 \dots M$  for each  $j=1, 2 \dots M$ , i.e. we have a set of M equations for each spatial function  $\psi_j$ . Roothaan-Hall equations can be written also in matrix form:

$$Fc = Sc\varepsilon \quad (1.150)$$

Where  $F$  is the Fock matrix with elements  $F_{r,s}$ ,  $c$  is the coefficient matrix with elements  $c_{s,j}$ ,  $S$  is the overlap matrix with elements  $S_{r,s}$  and  $\epsilon$  is the energy matrix with elements  $\epsilon_j$ .  $F$ ,  $c$  and  $S$  are  $M \times M$  Hermitian square matrices and  $\epsilon$  is an  $M \times M$  Hermitian diagonal matrix.

Eq. (1.150) cannot be solved directly because the Fock matrix  $F$  depends on the spatial wave functions. Therefore, Eq. (1.150) should be solved using the self-consistent field approach (SCF) technique obtaining in each iteration as a new set of coefficients  $c_{s,j}$  and continuing until a convergence criterion has been reached.

## 1.11 Restricted and unrestricted Hartree-Fock calculations

In restricted Hartree-Fock (RHF) [20, 21] theory, the electronic state is represented by single configuration state functions (CSF), which can be constructed from a linear combination of Slater determinants as

$$|CSF\rangle = \sum_i c_i |i\rangle \quad (1.151)$$

where, the  $|i\rangle$  is Slater determinants, with coefficients  $c_i$  fixed by the spin symmetry of the wave function. The Slater determinants in Eq. (1.151) belong to the same orbital configuration which means that they have identical orbital occupation numbers but different spin-orbital occupation numbers. In unrestricted Hartree-Fock theory [16], the wave function is represented by a single Slater determinant where the wave function is not required to be a spin eigenfunction, and different spatial orbitals are used for different spins, which means that no restrictions are enforced on the total spin of the system and the wave function is not required to transform as an irreducible representation of the molecular point

group. Since the alpha and beta spin orbitals are separately optimized, they will in general have different spatial forms.

## **1.12 Configuration interaction**

The configuration interaction method is the conceptually simplest of the common many-body techniques based on second quantization and the most accurate one, in the sense that it converges to the exact solution, and that the other methods are approximations to the Full (CI) method. The purpose of CI method is to treat the electron correlation better than does the HF method. The CI method [22, 23] is based on the simple idea that one can improve on the HF wavefunction, and hence energy, by adding on the HF wavefunctions terms that represents promotion (i.e. excitation) of electrons from occupied to virtual spin orbital's. The method is flexible and can give highly accurate wave functions for small closed and open shell systems with electron correlation. The principle shortcomings of the CI method is that it is difficult to implement for large molecules because of the rapid growth in the number of configurations needed to recover a substantial part of the correlation energy for larger systems.

### **1.12.1 The CI Wave Functions**

Since the HF wavefunction consists of the  $N$  lowest-energy spin orbitals, but it is not a complete representation of the total electronic wavefunction. The idea behind the CI calculation is that a better total wavefunction, and from this a better energy, is obtained if the electrons are confined not just to the  $N$  lowest-energy spin orbitals but are allowed to roam over all, or at least some, of the virtual spin orbitals. To permit this therefore there is a possibility of improving a trial

wavefunction by constructed as a linear combination of determinants or configuration state functions CSFs

$$\begin{aligned}
 |\Psi\rangle &= c_0|\psi\rangle_0 + \sum_s c_s|\psi_s\rangle \\
 &= c_0|\psi\rangle_0 + \sum_{ar} c_a^r |\psi_a^r\rangle + \sum_{\substack{a<b \\ r>s}} c_{ab}^{rs} |\psi_{ab}^{rs}\rangle + \sum_{\substack{a<b<c \\ r<s<t}} c_{abc}^{rst} |\psi_{abc}^{rst}\rangle \\
 &+ \dots
 \end{aligned} \tag{1.152}$$

In the following, the occupied orbitals will be denoted by indices  $a, b, c, \dots$  etc, and the virtual with indices  $r, s, t, \dots$  etc. where  $|\psi\rangle_0$  is the HF determinant and  $|\psi_a^r\rangle, |\psi_{ab}^{rs}\rangle, |\psi_{abc}^{rst}\rangle, \dots$  are determinants corresponding to the excitation of electrons into virtual orbitals. By replacing occupied spin orbitals in the HF determinant by virtual orbitals, a whole series of determinants may be generated. These can be denoted according to how many occupied HF spin orbitals have been replaced by unoccupied spin orbitals i.e. these determinants represent the ground state, singly excited, doubly excited, and triply excited state determinants, etc., excited relative to the HF determinant, up to a maximum of N excited electrons.

### 1.12.2 Optimization of the CI Wave Functions

If we can include all possible determinants in the expansion, then the wave function would be the full configuration interaction (FCI) wave functions. Full CI calculations are possible only for very small molecules because the promotion of electrons into virtual orbitals can generate a large number of states unless we have only few electrons and orbitals [24, 25]. The linear coefficients  $c$  determined by a

variational optimization of the expectation value of the electronic energy are obtained by

$$E_{CI} = \min \frac{\langle C|H|C \rangle}{\langle C|C \rangle} \quad (1.153)$$

$$\frac{\partial}{\partial c} \frac{\langle C|H|C \rangle}{\langle C|C \rangle} = 0 \quad (1.154)$$

The CI procedures, on a linear variation method are equivalent to an eigenvalue problem for the coefficients and the energy

$$\mathbf{HC} = \mathbf{EC} \quad (1.155)$$

where  $\mathbf{H}$  is the Hamiltonian matrix with the elements

$$H_{ij} = \langle i|H|j \rangle \quad (1.156)$$

and  $\mathbf{C}$  is a vector containing the expansion coefficients  $C_i$ . The Eq.(1.155) corresponds to a standard Hermitian eigenvalue problem of linear algebra. The construction of the CI wavefunction may therefore be accomplished by diagonalizing of the Hamiltonian matrix in the usual manner, or by other special iterative techniques are employed for extracting selected eigenvalues and eigenvectors.

If every possible idealized electronic state of the system, *i.e.* every possible determinant, were included in Eq. (1.151), then the wavefunctions  $\Psi$  would be full CI wavefunctions. Full CI wavefunctions with an infinitely large basis set would give the exact energies of all the electronic states *i.e.* full CI wavefunctions with a large basis set gives good energies for the ground and many excited states. But full CI calculations are possible only for very small molecules, because the excitation

of electrons into virtual orbitals can generate a huge number of states unless we have only a few electrons and orbitals. Since the full CI calculation is possible only for small molecules, then for large molecules the expansion should be limited and should include only the most important elements. It then becomes necessary to truncate the CI expansion so that only a small set of the determinants is included. The truncated CI expansion should preferably recover a large part of the correlation energy and provide a uniform description of the electronic structure over the whole potential energy surface.

### 1.13 Davidson correction

The Davidson correction [26, 27] is sometimes added to a variationally determined truncated CI energy such as the CI singles and doubles (CISD), which actually indirectly includes triply and quadruply excited states. But in case of large molecules the (SDCI) is not enough. Therefore, the Davidson correction is included when quadruple excited determinants can be important in completing the correlation energy. Thus, this correction is given by

$$\Delta E_a = (1 - c_1^2)(E_{DCI} - E_{SCF}) \quad (1.157)$$

where  $\Delta E_a$  is the contribution of quadruple excited determinants to correlation energy,  $E_{DCI}$  is the ground state energy computed in a CI calculation using  $|\psi\rangle_0$  and all its doubly excitations. The set  $c$  is the coefficients of  $|\psi\rangle_0$  for the normalized wavefunction of Eq. (1.151) obtained in the (CISD) calculation.  $E_{SCF}$  is the ground state energy associated with  $|\psi\rangle_0$  obtained in HF SCF calculations.

## 1.14 Basis set

The usual method to obtain a molecular wavefunction is to expand this wavefunction in terms of products of linear combinations of atomic orbitals. In order to limit the computational expense, a fast convergence of the calculation is desirable. The convergence essentially depends on the choice of the atomic basis set. This is a set of mathematical functions used to formulate the spatial wave function. Hence, the spatial wave function is a linear combination of these functions as shown in Eq. (1.145). The basis set functions are usually centered on the atomic nuclei. Several basis functions describe the electron distribution around an atom and combining the atomic basis functions yields the electron distribution in a molecule as a whole.

There are two types of basis set functions commonly used in electronic structural calculations: The Slater type orbital (STO) [28] and the Gaussian type orbital (GTO) [29]. The (STO) has the form

$$\theta_{\zeta,n,l,m}(r, \vartheta, \phi) = NY_{l,m}(\vartheta, \phi)r^{n-l}e^{-\zeta r} \quad (1.158)$$

where  $N$  is the normalization coefficient and  $Y_{l,m}$  is the usual spherical harmonic functions. Although Slater orbitals were used for many years, the basis set consists of functions that can adjust the shape of the atomic orbital by expressing each atomic orbital as a sum of two Slater type orbitals that differ only in the value of their exponent  $\zeta$ , this basis set is called double-zeta. If the valence orbitals are expressed by a double zeta representation, and the inner-shell electrons are still described by a single Slater orbital, the basis set is called split-valence basis set. In particular, integrals involving more than one nuclear center,

called multicenter integrals, are awkward to calculate using Slater orbitals. When using Gaussian functions instead of Slater orbitals, however, all the multicenter integrals are very easy to evaluate. Thus, it would see desirable to use Gaussian-type orbitals [29] of the form

$$\left\{ \begin{array}{l} \theta_{\zeta,n,l,m}(r, \vartheta, \phi) = NY_{l,m}(\vartheta, \phi)r^{(2n-2-l)}e^{-\zeta r^2} \\ \text{and} \\ \theta_{\zeta,l_x,l_y,l_z}(x, y, z) = Nx^{l_x}y^{l_y}z^{l_z}e^{-\zeta r^2} \end{array} \right. \quad (1.159)$$

where  $l_x+l_y+l_z$  determine the type of the orbital. The  $r^2$  dependence in the exponential makes the (GTO) inferior to the (STO) in two aspects. The first one is that (GTO) has a zero slope at the nucleus while (STO) has a discontinuous derivative this creates a problem for (GTO) in representing the proper behavior near to the nucleus. The second one is that (GTO) falls off too rapidly far from the nucleus compared with an (STO) so that the tail of the wavefunction is represented poorly. Both (GTO) and (STO) are used to form a complete basis set but according to the two aspects mentioned above we need more (GTO) to get the same level of accuracy achieved by (STO). Since the evaluation of two electron integrals requires more excessive computer time if we use (STO), this is why we use a linear combination of (GTO) instead of (STO) in all electronic structure calculations. In general, we would like to use the largest available basis set with the maximum possible consideration of electron correlation. The computer hardware (memory, disk storage, processor speed) and inherent size of the calculation force compromise on the choice of the basis set.

## 1.15 Effective core potential (ECP)

From about the third row of the periodic table the large number of electrons has a considerable effect on conventional *ab-initio* calculations, because of the large number of two electron repulsion integrals. The usual way of avoiding this problem is to add to the Fock operator a one electron operator that takes into account the effect of the core electrons on the valence electrons, which latter are still considered explicitly. This average operator is called an effective core potential (ECP) [30]. With a set of valence orbital basis function optimized for use with it, it stimulates the effect of the atomic nuclei plus the core electrons.

## 1.16 Energy correlation (EC)

The HF method allows the exact calculation of the interaction effects between the electrons and the nuclei, and the approximate calculation of the overall interaction effects of the electrons among themselves. The electron correlation is the phenomenon of the motion of pairs of electrons in atoms and molecules being connected or correlated [31, 32]. Actually, the HF method allows for some electron correlation because it uses antisymmetric wavefunctions which ensures a zero probability to find two electrons of equal spin at the same point in space. Because of this zero probability, and since the wavefunction is continuous, the probability of finding them at a given separation should decrease smoothly with that separation. This means that even if electrons were uncharged, with no electrostatic repulsion between them, around each electron there would still be a region increasingly unfriendly to other electrons of the same spin. This quantum mechanically engendered “Pauli exclusion zone” around an electron is called a

Fermi hole. Besides the quantum mechanical Fermi hole, each electron in a real molecule, not in a HF molecule, is surrounded by a region unfriendly to the other electrons, regardless of the spin, because of the electrostatic (Coulomb) repulsion between electrons. This electrostatic exclusion zone is called a Coulomb hole. Since the HF method does not treat electrons as discrete point particles it essentially ignores the existence of the Coulomb hole, allowing electrons to get too close on the average. This is the main source of overestimation of electron-electron repulsion in the HF method.

HF calculations give an electronic energy that is too high. This is partly because of the overestimation of electronic repulsion and partly because of the fact that in any real calculation the basis set is not perfect. As the size of the basis increases the HF energy gets smaller i.e. more negative. The limiting energy that would be given by an infinitely large basis set is called the HF limit. A measure of the extent to which any particular *ab initio* calculation does not deal perfectly with electron correlation is the correlation energy. The correlation energy for a calculation on some molecule or atom is the energy calculated by some perfect quantum mechanical procedure minus the energy calculated by the HF method using a huge basis set [33-38]. Mathematically this can be written as

$$E_{Correl} = E(exact) - E(HF\ limit) \quad (1.160)$$

This energy will always be negative because the Hartree-Fock energy is an upper bound to the exact energy (this is guaranteed by the variational theorem).

### **1.17 Dynamic and non-dynamical correlation energy.**

For the majority of molecules, for example all molecules that can be assigned a single Lewis structure, the main error in the Hartree-Fock approximation comes from ignoring the correlated motion of each electron with all the other electrons. This is called dynamical correlation because it refers to the dynamical character of the electron-electron interactions. This kind of correlation energy is described with the configuration interaction (CI) method. Non-dynamical correlation is important for molecules where the ground state is well described only with more than one (nearly) degenerate determinant. In this case the Hartree-Fock wave function (only one determinant) is qualitatively wrong. This is recovered by the multi-configurational self-consistent field (MCSCF) method.

### **1.18 Pseudo-potential and relativistic pseudo-potential**

We have seen earlier that it is possible to expand almost any smooth function that goes to zero at infinity in terms of Gaussian functions, so that the natural first choice of the expansion of core potential is a linear combination of the Gaussians. We have seen how to generate the explicit numerical forms of the pseudo, Coulomb and exchange potential available from atomic calculations so that we may use both these forms and the Gaussian expansion method to guide our choice.

For system involving elements from third row or higher in the periodic table, there is a large number of core electrons which in general are unimportant in a chemical sense. From the fact that valence electrons determine most of the chemical properties of the molecules, an Effective Core Potential (ECP) in the chemical

community, while the physics community uses the term Pseudo-potential (PP), may be constructed to represent all the core electrons. Thus reduce all-electron molecular electronic structure calculations to one involving the valence electrons.

There are four major steps in designing pseudo-potential:

1. Generate a good-quality all-electron wave function for the atom. (Hartree-Fock or a density functional calculations) under consideration.
2. Replace the valence orbitals by a set of node less pseudo-orbitals.
3. Core electrons are then replaced by a potential parameterized by expansion into a suitable set of analytical functions.
4. Fit the parameters of the potential such that the solution of the Schrödinger equation produces pseudo-orbitals matching the all-electrons valence orbitals.

In all electron method, the basic constituents of a molecule are the  $N$  electrons and the nuclei. In all Pseudo-potential methods, the basic constituents of the system are assumed to be the  $N_v$  valence electrons of the molecule and the fixed ions of each atom consisting of the core electrons and the nucleus. The total valence Hamiltonian is given by

$$H_{ps} = \sum_{i=1}^{N_v} \left[ \frac{-1}{2} \Delta_{Ai} + \sum W_{ps,A}(i) \right] + \sum_{i<j}^{N_v} \frac{1}{r_{ij}} + \sum_{A<B} \frac{Z_A Z_B}{R_{AB}} \quad (1.161)$$

where,  $R_{AB}$  is the distance between the nuclei A and B,  $Z_A = Z_A - N + N_v = Z_A - N_c$  is the net charge of the atomic core  $A$ , with  $Z_A$  the atomic charge of the atom A, and  $W_{ps,A}$  is the Pseudo-potential associated with the core A.  $W_{ps,A}$  takes into account the interaction of valence electrons with the atomic core  $A$  [39].

Various effective core potential methods have been developed to determine atomic *Pseudo-potentials* [40-45]. Semi-local potentials has the form [46-51]

$$W_{ps} = \frac{-Z}{r} + \sum_l W_l(r) P_l \quad (1.162)$$

$$P_l = \sum_{m_l=-l}^l |Y_{lm_l}\rangle \langle Y_{lm_l}| \quad (1.163)$$

Is the angular projection over the  $l^{th}$  sub-space of the spherical harmonics, and

$$W_l(r) = \sum_i c_i \frac{e^{-\alpha_i r^2 (ar)}}{r^{n_i}} \quad (1.164)$$

are functions of  $r$ . The  $r^2$  Gaussian dependence of the exponential function is generally chosen to simplify further molecular calculations, based on Gaussian type functions.

Non-local *pseudo-potentials* have the form [39]

$$W_{ps} = f(r) + \sum_l \sum_{i,j} c_{ij,l} \sum_{m_l=-l}^l |Y_{ilm_l}\rangle \langle Y_{ilm_l}| \quad (1.165)$$

where  $f(r)$  is a function which tends to  $\frac{-Z}{r}$  for  $r \gg R_c$  (core radius). The function  $\chi_{ilm_l} = R_i(r)Y_{lm_l}(\vartheta, \varphi)$  is generally Gaussian functions.

Expression (1.162) of  $W_{ps}$  has the great advantage that molecular calculations require only calculation of overlap integrals between the valence basis sets and the functions  $\chi_{ilm_l}$ .

The direct generalization of the non-relativistic semi-local form (1.162) is to define  $W_{ps}$  by

$$W_{ps} = \frac{-Z}{r} + \sum_{lj} W_{lj}(r) P_{lj} ; \quad \text{with } j = l \pm \frac{1}{2} \quad (1.166)$$

$P_{lj} = \sum_{m=-j}^l |ljm\rangle \langle ljm|$  is the operator on two-component spinors [40]. The  $W_{lj}$  expressions are most often linear combinations of Gaussian functions.

## 1.19 The Self-Consistent Field Method (SCF)

The Self-consistent Field (*SCF*) procedure is a computational procedure for obtaining restricted closed-shell Hartree-Fock wave function for atoms or molecules, as shown in figure 1.2.

**Step (1):** Specify a molecule (a set of nuclear coordinates  $\{R_A\}$ , atomic numbers  $\{Z_A\}$ , and number of electrons  $N$ ).

**Step (2):** Choose a basis function set  $\theta_j$ .

**Step (3):** we formulate the overlap matrix  $S$  according to Eq. (1.148).

**Step (4):** Constructing a trial wave function and a trial coefficient matrix  $c$  using Eq. (1.145).

**Step (5):** Using Eq. (1.148) we formulate a trial Fock matrix  $F$ .

**Step (6):** We solve equation Eq. (1.150) where a new set of coefficients and energies are obtained.

**Step (7):** program compares  $c$ 's with the previous  $c$ . If the match is not enough, the procedures return to step (3) with another SCF cycle inside.

**Step (8):** we repeat, in each iteration, steps 3 to 5 using the new coefficients obtained from the previous iteration till convergence are achieved.

At the end of these steps we get the best coefficients  $c_{s,j}$  used to formulate the spatial wave function and the corresponding energies  $\epsilon_j$  for each spatial orbital.

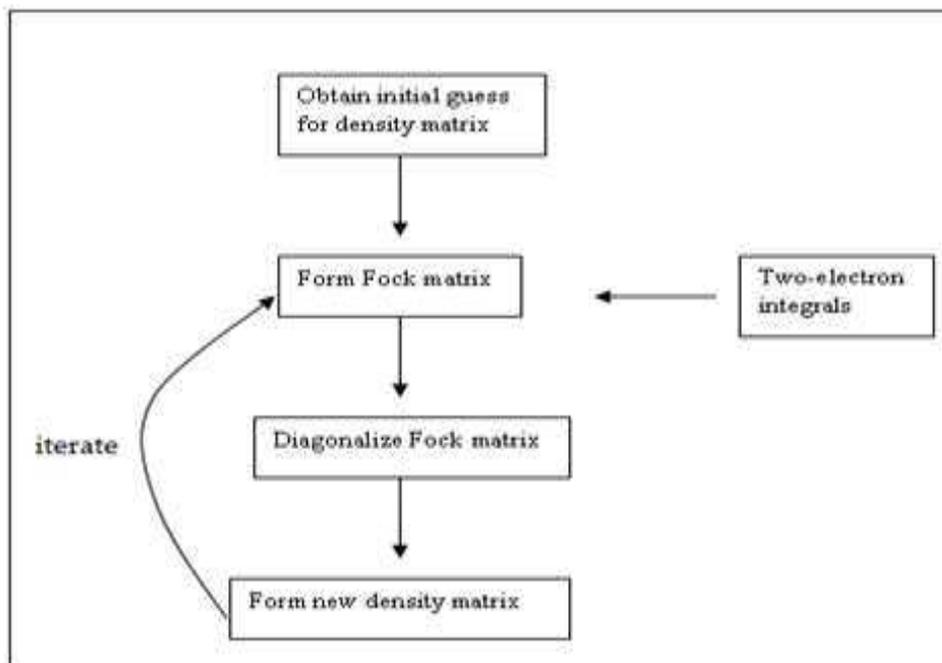


Fig 1.2. Illustration of SCF procedure

## 1.20 Multi-Configuration and Multi-Reference Methods

In many situations, the electron correlation effects are purely of the “dynamic” type, in the sense that Hartree-Fock is a good zero-order approximation, and under such circumstances, single-reference methods provide an efficient and accurate way to get correlation energies and correlated wavefunctions. However, wherever bonds are being broken, and for many excited states, the Hartree-Fock determinant does not dominate the wavefunction, and may sometimes be just one of a number of important electronic configurations. If this is the case, single-reference methods, which often depend formally on perturbation arguments for their validity, are inappropriate, and one must seek from the outset to have a first description of the system that is better than Hartree-Fock. In these cases the most straightforward way to give a qualitative correct description of the electronic structure providing

the entire necessary configuration included is the multi-reference SCF (MCSCF) method [52-54] , which are the most widely used implementation of CI and provide a qualitatively correct description of the system. In this approach, a selected set of determinants is used instead of single determinant. The wave function has the form

$$|\Psi\rangle = \sum_i c_i |i\rangle \quad (1.167)$$

where,  $|i\rangle$  is a spin-and space-symmetry adapted CSF consisting of Slater determinants. The orbital coefficients are optimized simultaneously with the CI coefficients in a variational procedure. Then the problem of finding the ground state MCSCF optimum wave function can be obtained by minimizing the energy with respect to the variational parameters

$$E_{MC} = \min \frac{\langle \Psi | H | \Psi \rangle}{\langle \Psi | \Psi \rangle} \quad (1.168)$$

the major problem with *MCSCF* method is selecting the necessary configurations. This can be achieved by the so-called Complete Active-Space self-Consistent Field (CASSCF) [55-57] method. In this approach, the molecular orbitals are divided into three classes:

1. A set of inactive orbitals composed of the lowest energy orbitals which are doubly occupied in all determinants.
2. A set of virtual orbitals of very high energy which are unoccupied in all determinants.
3. A set of active orbitals which are energetically intermediate between the inactive doubly occupied and highly excited virtual orbitals. This set

contains the spin orbitals that are considered to be the most important ones for the process under study.

The active electrons are the electrons that are not in the doubly occupied inactive orbital set. The CSFs included in the CASSCF calculations are configurations (of the appropriate symmetry and spin) that arise from all possible ways of distributing the active electrons over the active orbitals.

CASSCF calculations are used to study chemical reactions and to calculate electronic spectra. They require judgment in the proper choice of the active space and are not essentially algorithmic like other methods [58]. An extension of the (MCSCF) method is multireference CI (MRCI).

In Multi-Reference Configuration Interaction (MRCI), a MCSCF wave function is chosen as a reference from which excited determinants are formed for the use in CI calculation. The reference determinants will themselves often be singly and doubly excited with respect to  $\Psi_{HF}$ . In this case, a CISD will include determinants that are triply and quadruply excited from  $\Psi_{HF}$ . Then CI is performed, optimizing all the coefficients of the determinants that have been included. MRCI methods are among the most powerful tools for calculating accurate potential energy functions and molecular properties [59]. Benchmark calculations, in which MRCI results are compared with those from full CI in the same basis, indicate that MRCI is the *ab initio* method of choice for all circumstances in which single determinant descriptions do not work, and that very high accuracy may be obtained [60-69].

The methods we have been outlining are to be evaluated by two general criteria:

- Agreement with experimental measurements where the experimental results are available.
- Explanation of phenomena in terms of a set of concepts generated by a combination of intuition and theoretical analysis.

Clearly the second of these is of little value unless the first is satisfied within some well-defined and well-understood hierarchy of approximation; the models for molecular electronic structure we have been using fall into a more-or-less strict hierarchy:

1. The potential energy-terms in the Hamiltonian are only those due to Coulomb's law. We exclude magnetic and relativistic effects completely.
2. The Born-Oppenheimer (fixed nucleus) model is assumed throughout.
3. The algebraic approximation is the key numerical approximation to make the whole project feasible.
4. The use of only atom-centered basis functions is based on our intuitions about the likely distribution of electrons in molecules.
5. The number and the type of basis sets functions have to be chosen as a compromise between accuracy and convenience.
6. Core potentials are often used both for reasons of economy and to avoid difficulties with the description of core electrons.

The natural question to ask is “can we extend our use of intuitive information and physical interpretation to numerical approximations within the calculation?” If the answer is, “yes” then there are two possible ways in which we might go forward which are not mutually exclusive

- We can use the physical interpretation of the energy integrals appearing in the algebraic approximation to estimate their relative sizes and to make numerical estimates of their values.

The values (or functional forms) of the energy integrals may be used as a method of forcing a particular model of molecular electronic structure to agree with experiment. That is, we can calibrate a particular model against experiment for some chosen property.

## 1.21 Multireference CI Wave Function MRSDCI

The Multireference CI (MRCI) wave function is generated by including in the wave function all configurations arising from the single and double excitations from the reference space, thus resulting in the multireference singles and doubles configuration interaction (MRSDCI) wave function

$$|\Psi_{MRSDCI}\rangle = (1 + \sum_{AI} X_I^A + \sum_{A>B,I>J} X_{IJ}^{AB})|\Psi_0\rangle \quad (1.169)$$

In second quantization the single and double excitation operators are represented by

$$X_I^A |\Psi_0\rangle = C_I^A a_A^\dagger a_I |\Psi_0\rangle, \quad X_{IJ}^{AB} |\Psi_0\rangle = C_{IJ}^{AB} a_A^\dagger a_B^\dagger a_I a_J |\Psi_0\rangle. \quad (1.170)$$

The construction of a multireference CI wave function begins with the generation of a set of orbitals and a reference space of configurations  $|\Psi_0\rangle$ , which are best generated by the CASSCF Method. The CASSCF method writes the wave function as a linear combination of determinants or CSFs, whose expansion coefficients are optimized simultaneously with the MOs according to the variation principle. The fully optimized wave functions in the CASSCF method are then used as a reference state in the MRSDCI technique, in which single and double excitations are included.

## 1.22 Spin Orbit Effects

We discussed in the previous sections the non-relativistic Schrödinger scheme, which is not complete because we need to take into account an additional terms to the intrinsic magnetic moment of the electron (spin) in molecular system, the exact solution of the non-relativistic Schrödinger equation does not reproduce the real

experimental energies. The difference arises from relativistic effects, which increase with the 4<sup>th</sup> power of the nuclear charge ( $Z^4$ ) [70]. In cases of lighter atoms we can neglect relativistic effects but have to be included when dealing with heavy elements. In non-relativistic quantum mechanics, for most measurements on the lighter elements in the periodic table, non-relativistic quantum mechanics is sufficient, since the velocity of an electron is small compared to the speed of light. For the heavier elements in the periodic table the picture is entirely different. For the heavy atoms, the inner electrons attain such high velocities, comparable to that of light, and non-relativistic quantum mechanics is far from adequate.

From all the different kinds of relativistic effects the spin-orbit interaction represented by the Briet-Pauli Hamiltonian is the most important part [70]. There is an important effect, in molecular spectroscopy as well, called the spin-orbit interaction which splits the levels. These effects alter the spectroscopic properties of molecules containing heavy elements to a considerable extent. Even if a molecule has a closed shell ground state the excited states may stem from open shell electronic configurations, in which case the spin-orbit interaction not only splits the excited states, but mixes different excited states which would not mix in the absence of spin-orbit interaction. Indeed, the yellow color of gold is due to orbital mixing occurring between the 5d<sup>10</sup> and 6s<sup>1</sup> orbitals [71]. This relativistic effect allows gold to absorb light in the violet and blue regions of the spectrum while it allows for the reflection to occur in the yellow and red regions [71]. In the last ten years, there have been numerous studies dealing with spin-orbit (SO) coupling calculations for rather heavy molecules (including atoms below the second line of the periodic table). One of the most convenient schemes in the calculations of  $\Lambda$ - $\Sigma$  coupling is the “atoms in molecule” approximation developed by Cohen and Schneider [72] which consists of building an effective matrix of  $H_e$

+  $H_{SO}$  in the basis of  $\Lambda$  electronic states  $\Psi_m$  correlated to a given atomic configuration. The SO matrix elements are assumed to be independent of internuclear distances and determined empirically from the atomic energy splitting. The magnitude of the spin orbit coupling Hamiltonian  $H_{SO}$  in atoms is:

$$H_{so} = \frac{1}{2}hcA(j(j+1) - l(l+1) - s(s+1)) \quad (1.171)$$

where  $j$  is the total angular momentum  $j = l + s$ ,  $l$  is the orbital angular momentum quantum number and  $s$  is the spin quantum number.  $A$  is the magnitude of the spin-orbit coupling constant. Expending Eq.(1.169) we get

$$\begin{aligned} H_{so} &= \frac{1}{2}hcA((l+s)(l+s+1) - l(l+1) - s(s+1)) \\ &= \frac{1}{2}hcA(l^2 + ls + l + s^2 + sl + s - l^2 - l - s^2 - s) \\ &= hcAl.s. \end{aligned} \quad (1.172)$$

then the magnitude of the spin orbit coupling operator can be calculated

$$H_{so} = hcAl.s = \frac{Z\alpha^2}{2} \left\langle \frac{1}{r^3} \right\rangle l.s, \quad (1.173)$$

$Z$  is the atomic number, representing the number of protons inside the nucleus and  $\alpha$  is the fine structure constant  $\alpha = \frac{e^2}{\hbar c 4\pi\epsilon_0}$ . If we imagine ourselves riding on an electron in an atom, from our viewpoint and because of the spherical symmetry of the atom, the nucleus is moving around the electron. This apparent motion gives rise to a magnetic field which interacts with the intrinsic spin magnetic moment of the electron, and hence is proportional to  $\mathbf{L} \cdot \mathbf{S}$  where  $\mathbf{S} = \sum_i^n \mathbf{S}_i$  (the total spin) and  $\mathbf{S}_i$

is the individual electron angular momentum. Unfortunately, the projection of  $S$  along the internuclear axis is also called  $\Sigma$ . For  $\Lambda = 0$ ,  $\Sigma$  is not defined, that is there are no torques on  $S$ . For  $\Lambda \neq 0$ ,  $\Sigma = S, S - 1, -S + 1, -S$ , and the internal magnetic field set up causes  $S$  to precess, coupling the orbital and spin momentum. The total angular momentum is called  $\Omega$  and  $\Omega = |\Lambda + \Sigma|$  the splitting between the sub-states arises from the spin-orbit interaction. An example is showing in Fig 1.3.

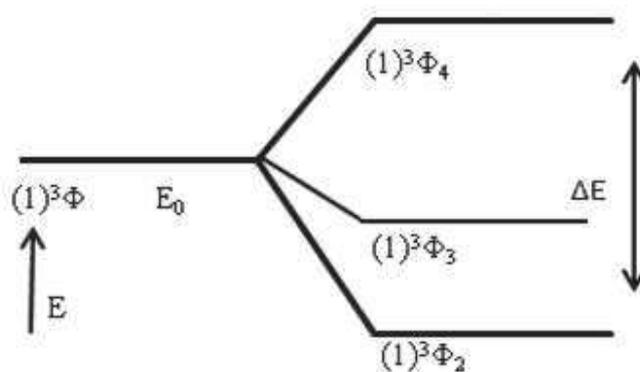


Fig.1.3. Energy level diagram for the multiplet states of  ${}^3\Phi$  state.

Teichtel and Speigelman [73] [74] developed a general algorithm in order to perform an *ab initio* CI calculations including relativistic terms within the quasi-degenerate perturbation theory [75]. The effective Hamiltonian thus introduced in the  $\Lambda$ - $\Sigma$  coupling representation is spanned in the basis of  $\Lambda$  states like in the Cohen and Schneider scheme [72] but the SO interactions between  $\Lambda$  states is calculated explicitly through the SO *ab initio* pseudopotentials, the averaged relativistic effects being taken into account at the mono-electronic level. Spin-orbit energy correction is very small in comparison with the total energy of the electron. It may be regarded as a small perturbation. So to calculate the energy correction is

sufficient to take the first-order perturbation theory using the previously found wavefunctions. The energy correction is then

$$\Delta E_{so} = \langle \Delta H_{so} \rangle = \int \Psi^* \Delta H_{so} \Psi d^3 x \quad (1.174)$$

we can calculate the value of  $l.s$  by

$$J^2 = J.J = l^2 + s^2 + l.s, \quad (1.175)$$

The average values of  $l^2$ ,  $s^2$  and  $j^2$  are  $l(l+1)\hbar^2$ ,  $s(s+1)\hbar^2$  and  $j(j+1)\hbar^2$ . Therefore, then acting on  $\Psi$

$$l.s \Psi = \frac{1}{2} \hbar^2 [j(j+1) - l(l+1) - s(s+1)] \Psi \quad (1.176)$$

the average value of  $1/r^3$  in a state characterized by quantum numbers  $n, l, j$  is given by

$$\left\langle \frac{1}{r^3} \right\rangle = \int \Psi_{n l j}^* \left( \frac{1}{r^3} \right) \Psi d\tau = \frac{Z^3}{a_0^3 n^3 l(l+\frac{1}{2})(l+1)} \quad (1.177)$$

In view of the results of Eqs.(1.174) and (1.175) the expression for spin orbit interaction energy becomes

$$\Delta E_{so} = \frac{1}{4} \frac{e^2 \hbar^2 Z^4}{4\pi \epsilon_0 m^2 c^2 a_0^3} \frac{j(j+1) - l(l+1) - s(s+1)}{n^3 l(l+\frac{1}{2})(l+1)} \quad l \neq 0 \quad (1.178)$$

then the term value of an energy level, by taking spin orbit energy into consideration, is

$$T = T_0 + T_{so} \tag{1.179}$$

where  $T_{so} = -\frac{\Delta E_{so}}{hc}$  and  $T_0$  is the term value of some reference level. If  $T_{so}$  is negative, the shift is upward and if  $T_{so}$  is positive, the shift of level is downward with respect to the reference level.

## 1.23 Conclusion

We present in this chapter a brief overview for the theoretical backgrounds of the computational methods used in the present work. The theoretical backgrounds for the electronic structure calculations in the Hartree-Fock method, followed by Complete Active Space Self-Consistent Field Calculations (CASSCF) and Multireference Configuration Interaction (MRCI) methods are written within the formalism of second quantization. A brief discussion for the theoretical background of spin orbit relativistic interactions in diatomic molecules has been also included within the context of this chapter.

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## CHAPTER 2

## The Vibration-Rotation Calculation In a Diatomic Molecule

### 2.1 Vibration-rotation canonical functions

**M**olecular spectra are more complex than atomic spectra. This is because atomic spectra are due to electronic transitions while molecular spectra are due to electronic, rotational and vibrational transitions. Since the electronic Schrödinger equation has solved in previous chapter, now it is possible to solve the radial Schrödinger equation. The vibration-rotation motion of a diatomic molecule is described by the wavefunction  $f_{v,J}$  and the energy  $E_{v,J}$  which are respectively the eigenfunction and eigenvalue of the radial Schrödinger Eq.[1]

$$\frac{d^2 f_{v,J}}{dr^2} + \left[ k \left( E_{v,J} - E_t(r) \right) - \frac{J(J+1)}{r^2} \right] f_{v,J}(r) = 0 \quad (2.1)$$

where  $v$  and  $J$  are the vibrational and rotational quantum numbers respectively,  $r$  is the internuclear distance,  $k = \frac{2\mu_r}{\hbar^2}$ , and  $E_t(r)$  is the total electronic energy. Eq. (2.1) can be simply represented as

$$f_{v,J}''(r) = P_{v,J}(x) f_{v,J}(x) \quad (2.2)$$

where  $x=r-r_e$  ( $r_e$  is the value of  $r$  at equilibrium), and

$$P(x) = -k \left( E_{v,J} - E_t(x) \right) + \frac{\lambda}{(r - r_e)^2} \quad (2.3)$$

with  $\lambda = J(J + 1)$ .

Eq. (2.2) is equivalent to the Volterra integral Eq. [2]

$$f_{v,J}(x) = f_{v,J}(0) + x' f'_{v,J}(0) + \int_0^x (x - t) P_{v,J}(t) f_{v,J}(t) dt \quad (2.4)$$

The energy factor  $P_{v,J}(x)$  can be associated with two functions  $\alpha(x)$  and  $\beta(x)$  called the canonical functions [3] and they are defined as

$$\left\{ \begin{array}{l} \alpha(x) = \sum_{i=0}^{\infty} A_i(x) \\ \text{and} \\ \beta(x) = \sum_{i=0}^{\infty} B_i(x) \end{array} \right. \quad (2.5)$$

where

$$\left\{ \begin{array}{l} A_i = \int_0^x (x - t) P_{v,J}(t) A_{i-1}(t) dt \\ \text{and} \\ B_i = \int_0^x (x - t) P_{v,J}(t) B_{i-1}(t) dt \end{array} \right. \quad (2.6)$$

with  $A_0(x)=1$  and  $B_0(x)=x$ . By using the properties of the Volterra integral equation (2.4) we obtain

1. The wavefunction  $f_{v,J}(x)$  is related to the functions  $\alpha(x)$  and  $\beta(x)$  by the relation:

$$f_{v,J}(x) = f_{v,J}(0)\alpha(x) + f'_{v,J}(0)\beta(x) \quad (2.7)$$

2.  $\alpha(x)$  and  $\beta(x)$  are two particular solutions of Eq.(2.2) with the well determined initial values

$$\begin{cases} \alpha(0) = 1 \text{ and } \alpha'(0) = 0 \\ \beta(0) = 0 \text{ and } \beta'(0) = 1 \end{cases} \quad (2.8)$$

3. The initial value  $f'_{v,J}(0)$  for the unnormalized wavefunction  $f_{v,J}(x)$  can be deduced from  $\alpha(x)$  and  $\beta(x)$  by using Eq.(2.7) on one hand and on the other hand the boundary conditions [4]

$$f_{v,J}(x) \rightarrow 0 \quad (2.9)$$

$\begin{matrix} x \rightarrow \infty \\ x \rightarrow r_e \end{matrix}$

one can find

$$\begin{cases} \frac{f'_{v,J}(0)}{f_{v,J}(0)} = \lim_{x \rightarrow \infty} \frac{-\alpha(x)}{\beta(x)} \\ \text{and} \\ \frac{f'_{v,J}(0)}{f_{v,J}(0)} = \lim_{x \rightarrow -r_e} \frac{-\alpha(x)}{\beta(x)} \end{cases} \quad (2.10)$$

## 2.2 The rotational Schrödinger equations

In the Rayleigh-Schrödinger perturbation theory (RSPT) the eigenvalue and eigenfunction of Eq.(2.1) are respectively given by

$$\begin{cases} E_\lambda = \sum_{n=0}^{\infty} e_n \lambda^n \\ \text{and} \\ f_{v,J}(x) = \sum_{n=0}^{\infty} \Phi_n \lambda^n \end{cases} \quad (2.11)$$

where  $e_0$  is the pure vibrational energy,  $e_1$  is the rotational constant,  $e_n$  ( $n > 1$ ) are the centrifugal distortion constants (CDC),  $\Phi_0$  is the pure vibrational wavefunction



where  $\Phi_n(x)$  depends on  $C_n(x)$ ,  $G_n(x)$  and  $I_n(x)$ . Taking the first term out of the series in the first line of Eq.(2.14), we can write

$$f_{v,J}(x) = \Phi_0(x) + \sum_{n=1}^{\infty} \Phi_n(x)\lambda^n \quad (2.17)$$

The first term on the right-hand side of Eq.(2.17) is independent of  $\lambda$ ; therefore this term is the pure vibrational wavefunction  $f_v(x)$ . Thus, Eq.(2.17) takes the form

$$f_{v,J}(x) = f_v(x) + \sum_{n=1}^{\infty} \Phi_n(x)\lambda^n \quad (2.18)$$

where  $\Phi_n(x)$  are the so-called rotation harmonics. Thus, the rotation effect  $\sum_{n=1}^{\infty} \Phi_n(x)\lambda^n$  in the vibration-rotation wave function  $f_{v,J}(x)$  is separated from the pure vibration wave function  $f_v(x)$ . Taking the second derivative of Eq.(2.18), we obtain

$$f_{v,J}''(x) = f_v''(x) + \sum_{n=1}^{\infty} \Phi_n''(x)\lambda^n \quad (2.19)$$

Substituting Eq.(2.18) into Eq.(2.2), we get

$$f_{v,J}''(x) = P_{v,J}(x) \left[ f_v(x) + \sum_{n=1}^{\infty} \Phi_n(x)\lambda^n \right] \quad (2.20)$$

Substituting Eq.(2.19) in Eq.(2.20) and after some mathematical manipulation we get

$$\left[ \sum_{n=0}^{\infty} \varepsilon_n(x)\lambda^n \right] \left[ \sum_{n=0}^{\infty} \Phi_n(x)\lambda^n \right] = \sum_{n=0}^{\infty} \Phi_n''(x)\lambda^n \quad (2.21)$$



### 2.3.2 Calculation of the rotational harmonics ( $\Phi_n(x)$ )

A rotational Schrödinger equation (last line in Eq.(2.22)) is given by

$$\Phi_n''(x) - \varepsilon_0(x)\Phi_n(x) = \sum_{m=1}^n \varepsilon_m(x)\Phi_{n-m}(x) \quad (2.24)$$

multiplying Eq. (2.24) by (x-t) and integrating the obtained equation between zero and x we get:

$$\Phi_n(x) = \Phi_n(0) + \Phi_n'(0)x + \sum_{m=1}^n \left[ \int_0^x (x-t)\varepsilon_m(t)\Phi_{n-m}(t)dt \right] \quad (2.25)$$

substituting the expression of  $\varepsilon_m(t)$  given by Eq.(2.13) in Eq.(2.24) we get [5-7]:

$$\Phi_n(x) = \Phi_n(0)\alpha_v(x) + \Phi_n'(0)\beta_v(x) + \sigma_n(x) \quad (2.26)$$

where

$$\sigma_n(x) = \sum_{m=0}^{\infty} k_m^n(x) \quad (2.27)$$

and

$$\left\{ \begin{array}{l} k_0^n(x) = \int_0^x (x-t)\varepsilon_n(t)\Phi_0(t)dt \\ k_1^n(x) = \int_0^x \int_0^t (x-t)(t-t_1)\varepsilon_n(t)\Phi_0(t)dt_1 dt \\ k_m^n(x) = \int_0^x (x-t)\varepsilon_n(t)k_{m-1}(t)dt \end{array} \right. \quad (2.28)$$

For  $x=0$ :

$$\begin{cases} k_0^n(0) = k_1^n(0) = \dots = k_m^n(0) = \dots = 0 \\ k_0^{n'}(0) = k_1^{n'}(0) = \dots = k_m^{n'}(0) = \dots = 0 \end{cases}$$

Therefore:

$$\sigma_n(0) = \sigma_n'(0) = 0$$

For the  $i^{\text{th}}$  order derivative (i.e.  $i>1$ ) we can write:

$$\begin{cases} \frac{d^i\{k_m^n(0)\}}{dx^i} = 0 \\ \text{and} \\ \frac{d^i\{\sigma_n(0)\}}{dx^i} \neq 0 \end{cases}$$

For the unnormalized wavefunction, we chose  $f_v(0)=\Phi(0)=1$  and by using Eq.(2.18) we get

$$\Phi_n(0) = 0$$

Substituting  $\Phi_n(0)$  by its value in Eq.(2.26) [7] we obtain:

$$\Phi_n(x) = \Phi_n'(0)\beta_v(x) + \sigma_n(x) \quad (2.29)$$

On the other hand, the rotation harmonics must be vanished at the boundaries (2.9), thus Eq.(2.29) becomes

$$\Phi_n'(0) = \lim_{\substack{x \rightarrow \infty \\ x \rightarrow -r_e}} \frac{-\sigma_n(x)}{\beta_v(x)} = l_n \quad (2.30)$$

and the rotational harmonic  $\Phi_n(x)$  is given by [6]:

$$\Phi_n(x) = \sigma_n(x) + l_n\beta_v(x) \quad (2.31)$$

This expression is valid without any restriction on the form of the given potential function.

## 2.4 Numerical method

### 2.4.1 Calculation of the vibration wavefunction $\Phi_0(x)$

For one electronic state and for a given potential, the vibrational wavefunction is given by

$$\Phi_0(x) = \Phi_0(0)\alpha_v(x) + \Phi_0'(0)\beta_v(x) \quad (2.32)$$

Therefore, the determination of  $\Phi_0(x)$  requires the calculation of  $\alpha_v(x)$ ,  $\beta_v(x)$  and  $\Phi_0'(x)$ .

### 2.4.2 Calculation of $\alpha_v(x)$ and $\beta_v(x)$

On one interval  $I_i = [r_i, r_{i+1}]$  a given potential has a polynomial form

$$E_t(r) = \sum_{n=0}^N \gamma_n(i)(r - r_i)^n \quad (2.33)$$

The canonical functions  $\alpha(x)$  and  $\beta(x)$  are particular solutions of the vibrational Schrödinger equation (first line in Eq.(2.22)); because  $E_t(x)$  is expanded in polynomial [8];  $\alpha(x)$  and  $\beta(x)$  also can be expanded as

$$\left\{ \begin{array}{l} \alpha(r) = \sum_{n=0}^{\infty} a_n (r - r_i)^n \\ \text{and} \\ \beta(r) = \sum_{n=0}^{\infty} b_n (r - r_i)^n \end{array} \right. \quad (2.34)$$

By representing  $\alpha(r)$  and  $\beta(r)$  by the same function  $y(r)$  for a given potential  $E_t(r)$  and energy  $E$ , the function  $y(r)$  is given by

$$y(r) = \sum_{n=0}^{\infty} C_n(i)(r - r_i)^n \quad (2.35)$$

By using the vibrational Schrödinger equation (first line in Eq.(2.22)), we obtain the following recursion relation [7]

$$(n + 2)(n + 1)C_{n+2}(i) = -kEC_n(i) + k \sum_{m=0}^n C_m(i)\gamma_{n-m}(i) \quad (2.36)$$

where

$$\begin{cases} C_0(i) = y(r_i) \\ \text{and} \\ C_1(i) = y'(r_i) \end{cases} \quad (2.37)$$

The initial values  $y(r_i)$  and  $y'(r_i)$  are given by:

$$\begin{cases} y(r_i) = \sum_{n=0}^{\infty} C_n(i-1)(r_i - r_{i-1})^n \\ \text{and} \\ y'(r_i) = \sum_{n=0}^{\infty} nC_n(i-1)(r_i - r_{i-1})^{n-1} \end{cases} \quad (2.38)$$

where

$$\begin{cases} \text{for } \alpha: y(0) = 1, & y'(0) = 0 \\ \text{and} \\ \text{for } \beta: y(0) = 0, & y'(0) = 1 \end{cases} \quad (2.39)$$

Therefore, the canonical functions  $\alpha(r)$  and  $\beta(r)$  are well determined at any point  $r$ .

### 2.4.3 Calculation of $\Phi'_0(x)$

From Eq.(2.7), the wavefunction  $\Phi_0(x)$  is given by:

$$\Phi_0(r) = \alpha(r) + \Phi'_0(0)\beta(r) \quad (2.40)$$

By using the boundary conditions (Eq.(2.9)) we can write:

$$\frac{\Phi'_0(0)}{\Phi_0(0)} = \lim_{\substack{r \rightarrow \infty \\ r \rightarrow -r_e}} \frac{-\alpha(r)}{\beta(r)} = \lim_{\substack{r \rightarrow \infty \\ r \rightarrow -r_e}} \frac{\alpha'(r)}{\beta'(r)} \quad (2.41)$$

For unnormalized wavefunction  $\Phi_0(0)=1$ , therefore the vibration wavefunction  $\Phi_0(r)$  is determined for any point  $r$ .

## 2.5 Diatomic centrifugal distortion constants (CDC)

For a diatomic molecule in a given electronic state, and for a given vibration-rotation level, the vibration-rotation energy  $E_{v,J}$  is commonly represented by the empirical relation

$$E_{v,J} = E_v + \lambda B_v - \lambda^2 D_v + \lambda^3 H_v + \dots \quad (2.42)$$

where  $\lambda=J(J+1)$ ,  $E_v$  is the pure vibrational energy,  $B_v$  is the rotational constant,  $D_v$ ,  $H_v$  are the centrifugal distortion constants (CDC) related to the potential energy  $E_t(r)$ .

The first explicit analytical expression of the distortion constants have been derived since 1973 by Albritton *et al.* [9] using the Rayleigh-Schrödinger perturbation theory (RSPT) [10] in its conventional approach. The expressions

derived by Albritton are complicated and their computation is tedious, Hutson's algorithm [11] allows the determination of  $D_v$ ,  $H_v$ ,  $L_v$ , and  $M_v$  only. The improvements of Hutson's algorithm introduced by Tellinghuisen [12-16], were not sufficient to accede to high orders. Korek *et al.* [17, 18] showed that by one single and simple routine (similar to that integrating the radial Schrödinger equation) is sufficient to reach any level and any order, which we represent, bellow. The rotational Eqs.(2.22) are all of the form:

$$z'' + k(e_0 - E_t)z = S(r) \quad (2.43)$$

Multiplying Eq.(2.43) by  $\Phi_0$  and integrating between  $r_0$  and  $\infty$  and making use of Eq.(2.22), we obtain

$$\int_{r_0}^{\infty} (z''\Phi_0 - z\Phi_0'')dr = \int_{r_0}^{\infty} s(r)\Phi_0(r)dr \quad (2.44)$$

Then we make use of the boundary conditions for  $\Phi_0$  and  $z$  (at  $r \rightarrow \infty$ ) on one hand, and of Eq.(2.9) on the other hand, we find:

$$z'(r_0) = - \int_{r_0}^{\infty} s(r)\Phi_0(r)dr \quad (2.45)$$

And similarly for the other boundary condition (at  $r \rightarrow \infty$ )

$$z'(r_0) = - \int_{r_0}^{\infty} s(r)\Phi_0(r)dr \quad (2.46)$$

The continuity equation for  $s(r)$  implies the equality of  $z'(r_0)$  given by Eqs. (2.45) and (2.46), *i.e.*:





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# Results

## Theoretical calculation of the low-lying electronic states of the molecule BN

### 3.1 Introduction:

The accurate determination of the ground electronic state of BN molecule has been a very difficult task. The two lowest electronic states,  $^1\Sigma^+$  and  $^3\Pi$  are separated by only few tenths of electron volts and both theory and experiment works have had difficulty in discerning which the lowest electronic state is. Thus this small separation between singlet and triplet states should be a sensitive test of the performance of different computational methods. The detailed knowledge of molecular and spectroscopic properties can help to clarify the chemical process involved. In order to acquire the accurate molecular and spectroscopic properties of the BN molecule, a number of experimental and theoretical investigations have been made in the past several decades. The potential energy curves (PECs) for the  $X^3\Pi$ ,  $a^1\Sigma^+$ ,  $b^1\Pi$  and  $A^3\Sigma^+$  electronic states of the BN molecule have been performed, in early calculation, by Verhaegen *et al.* [1] and Melrose and Russell [2] using the linear combination atomic orbitals self-consistent field (LCAO-MO-SCF) approach and the variational calculations respectively. Melrose and Russell [3] re-calculated the term value and the equilibrium internuclear separation of the  $D^3\Pi$  electronic state of the molecule BN [2] while Moffat [4] performed an *ab initio* calculation for the  $a^1\Sigma^+$  electronic state of this molecule. In 1985 an *ab initio* study of large number of valence states of the BN molecule have been performed by karma and Grein (KG) [5], their computational work was instrumental in correcting the original measurements of the band distance for the lowest  $^3\Pi$ . They concluded that BN molecule has  $a^3\Pi$  ground state and they found that the energy difference between the  $^3\Pi$  and  $^1\Sigma^+$  states is of the order  $800\text{ cm}^{-1}$ , and in 1988 they

investigated the potential energy curves (PECs) of three quintuple electronic states [6]. Martin *et al.* [7] carried out a theoretical study of BN using large basis set and extensive electron correlation of the lowest lying  $^3\Pi$  and  $^1\Sigma^+$  state. These calculations support the ground state assignment as  $^3\Pi$  and found that  $^1\Sigma^+$  is the next excited state lies at  $381\text{ cm}^{-1}$  above the ground state.

In the literature most of the theoretical calculations focus on the studies of the spectroscopic properties of the  $X^3\Pi$  and  $a^1\Sigma^+$  electronic states [1, 2, 5, 7-23]. Only few results concerned the excited electronic states [1-3, 5, 9, 11, 21, 17, 20, 22]. An accurate determination of  $T_e$  for the electronic state  $a^1\Sigma^+$  of the molecule BN is a very difficult task not only by experimental methods, but also theoretically as well. The reasons are two-folds: one is that the  $X^3\Pi$  and  $a^1\Sigma^+$  electronic states nearly degenerate, the other is that the combination of moderate multireference character in the  $X^3\Pi$  and pathological multireference character in the  $a^1\Sigma^+$  electronic state makes the  $T_e$  excessively sensitive to the electron correlation treatment [18]. In 1995 Peterson [10] computed the lowest  $^1\Sigma^+$  and  $^3\Pi$  of  $C_2$ ,  $CN^+$ , BN and  $BO^+$  molecules, he supported that the ground state is the lowest  $^3\Pi$  state of BN and predict that energy  $^1\Sigma^+$  and  $^3\Pi$  separation of  $190\text{ cm}^{-1}$ . Baushlischer and partridge [11] based on an ICMRCI calculation found that this energy separation is  $180\text{ cm}^{-1}$  supporting that  $^3\Pi$  is the ground electronic state. At the MRCI level, Gan [17] recommended that the energy separation between  $^1\Sigma^+$  and  $^3\Pi$  states is between the values of Martin *et al.* [7] and those of Peterson [10], and supported that the ground state is lowest  $^3\Pi$ . Karton and Martin [18] used the CCSDTQ theory and the correlation-consistent basis sets to estimate the value of  $T_e$  of the  $a^1\Sigma^+$  electronic state equal  $183 \pm 40\text{ cm}^{-1}$ . In 2012 Shi *et al.* [24] calculated in detail the PECs of seventeen electronic states by the complete active space self consistent field (CASSCF) method followed by the MRCI approach including the core–

valence correlation and relativistic corrections, their spectroscopic results are in reasonable agreement with the experimental data in literature.

Dauglas and Herzberg [25] reported the analysis of a  $^3\Pi-^3\Pi$  transition with three weaker bands which were left unassigned. Mosher and Frosch [26] observed the  $^3\Pi-^3\Pi$  transition and they suggested that the ground state of the BN molecule is a  $^3\Pi$ . In 1984 Bredohl *et al.* [27] analyzed the singlet transitions  $^1\Sigma^+-a^1\Sigma^+$  and  $^1\Sigma^+-b^1\Pi$ , observed under high resolution, and made a new analysis of the triplet transition  $A^3\Pi-X^3\Pi$  [23] [30]. Lorenz *et al.* [29] reported a Fourier-transform absorption and laser induced fluorescence spectrum of BN in a neon matrix and they showed that the ground state is a  $^3\Pi$  with the  $^1\Sigma^+$  state at  $15-182\text{ cm}^{-1}$  above the ground state with the identification of several excited electronic states. Asmis *et al.* [30] experimentally identified the ground state and three lowest excited states of the BN molecule by anion photoelectron spectroscopy of BN. More detail spectroscopic investigations for the higher excited electronic states would be of great value for better understanding of the electronic structure of BN molecule. In the present work, the PECs for 42 electronic states of the BN molecule are calculated along with spectroscopic parameters and the dipole moments. The comparison of these results with those available in literature showed a very good agreement.

## 3.2 Method of Calculations

The study of the 42 low-lying electronic states of the molecule BN has been performed by using the state averaged complete active space self-consistent field (CASSCF) procedure [31, 32] followed by a Multireference Configuration Interaction MRDSCI with Davidson correction [33, 34] treatment for the electron

correlation. The entire CASSCF configuration space was used as the reference in the MRDSCI calculations, which were done via the computational chemistry Program MOLPRO [35] taking advantage of the graphical user interface GABEDIT [36]. This software is intended for high accuracy correlated ab initio calculations. MOLPRO has been run on a PC-computer with LINUX-type operating systems. The boron and nitrogen species are treated in all electron scheme using basis sets for s, p, d, f, and g functions for each atom. The calculation has been done by using for B and N atoms the 3 types of basis sets: the correlation-consistent polarized triple zeta cc-pVTZ, the correlation-consistent polarized quadruple-zeta cc-pVQZ, and the augmented correlation-consistent basis set aug-cc-pVQZ from the library of MOLPRO. For these 3 bases and from the 12 electrons for BN molecule 4 inner electrons are frozen in subsequent calculations so that the remaining 8 valance electrons are explicitly treated. The corresponding active space is  $5\sigma(B:2s,2p_0;N:2s,3s,2p_0)$  and  $2\pi(B:2p_{\pm 1};N:2p_{\pm 1})$  orbitals in the  $C_{2v}$  symmetry where the active molecular orbitals are distributed into the irreducible representation  $a_1, b_1, b_2$  and  $a_2$  in the following way  $5a_1, 2b_1, 2b_2$  noted [5, 2, 2, 0].

### 3.3 Results and discussion

The calculation of the potential energy curves (PECs) for 14 singlet, 15 triplet and 13 quintet electronic states, in the representation  $^{2s+1}\Lambda^{(\pm)}$  of the molecule BN, has been performed for 63 internuclear distances in the range  $1.0\text{\AA} \leq R \leq 3.22\text{\AA}$  and the energy separation between the lowest and the highest obtained electronic quintet state is  $90501.45\text{ cm}^{-1}$ . These curves are given in Figs. (3.1-3.4) using the basis cc-pVTZ.

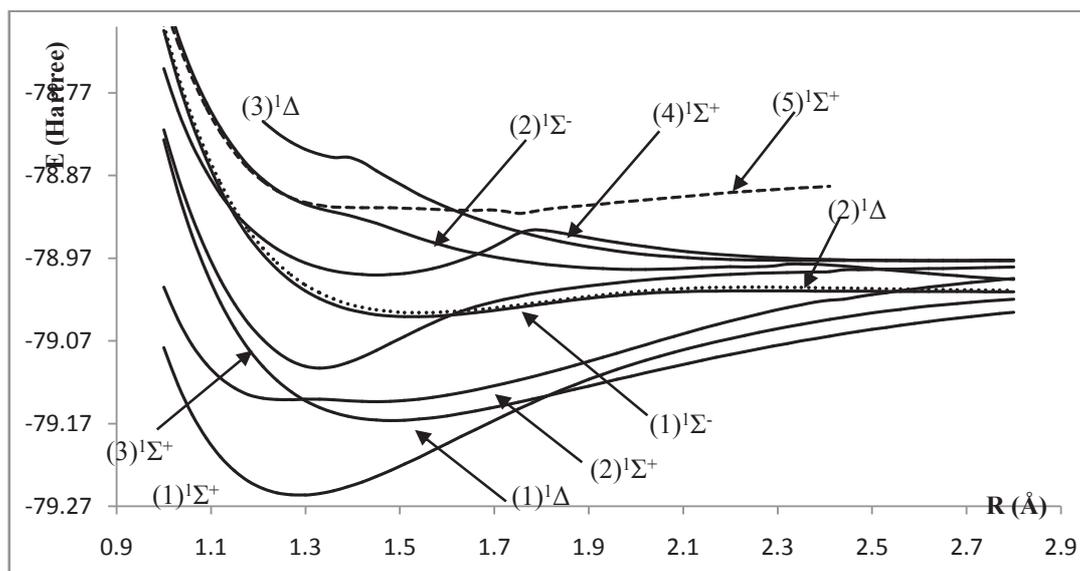


Fig. 3.1: Potential energy curves of the states  $^1\Sigma^+$  and  $^1\Delta$  using the basis cc-pVTZ of the molecule BN.

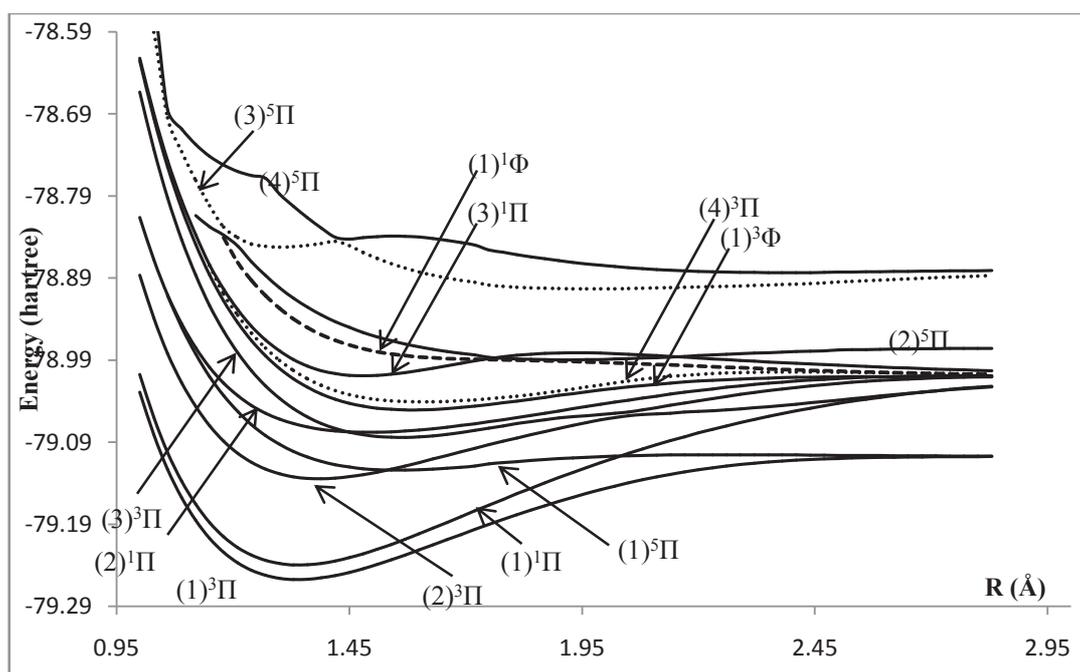


Fig.3.2: Potential energy curves of the states  $^{1,3,5}\Pi$ , and  $^{1,3}\Phi$  using the basis cc-pVTZ of the molecule BN.

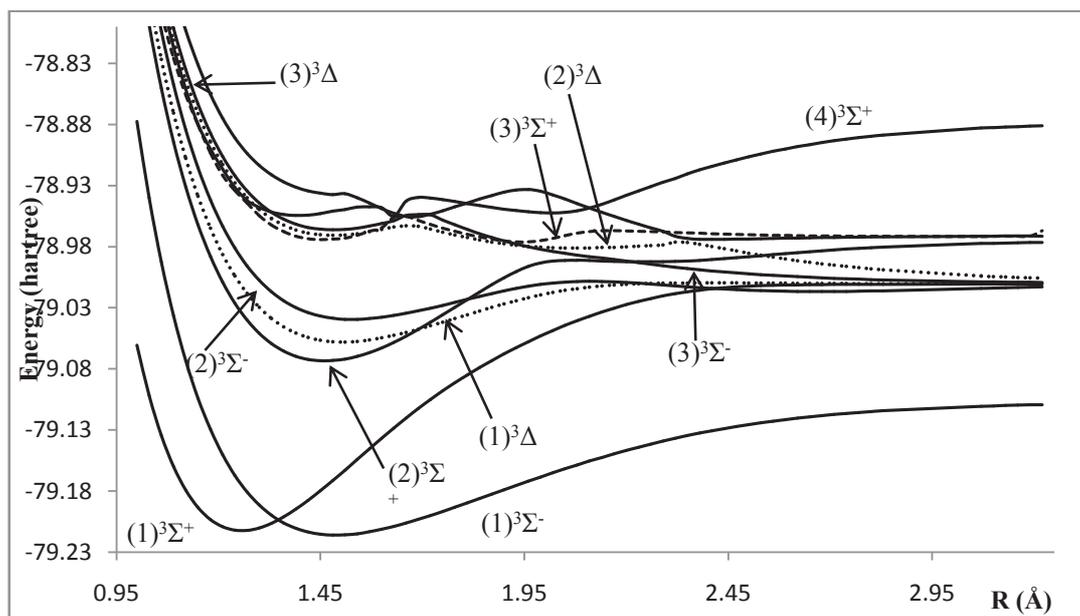


Fig. 3.3: Potential energy curves of the states  ${}^3\Sigma^+$  and  ${}^3\Delta$  using the basis cc-pVTZ of the molecule BN.

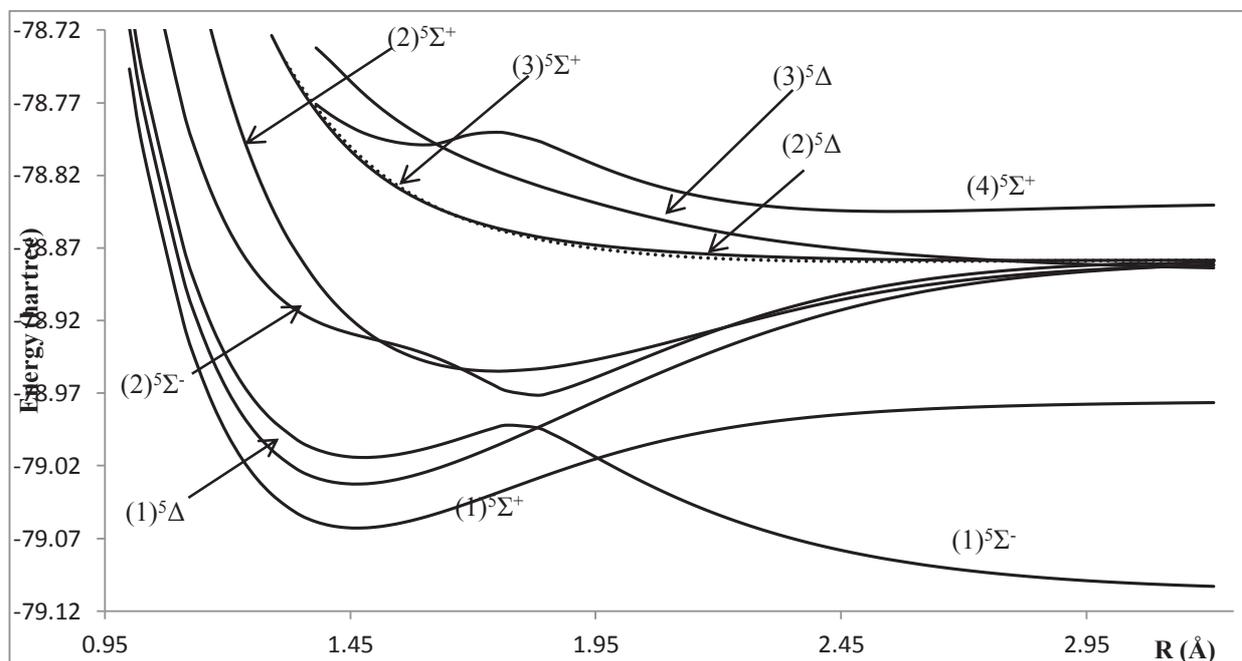


Fig. 3.4: Potential energy curves of the states  ${}^5\Sigma^+$  states and  ${}^5\Delta$ , using the basis cc-pVTZ of the molecule BN.

Table 3.1:  $R_c$  and  $R_{av}$  are respectively the positions of crossings and avoided crossings and  $\Delta E_{AC}$  is the energy difference at the positions of avoided crossings.

State(1)	State(2)	Crossing		Avoided crossing	
		$n_1$ state(1)/ $n_2$ state(2)	$R_c(\text{\AA})$	$R_{av}(\text{\AA})$	$\Delta E_{AC}(\text{cm}^{-1})$
$X^1\Sigma^+$	$^1\Delta$	1/1	1.84		
$^1\Sigma^+$	$^1\Delta$	2/1	1.3		
		3/2	1.63		
		2/2	2.59		
		4/2	1.18		
		4/3	1.75		
		4/3	2.35		
		5/3	1.63		
$^3\Pi$	$^5\Pi$	1/1	2.59		
		2/1	1.54		
$^3\Pi$	$^1\Pi$	2/1	2.65		
		3/2	1.45		
		4/3	1.15		
$^1\Pi$	$^5\Pi$	1/1	2.05		
		2/1	1.09		
		3/2	1.78		
		3/2	2.14		
$^1\Pi$	$^1\Phi$	3/1	1.75		
$^3\Sigma^+$	$^3\Delta$	2/1	1.72		
		2/2	2.53		
		3/2	1.57		
		4/2	1.3		
		4/3	1.6		
		4/3	1.66		
		4/3	1.81		
		4/3	2.11		
		3/3	2.29		
$^3\Sigma^-$	$^3\Sigma^-$	1/1	1.36		
		1/2	2.41		
		2/2	1.81		
		2/3	2.20		
		4/3	1.33		
$^3\Sigma^-$	$^3\Delta$	2/1	2.26		
		3/2	1.96		
		3/3	1.66		
		3/3	1.72		
$^5\Sigma^+$	$^5\Sigma^-$	1/1	1.95		
		2/2	1.53		
		2/2	1.68		
		2/2	2.25		
$^5\Sigma^{\square}$	$^5\Delta$	3/2	2.79		
		2/2	3.09		
		3/2	1.65		
		4/3	1.62		
$^5\Sigma^-$	$^5\Delta$	1/1	1.83		
		2/2	3.00		
$^3\Pi$	$^3\Pi$	2/3		2.05	1056.656
$^3\Pi$	$^5\Pi$	3/4		1.47	1099.54
$^3\Sigma^+$	$^3\Sigma^+$	3/4		1.63	200.81
$^3\Delta$	$^3\Delta$	2/3		1.66	1711.12
$^3\Delta$	$^3\Delta$	2/3		2.35	726.68
$^5\Delta$	$^5\Delta$	2/3		2.76	12.51

Such crossings or avoided crossings can dramatically alter the stability of molecules. By fitting the calculated energy values of the different investigated electronic states, calculated by using the 3 different basis, into a polynomial in  $R$  around the internuclear distance at equilibrium  $R_e$ , the harmonic vibrational frequencies  $\omega_e$ , the relative energy separations  $T_e$ , and the rotational constants  $B_e$ , have been calculated. These values with the available data in literature are given in Table 3.2.

Table 3.2: Spectroscopic constants of the different electronic states of the molecule BN.

$^{2S+1}\Lambda$ states	$T_e$ ( $\text{cm}^{-1}$ )	$\Delta T_e/T_e$ %	$R_e$ ( $\text{\AA}$ )	$\Delta R_e/R_e$ %	$B_e$ ( $\text{cm}^{-1}$ )	$\Delta B_e/B_e$ %	$\omega_e$ ( $\text{cm}^{-1}$ )	$\Delta\omega_e/\omega_e$ %			
$\chi^2\Pi$	$0^{(a1)}$	0.0	1.340 <sup>(a1)</sup>		1.53 <sup>(a1)</sup>	8.16	1482.82 <sup>(a1)</sup>				
	$0^{(a2)}$		1.334 <sup>(a2)</sup>		1.55 <sup>(a2)</sup>		1490.60 <sup>(a2)</sup>				
	$0^{(a3)}$		1.334 <sup>(a3)</sup>		1.55 <sup>(a3)</sup>		1494.65 <sup>(a3)</sup>				
	$0^{(b)}$		1.281 <sup>(b)</sup>		4.6		1.666 <sup>(b)</sup>		1514.6 <sup>(b)</sup>	2.09	
	$0^{(c)}$		1.329 <sup>(c)</sup>		0.8						
	$0^{(d)}$		1.329 <sup>(d)</sup>		0.8					1519.2 <sup>(d)</sup>	2.45
	$0^{(e)}$		1.305 <sup>(e)</sup>		2.6					1750 <sup>(e)</sup>	15.26
	$0^{(f)}$		1.327 <sup>(f)</sup>		0.9		1.552 <sup>(f)</sup>		1.41	1518.1 <sup>(f)</sup>	2.37
	$0^{(g)}$		1.325 <sup>(g)</sup>		1.1		1.557 <sup>(g)</sup>		1.73	1529.5 <sup>(g)</sup>	3.05
	$0^{(h)}$		1.330 <sup>(h)</sup>		0.7					1491 <sup>(h)</sup>	0.54
	$0^{(i)}$		1.333 <sup>(i)</sup>		0.5		1.537 <sup>(i)</sup>		0.45	1488 <sup>(i)</sup>	0.34
	$0^{(j1)}$		1.33 <sup>(j1)</sup>		0.7		1.547 <sup>(j1)</sup>		1.09	1508.2 <sup>(j1)</sup>	1.71
	$0^{(j2)}$		1.325 <sup>(j2)</sup>		1.1					1526 <sup>(j2)</sup>	2.83
	$0^{(k)}$		1.33 <sup>(k)</sup>		0.7						
	$0^{(l)}$		1.331 <sup>(l)</sup>		0.6					1529 <sup>(l)</sup>	3.02
	$0^{(m1)}$		1.33 <sup>(m1)</sup>		0.7		1.546 <sup>(m1)</sup>		1.03	1508.6 <sup>(m1)</sup>	1.70
	$0^{(m2)}$		1.33 <sup>(m2)</sup>		0.7					1508.7 <sup>(m2)</sup>	1.71
	$0^{(n)}$		1.329 <sup>(n)</sup>		0.8					1518 <sup>(n)</sup>	2.31
	$0^{(o)}$		1.329 <sup>(o)</sup>		0.8					1531.6 <sup>(o)</sup>	3.18
	$0^{(p)}$		1.329 <sup>(p)</sup>		0.8					1510 <sup>(p)</sup>	1.80
	$0^{(q)}$		1.327 <sup>(q)</sup>		0.9						
	$0^{(r)}$		1.329 <sup>(r)</sup>		0.8					1557 <sup>(r)</sup>	4.76
	$0^{(s1)}$		1.325 <sup>(s1)</sup>		1.1		1.557 <sup>(s1)</sup>		1.73	1520 <sup>(s1)</sup>	2.44
	$0^{(s2)}$		1.326 <sup>(s2)</sup>		1.05		1.554 <sup>(s2)</sup>		1.54	1515.49 <sup>(s2)</sup>	2.15
$(1)^1\Sigma^+$	129.74 <sup>(a1)</sup>		1.286 <sup>(a1)</sup>		1.669 <sup>(a1)</sup>		1688.72 <sup>(a1)</sup>				
	220.94 <sup>(a2)</sup>		1.281 <sup>(a2)</sup>		1.682 <sup>(a2)</sup>		1687.72 <sup>(a2)</sup>				
	290.17 <sup>(a3)</sup>		1.281 <sup>(a3)</sup>		1.682 <sup>(a3)</sup>		1680.34 <sup>(a3)</sup>				
	15<a<182 <sup>(d)</sup>						1700.9 <sup>(d)</sup>	0.71			
	98.6 <sup>(e)9</sup>		1.279 <sup>(e)</sup>	0.54	1.670 <sup>(e)</sup>	0.06	1737.6 <sup>(e)</sup>	2.81			
	381±100 <sup>(h)</sup>		1.284 <sup>(h)</sup>	0.15	1.610 <sup>(h)</sup>	3.66	1686 <sup>(h)</sup>	0.16			
	241.97 <sup>(i)</sup>		1.283 <sup>(i)</sup>	0.23	1.671 <sup>(i)</sup>	0.12	1660 <sup>(i)</sup>	1.73			
	310.7 <sup>(j1)</sup>		1.287 <sup>(j1)</sup>	0.07	1.674 <sup>(j1)</sup>	0.29	1697.5 <sup>(j1)</sup>	0.51			
	190±100 <sup>(j2)</sup>		1.285 <sup>(j2)</sup>	0.07			1705 <sup>(j2)</sup>	0.95			
	178 <sup>(l)</sup>		1.275 <sup>(l)</sup>	0.86			1709 <sup>(l)</sup>	1.18			
	269 <sup>(n)</sup>		1.277 <sup>(n)</sup>	0.70			1700 <sup>(n)</sup>	0.70			
	242 <sup>(o)</sup>		1.28 <sup>(o)</sup>	0.46			1725.1 <sup>(o)</sup>	2.10			
	164 <sup>(p)</sup>		1.274 <sup>(p)</sup>	0.94			1722 <sup>(p)</sup>	1.93			
			1.276 <sup>(q)</sup>	0.78							
	111.49 <sup>(s1)</sup>		1.273 <sup>(s1)</sup>	0.01	1.698 <sup>(s1)</sup>	1.7	1706.97 <sup>(s1)</sup>	1.06			
	134.32 <sup>(s2)</sup>		1.274 <sup>(s2)</sup>	0.94	1.693 <sup>(s2)</sup>	1.41	1703.22 <sup>(s2)</sup>	0.85			
	158±36 <sup>(u)</sup>		1.274 <sup>(u)</sup>	0.94							
	180±110 <sup>(v)</sup>		1.286 <sup>(v)</sup>	0.00			1694 <sup>(v)</sup>	0.31			
183±40 <sup>(x)</sup>		1.274 <sup>(w)</sup>	0.94								
$(1)^1\Pi$	3885.58 <sup>(a1)</sup>		1.341 <sup>(a1)</sup>		1.535 <sup>(a1)</sup>		1504.65 <sup>(a1)</sup>				



Chapter three: Theoretical calculation of the low-lying electronic states of the molecule BN

	38984.40 <sup>(s1)</sup>	2.53	1.544 <sup>(s1)</sup>	0.96	1.145 <sup>(s1)</sup>	0.87	1050.08 <sup>(s1)</sup>	1.15
	38862.37 <sup>(s2)</sup>	2.23	1.545 <sup>(s2)</sup>	0.90	1.143 <sup>(s2)</sup>	0.70	1048.15 <sup>(s2)</sup>	0.97
	38135 <sup>(v)</sup>	0.36	1.556 <sup>(v)</sup>	0.19	1.556 <sup>(v)</sup>	27.05		
(2) <sup>1</sup> π	39390.93 <sup>(a1)</sup>		1.492 <sup>(a1)</sup>		1.240 <sup>(a1)</sup>		825.94 <sup>(a1)</sup>	
	39633.45 <sup>(a2)</sup>		1.486 <sup>(a2)</sup>		1.250 <sup>(a2)</sup>		826.80 <sup>(a2)</sup>	
	39277.35 <sup>(a3)</sup>		1.487 <sup>(a3)</sup>		1.249 <sup>(a3)</sup>		814.66 <sup>(a3)</sup>	
	40892.29 <sup>(f)</sup>	3.67	1.468 <sup>(f)</sup>	1.63	1.269 <sup>(f)</sup>	2.28	970.3 <sup>(f)</sup>	14.87
	40244.19 <sup>(s1)</sup>	2.12	1.463 <sup>(s1)</sup>	1.98	1.276 <sup>(s1)</sup>	2.82	852.46 <sup>(s1)</sup>	3.11
	39637 <sup>(s2)</sup>	0.62	1.466 <sup>(s2)</sup>	1.77	1.270 <sup>(s2)</sup>	2.41	848.23 <sup>(s2)</sup>	2.62
	38135 <sup>(v)</sup>	3.29	1.491 <sup>(v)</sup>	0.06				
(2) <sup>3</sup> Σ <sup>+</sup>	40335.16 <sup>(a1)</sup>		1.460 <sup>(a1)</sup>		1.294 <sup>(a1)</sup>		1265.05 <sup>(a1)</sup>	
	40626.32 <sup>(a2)</sup>		1.459 <sup>(a2)</sup>		1.298 <sup>(a2)</sup>		1247.42 <sup>(a2)</sup>	
	40603.02 <sup>(a3)</sup>		1.457 <sup>(a3)</sup>		1.300 <sup>(a3)</sup>		1235.66 <sup>(a3)</sup>	
	41940.81 <sup>(f)</sup>	3.82	1.467 <sup>(f)</sup>	0.47	1.270 <sup>(f)</sup>	1.88	1195.8 <sup>(f)</sup>	5.79
	41466.88 <sup>(s1)</sup>	2.72	1.447 <sup>(s1)</sup>	0.89	1.304 <sup>(s1)</sup>	0.76	1272.12 <sup>(s1)</sup>	0.55
	41361.09 <sup>(s2)</sup>	2.48	1.448 <sup>(s2)</sup>	0.82	1.303 <sup>(s2)</sup>	0.69	1271.32 <sup>(s2)</sup>	0.49
	41108 <sup>(v)</sup>	1.88	1.458 <sup>(v)</sup>	0.13				
(1) <sup>5</sup> Σ <sup>+</sup>	42666.42 <sup>(a1)</sup>		1.463 <sup>(a1)</sup>		1.291 <sup>(a1)</sup>		1143.54 <sup>(a1)</sup>	
	43454.84 <sup>(a2)</sup>		1.489 <sup>(a2)</sup>		1.243 <sup>(a2)</sup>		977.46 <sup>(a2)</sup>	
	43519.72 <sup>(a3)</sup>		1.464 <sup>(a3)</sup>		1.288 <sup>(a3)</sup>		1100.98 <sup>(a3)</sup>	
	44769.31 <sup>(s1)</sup>	4.69	1.444 <sup>(s1)</sup>	1.31	1.311 <sup>(s1)</sup>	1.52	1160.47 <sup>(s1)</sup>	1.45
	44586.93 <sup>(s2)</sup>	4.30	1.445 <sup>(s2)</sup>	1.24	1.308 <sup>(s2)</sup>	1.29	1156.76 <sup>(s2)</sup>	1.14
	42666.71 <sup>(ab)</sup>	0.00	1.477 <sup>(ab)</sup>	0.94	1.255 <sup>(ab)</sup>	2.86	1386.2 <sup>(ab)</sup>	17.5
(1) <sup>3</sup> Δ	43721.33 <sup>(a1)</sup>		1.503 <sup>(a1)</sup>		1.222 <sup>(a1)</sup>		1037.42 <sup>(a1)</sup>	
	43869.96 <sup>(a2)</sup>		1.498 <sup>(a2)</sup>		1.229 <sup>(a2)</sup>		1037.24 <sup>(a2)</sup>	
	43714.60 <sup>(a3)</sup>		1.499 <sup>(a3)</sup>		1.228 <sup>(a3)</sup>		1020.35 <sup>(a3)</sup>	
	45489.65 <sup>(f)</sup>	3.88	1.511 <sup>(f)</sup>	0.52	1.198 <sup>(f)</sup>	2.00	1138.8 <sup>(f)</sup>	8.90
	44406.52 <sup>(s1)</sup>	1.54	1.485 <sup>(s1)</sup>	1.21	1.239 <sup>(s1)</sup>	1.37	1068.17 <sup>(s1)</sup>	2.87
	44301.61 <sup>(s2)</sup>	1.30	1.486 <sup>(s2)</sup>	1.14	1.237 <sup>(s2)</sup>	1.21	1064.78 <sup>(s2)</sup>	2.56
	44197 <sup>(v)</sup>	1.07	1.499 <sup>(v)</sup>	0.26				
(1) <sup>3</sup> Φ	45337.0 <sup>(a1)</sup>		1.585 <sup>(a1)</sup>		1.099 <sup>(a1)</sup>		909.99 <sup>(a1)</sup>	
	45151.93 <sup>(a2)</sup>		1.580 <sup>(a2)</sup>		1.106 <sup>(a2)</sup>		917.41 <sup>(a2)</sup>	
	45046.41 <sup>(a3)</sup>		1.580 <sup>(a3)</sup>		1.105 <sup>(a3)</sup>		915.03 <sup>(a3)</sup>	
(1) <sup>1</sup> Σ <sup>-</sup>	47486.62 <sup>(a1)</sup>		1.524 <sup>(a1)</sup>		1.188 <sup>(a1)</sup>		953.24 <sup>(a1)</sup>	
	47298.94 <sup>(a2)</sup>		1.520 <sup>(a2)</sup>		1.195 <sup>(a2)</sup>		952.17 <sup>(a2)</sup>	
	46989.35 <sup>(a3)</sup>		1.523 <sup>(a3)</sup>		1.189 <sup>(a3)</sup>		947.35 <sup>(a3)</sup>	
(4) <sup>3</sup> π	47509.41 <sup>(a1)</sup>		1.604 <sup>(a1)</sup>		1.073 <sup>(a1)</sup>		783.68 <sup>(a1)</sup>	
	48205.37 <sup>(a2)</sup>		1.505 <sup>(a2)</sup>		1.219 <sup>(a2)</sup>		782.31 <sup>(a2)</sup>	
	48094.12 <sup>(a3)</sup>		1.593 <sup>(a3)</sup>		1.088 <sup>(a3)</sup>		787.31 <sup>(a3)</sup>	
	47022.10 <sup>(f)</sup>	1.03	1.517 <sup>(f)</sup>	5.73	1.188 <sup>(f)</sup>	9.68	1428.3 <sup>(f)</sup>	45.13
	45497.75 <sup>(s1)</sup>	4.42	1.566 <sup>(s1)</sup>	2.42	1.113 <sup>(s1)</sup>	3.59	934.80 <sup>(s1)</sup>	16.16
	45051 <sup>(s2)</sup>	5.45	1.568 <sup>(s2)</sup>	2.29	1.111 <sup>(s2)</sup>	3.42	931.29 <sup>(s2)</sup>	15.85
	38135 <sup>(v)</sup>	24.58	1.582 <sup>(v)</sup>	1.39				
(2) <sup>3</sup> Σ <sup>-</sup>	47782.97 <sup>(a1)</sup>		1.526 <sup>(a1)</sup>		1.185 <sup>(a1)</sup>		959.98 <sup>(a1)</sup>	
	47774.64 <sup>(a2)</sup>		1.522 <sup>(a2)</sup>		1.191 <sup>(a2)</sup>		960.55 <sup>(a2)</sup>	
	47526.55 <sup>(a3)</sup>		1.522 <sup>(a3)</sup>		1.191 <sup>(a3)</sup>		951.88 <sup>(a3)</sup>	
	50974.22 <sup>(f)</sup>	6.26	1.533 <sup>(f)</sup>	0.45	1.164 <sup>(f)</sup>	1.8	1006.9 <sup>(f)</sup>	4.65
	48596.73 <sup>(s1)</sup>	1.67	1.505 <sup>(s1)</sup>	1.39	1.207 <sup>(s1)</sup>	1.82	985.403 <sup>(s1)</sup>	2.57
	48493.80 <sup>(s2)</sup>	1.46	1.506 <sup>(s2)</sup>	1.32	1.204 <sup>(s2)</sup>	1.57	981.88 <sup>(s2)</sup>	2.23
	48272 <sup>(v)</sup>	1.01	1.520 <sup>(v)</sup>	0.39				
(2) <sup>1</sup> Δ	48781.54 <sup>(a1)</sup>		1.542 <sup>(a1)</sup>		1.162 <sup>(a1)</sup>		894.28 <sup>(a1)</sup>	
	48537.65 <sup>(a2)</sup>		1.538 <sup>(a2)</sup>		1.167 <sup>(a2)</sup>		894.58 <sup>(a2)</sup>	
	48184.48 <sup>(a3)</sup>		1.539 <sup>(a3)</sup>		1.165 <sup>(a3)</sup>		898.20 <sup>(a3)</sup>	
(1) <sup>5</sup> Δ	49277.56 <sup>(a1)</sup>		1.461 <sup>(a1)</sup>		1.293 <sup>(a1)</sup>		1170.27 <sup>(a1)</sup>	
	49634.20 <sup>(a2)</sup>		1.492 <sup>(a2)</sup>		1.239 <sup>(a2)</sup>		996.16 <sup>(a2)</sup>	
	49566.86 <sup>(a3)</sup>		1.468 <sup>(a3)</sup>		1.281 <sup>(a3)</sup>		1097.57 <sup>(a3)</sup>	
(3) <sup>1</sup> π	54491.08 <sup>(a1)</sup>		1.481 <sup>(a1)</sup>		1.259 <sup>(a1)</sup>		1222.432 <sup>(a1)</sup>	
	54248.10 <sup>(a2)</sup>		1.477 <sup>(a2)</sup>		1.265 <sup>(a2)</sup>		1235.026 <sup>(a2)</sup>	
	53890.11 <sup>(a3)</sup>		1.473 <sup>(a3)</sup>		1.272 <sup>(a3)</sup>		1251.93 <sup>(a3)</sup>	
(5) <sup>1</sup> Σ <sup>+</sup>	(F)58590.36 <sup>(a1)</sup>		1.451 <sup>(a1)</sup>		1.311 <sup>(a1)</sup>		1161.97 <sup>(a1)</sup>	
	(S)62425.61 <sup>(a1)</sup>		2.548 <sup>(a1)</sup>		0.413 <sup>(a1)</sup>		185.20 <sup>(a1)</sup>	
	(F)58802.35 <sup>(a2)</sup>		1.441 <sup>(a2)</sup>		1.329 <sup>(a2)</sup>		1176.59 <sup>(a2)</sup>	
	(F)58651.12 <sup>(a3)</sup>		1.446 <sup>(a3)</sup>		1.319 <sup>(a3)</sup>		1148.88 <sup>(a3)</sup>	
(2) <sup>5</sup> π	58748.56 <sup>(a1)</sup>		1.995 <sup>(a1)</sup>		0.693 <sup>(a1)</sup>		479.34 <sup>(a1)</sup>	
	59958.24 <sup>(a2)</sup>		2.007 <sup>(a2)</sup>		0.685 <sup>(a2)</sup>		492.25 <sup>(a2)</sup>	
	59920.43 <sup>(a3)</sup>		2.008 <sup>(a3)</sup>		0.684 <sup>(a3)</sup>		495.18 <sup>(a3)</sup>	
(2) <sup>1</sup> Σ <sup>-</sup>	60063.95 <sup>(a1)</sup>		2.009 <sup>(a1)</sup>		0.682 <sup>(a1)</sup>		579.37 <sup>(a1)</sup>	
(5) <sup>3</sup> Σ <sup>+</sup>	(F)62005.23 <sup>(a1)</sup>		1.459 <sup>(a1)</sup>		1.297 <sup>(a1)</sup>		1298.94 <sup>(a1)</sup>	
	(S)61680.23 <sup>(a1)</sup>		1.942 <sup>(a1)</sup>		0.732 <sup>(a1)</sup>		1128.00 <sup>(a1)</sup>	
	(F)61934.53 <sup>(a2)</sup>		1.438 <sup>(a2)</sup>		1.336 <sup>(a2)</sup>		1093.34 <sup>(a2)</sup>	
	(F)62226.18 <sup>(a3)</sup>		1.467 <sup>(a3)</sup>		1.272 <sup>(a3)</sup>		1268.74 <sup>(a3)</sup>	
(3) <sup>1</sup> Δ	62509.25 <sup>(a1)</sup>		2.735 <sup>(a1)</sup>		0.368 <sup>(a1)</sup>			
(2) <sup>3</sup> Δ	(F)62864.17 <sup>(a1)</sup>		1.481 <sup>(a1)</sup>		1.257 <sup>(a1)</sup>		1080.96 <sup>(a1)</sup>	

	(S)60586.28 <sup>(a1)</sup> (F)62598.60 <sup>(a2)</sup> (F)62333.67 <sup>(a3)</sup>		2.070 <sup>(a1)</sup> 1.477 <sup>(a2)</sup> 1.479 <sup>(a3)</sup>		0.646 <sup>(a1)</sup> 1.264 <sup>(a2)</sup> 1.261 <sup>(a3)</sup>		0.438 <sup>(a1)</sup> 1061.83 <sup>(a2)</sup> 1055.08 <sup>(a3)</sup>	
(3) <sup>3</sup> $\Sigma^-$	63877.55 <sup>(a1)</sup> 63620.19 <sup>(a2)</sup>		1.479 <sup>(a1)</sup> 1.471 <sup>(a2)</sup>		1.263 <sup>(a1)</sup> 1.281 <sup>(a2)</sup>		1032.18 <sup>(a1)</sup> 1035.19 <sup>(a2)</sup>	
(4) <sup>5</sup> $\Sigma^+$	66384.50 <sup>(a1)</sup> 67209.38 <sup>(a2)</sup> 67211.01 <sup>(a3)</sup>		1.750 <sup>(a1)</sup> 1.761 <sup>(a2)</sup> 1.759 <sup>(a3)</sup>		0.901 <sup>(a1)</sup> 0.889 <sup>(a2)</sup> 0.891 <sup>(a3)</sup>		783.28 <sup>(a1)</sup> 818.33 <sup>(a2)</sup> 721.55 <sup>(a3)</sup>	
(7) <sup>3</sup> $\Sigma^+$	(F)66440.45 <sup>(a1)</sup> (S)66904.66 <sup>(a1)</sup> (F)66713.82 <sup>(a2)</sup> (F)66415.20 <sup>(a3)</sup>		1.392 <sup>(a1)</sup> 2.010 <sup>(a1)</sup> 1.373 <sup>(a2)</sup> 1.386 <sup>(a3)</sup>		1.423 <sup>(a1)</sup> 0.684 <sup>(a1)</sup> 1.465 <sup>(a2)</sup> 1.436 <sup>(a3)</sup>		1228.48 <sup>(a1)</sup> 937.41 <sup>(a1)</sup> 1217.13 <sup>(a2)</sup> 1170.90 <sup>(a3)</sup>	
(3) <sup>5</sup> $\Pi$	77741.38 <sup>(a1)</sup> 78746.32 <sup>(a2)</sup> 78776.76 <sup>(a3)</sup>		2.046 <sup>(a1)</sup> 2.062 <sup>(a2)</sup> 2.066 <sup>(a3)</sup>		0.661 <sup>(a1)</sup> 0.649 <sup>(a2)</sup> 0.646 <sup>(a3)</sup>		397.46 <sup>(a1)</sup> 349.72 <sup>(a2)</sup> 332.38 <sup>(a3)</sup>	
(4) <sup>5</sup> $\Pi$	82073.35 <sup>(a1)</sup> 82617.75 <sup>(a2)</sup>		2.459 <sup>(a1)</sup> 2.492 <sup>(a2)</sup>		0.456 <sup>(a1)</sup> 0.443 <sup>(a2)</sup>		279.84 <sup>(a1)</sup> 228.72 <sup>(a2)</sup>	
(5) <sup>5</sup> $\Sigma^+$	82970.68 <sup>(a1)</sup>		2.539 <sup>(a1)</sup>		0.432 <sup>(a1)</sup>		151.42 <sup>(a1)</sup>	
(6) <sup>5</sup> $\Sigma^+$	90501.45 <sup>(a1)</sup> 90947.56 <sup>(a2)</sup>		2.559 <sup>(a1)</sup> 2.620 <sup>(a2)</sup>		0.422 <sup>(a1)</sup> 0.402 <sup>(a2)</sup>		292.37 <sup>(a1)</sup> 278.70 <sup>(a2)</sup>	

a1) the first entry is for the present work where we use the cc-pVTZ basis set for the two atoms, a2) the second entry is for the present work where we use the cc-pVQZ basis set for the two atoms, a3) the third entry is for the present work where we use the aug-cc-pVQZ basis set for the two atoms, b) Ref<sup>exp</sup> [25], c) Ref<sup>theo</sup> [28], d) Ref<sup>exp</sup> [29], e) Ref<sup>theo</sup> [1], f) Ref<sup>theo</sup> [5], g) Ref<sup>theo</sup> [7], h) Ref<sup>theo</sup> [8], i) Ref<sup>theo</sup> [9], j1.j2) Theory, Ref<sup>theo</sup> [10], k) Theory, Ref<sup>theo</sup> [14], l) Ref<sup>theo</sup> [15], m1.m2) Ref<sup>theo</sup> [16], n) Ref<sup>theo</sup> [19], o) Ref<sup>theo</sup> [20], p) Ref<sup>theo</sup> [21], q) Ref<sup>theo</sup> [22], r) Ref<sup>theo</sup> [23], s1.s2) Ref<sup>theo</sup> [24], u) Ref<sup>exp</sup> [30], v) Ref<sup>theo</sup> [11], w) Ref<sup>theo</sup> [17], x) Ref<sup>theo</sup> [18], y) Ref<sup>theo</sup> [2], z) Ref<sup>theo</sup> [12], ab) Ref<sup>theo</sup> [6], (F) is in our work represent the first minimum and (S) represent the second minimum

One can notice the absence of our calculated data for the unbound states and for electronic states having crossing or avoided crossing at their equilibrium internuclear distance positions  $R_e$ .

An accurate determination of the value of  $T_e$  for the first excited electronic state  $a^1\Sigma^+$  of the molecule BN is a very difficult task not only by experimental techniques, but also theoretically as well. One can find that the values of  $T_e$  published in literature vary between  $15 \text{ cm}^{-1}$  [29] and  $481 \text{ cm}^{-1}$  [8]. Our calculated values of  $T_e$  by the 3 different basis sets are within this range. The reasons for this disagreement can be explained by: i) the  $X^3\Pi$  and  $a^1\Sigma^+$  electronic states are nearly degenerate ii) the combination of moderate multireference character in the  $X^3\Pi$  and pathological multireference character in the  $a^1\Sigma^+$  electronic state makes the  $T_e$

excessively sensitive to the electron correlation treatment [18]. The comparison of our calculated values of this constant  $T_e$ , using the basis cc-pVTZ, with those given in literature for 14 electronic states shows a very good agreement with relative difference  $0.00\% (\text{Ref.}[6]) \leq \Delta T_e/T_e \leq 11.8\% (\text{Ref.}[6])$  except the 2 values given in Refs.[5, 11] for the 2 states  $(1)^3\Sigma^+$  and  $(4)^3\Pi$  where the relative differences are respectively 14.9% and 24.6%.

By comparing our calculated values of  $R_e$  and  $B_e$  with those published for 16 electronic states in literature we can find respectively an excellent agreement with the relative differences  $0.0\%((1)^3\Sigma^-, \text{Ref.}[11]) \leq \Delta R_e/R_e \leq 5.73\%((4)^3\Pi, \text{Ref.}[11])$  and  $0.06\%((1)^1\Sigma^+, \text{Ref.}[7]) \leq \Delta B_e/B_e \leq 9.68\%((4)^3\Pi, \text{Ref.}[5])$  except the value of  $T_e$  given in Ref.[1] for the state  $(3)^3\Pi$  where the relative difference is 27.05%. Similar results can be obtained by comparing the present results of  $\omega_e$  with those given in literature for 15 electronic states where  $0.31\%((1)^1\Sigma^+, \text{Ref.}[11]) \leq \Delta\omega_e/\omega_e \leq 10.2\%((1)^1\Sigma^+, \text{Ref.}[24])$ . A less agreement is obtained for some calculated values by different techniques of  $\omega_e$  given in Refs.[1, 5, 7] for the states  $X^3\Pi$ ,  $(1)^3\Sigma^+$ ,  $(1)^5\Pi$ , and  $(2)^1\Pi$  where the relative difference is  $12.11\%(\text{Ref.}[7]) \leq \Delta\omega_e/\omega_e \leq 16.6\%(\text{Ref.}[24])$ . The agreement deteriorate by comparing our calculated value of  $\omega_e$  to those calculated in Ref. [5] for the states  $(2)^3\Pi$  and  $(4)^3\Pi$  where the relative differences are respectively 26.3% and 45.13%. The overall good agreement between our investigated values and those given in literature may confirm the accuracy and the validity of the results for the new studied states obtained in the present work.

### 3.4 Dipole Moment

The static dipole moment is a fundamental electrostatic property of a neutral molecule, its importance lying in the description of numerous physical phenomena. The expectation value of this operator is sensitive to the nature of the least energetic and most chemically relevant valence electrons. By taking the boron atom at the origin, the values of the dipole moments have been calculated for the considered lowest-lying electronic states using the basis set cc-pVTZ. These values are plotted in term of the internuclear distance  $R$  in Figs. (3.5 - 3.8).

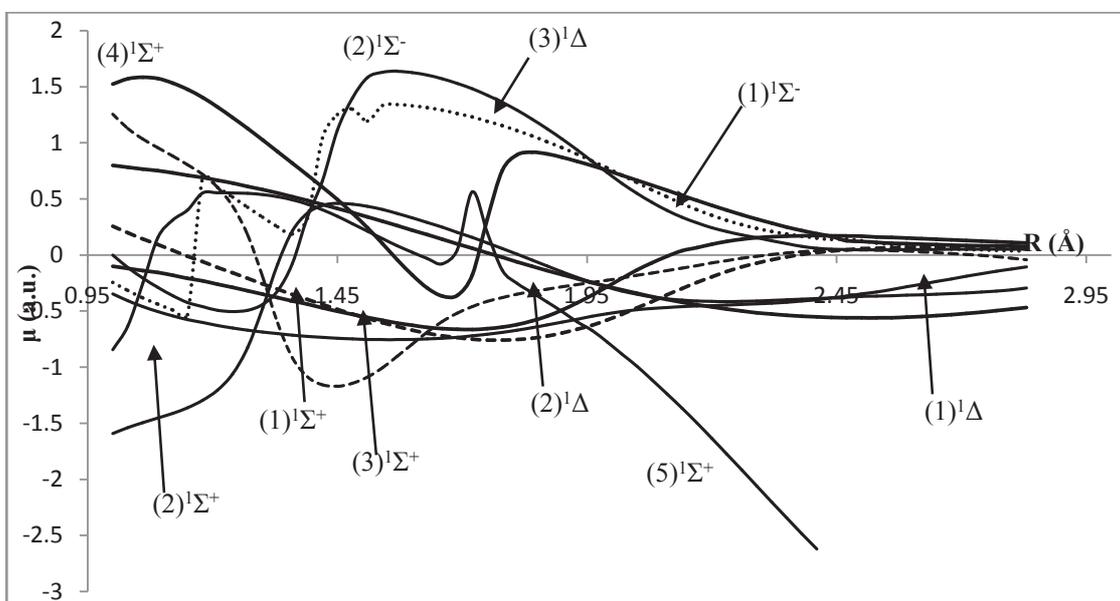


Fig.3.5: Static dipole moment curves of the  $1\Sigma$  and  $1\Delta$  states using the basis cc-pVTZ of the molecule BN

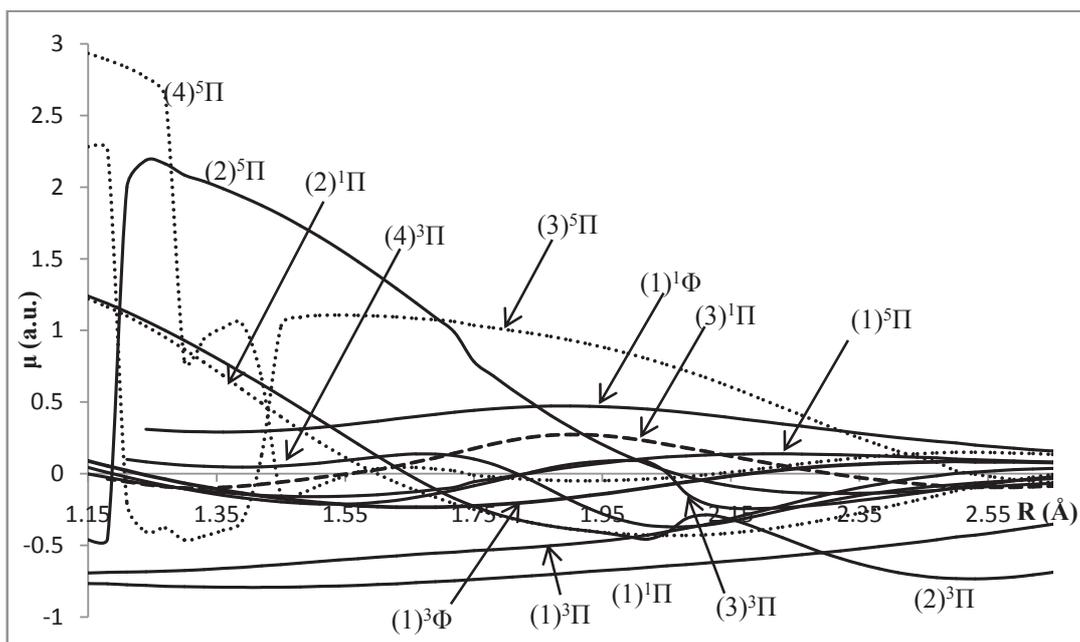


Fig. 3.6: Static dipole moment curves of the  $^{1,3,5}\Pi$ , and  $^{1,3}\Phi$  states using the basis cc-pVTZ of the molecule BN.

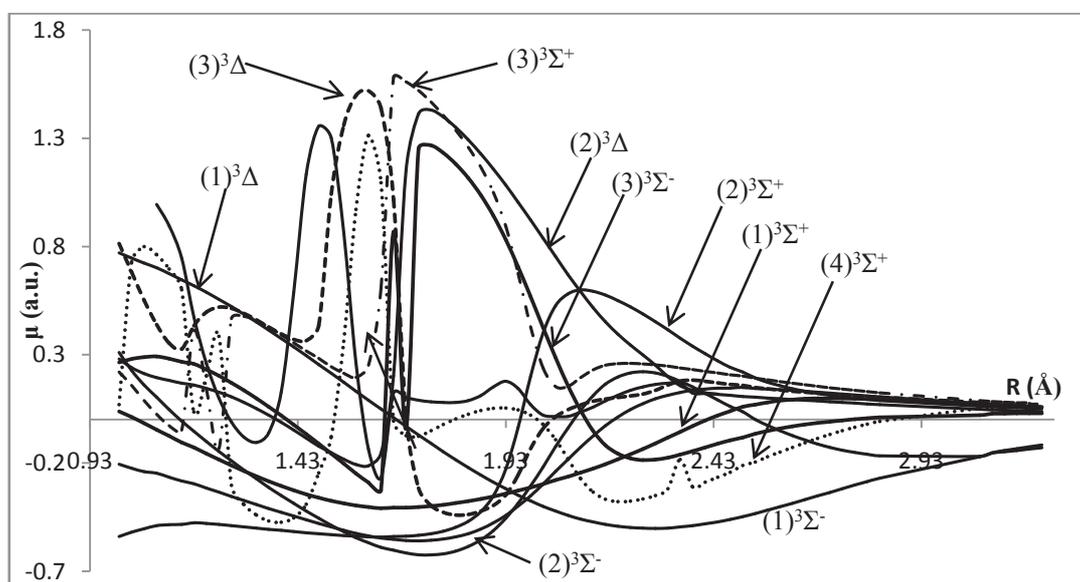


Fig.3.7: Static dipole moment curves of the  $^3\Sigma$  and  $^3\Delta$  states using the basis cc-pVTZ of the molecule BN

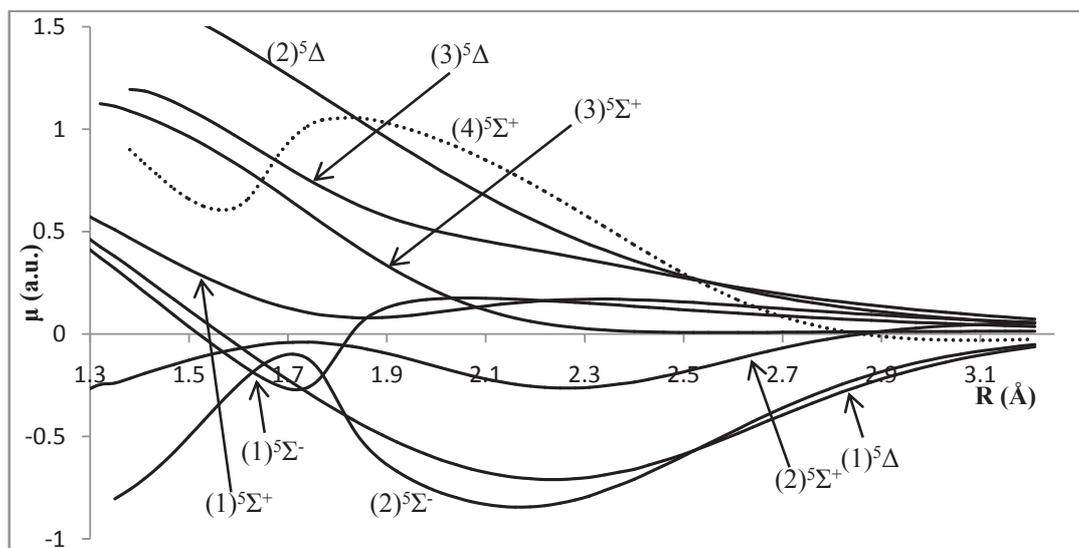


Fig.3.8: Static dipole moment curves of the  ${}^5\Sigma$  and  ${}^5\Delta$  states using the basis cc-pVTZ of the molecule BN

In these figures one can notice that, parts of the curves are positive where the dipole moments are oriented from B to N, and the other parts are negative where the dipole moments are oriented from N to B. By comparing these curves to the potential energy curves in Figs (3.2, 3.3, 3.4) one can notice the agreement between the 5 positions of the avoided crossing of the PECs and the crossings of dipole moment curves (Table 3.1). This agreement may confirm the validity and the accuracy of the calculation of the studied excited electronic states.

### 3.5 Conclusion

In the present work an *ab initio* calculation of 42 singlet, triplet, and quintet lowest electronic states in the  ${}^{2s+1}\Lambda^{(\pm)}$  representation up to  $95000\text{ cm}^{-1}$  has been performed via CASSCF/MRCI methods using 3 type of basis sets. The potential energy

curves have been calculated along with the spectroscopic constants  $T_e$ ,  $R_e$ ,  $B_e$ , and  $\omega_e$  for these states and the static dipole moment  $\mu$ . An accurate calculation of  $T_e$  of the first excited electronic state  $^1\Sigma^+$  of the molecule BN is a very difficult task since it is excessively sensitive to the electron correlation treatment. In literature there is a large discrepancy in the investigated values either theoretically or experimentally. Our calculated values of  $T_e$  using the 3 different bases sets are within the range of these values, but may be more experimental studies for this state can confirm its value of  $T_e$ . The comparison of our results with the theoretical and experimental data available in the literature for other states demonstrated an overall very good accuracy.

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## Theoretical calculation of the electronic structure of the SiN molecule

### 4.1 Introduction

The remarkable interest of silicon nitride reside in many properties such as strength, hardness, chemical inertness, good resistance to corrosion, high thermal stability, and good dielectric properties [1]. In literature many spectroscopic investigations have been focused on the ground and the first excited states where some spectroscopic constants have been obtained [2-12]. The spectroscopic constants  $R_e$ ,  $\omega_e$ ,  $\omega_e x_e$  and  $T_e$  have been investigated by different theoretical techniques for the doublet and quartet electronic states where the ground state is proved to be  $X^2\Sigma^+$  and the first excited state is  $A^2\Pi$  [13-38]. Recently Xing *et al.* [39] determined the spectroscopic parameters and the PECs of thirteen  $^{2s+1}A^{(\pm)}$  electronic states using the complete active space self-consistent field method followed by the internally contracted multireference configuration interaction approach with the Davidson modification (icMRCI+Q).

By using an *ab initio* calculation, we investigate in the present work, the potential energy curves (PEC's) for 29 doublet and quartet electronic states of the SiN molecule. The spectroscopic parameters (dissociation energy  $D_e$ , excitation energy term  $T_e$  referred to the ground state, equilibrium internuclear separation  $R_e$ , and harmonic frequency  $\omega_e$ ) are also calculated for the investigated electronic states. The comparison of these results with those reported in the literature showed a very good agreement.

### 4.2 Method of calculations

In the present work we study the low-lying doublet and quartet electronic states of the molecule SiN using state averaged complete active space self-consistent field (CASSCF) procedure followed by a multireference configuration interaction (MRDSCI with Davidson correction) treatment for the electron correlation. The entire CASSCF configuration space was used as the reference in the MRDSCI calculations, which were done via the computational chemistry program MOLPRO [41] taking advantage of the graphical user interface GABEDIT [42]. This software is intended for high level accuracy correlated *ab initio* calculations. MOLPRO has been run on a PC-computer with LINUX-type operating systems. Silicon species are treated in all electron schemes; the 14 electrons of the silicon atom are considered using a aug-cc-pV5Z basis set for s, p, d and f functions. The Nitrogen species is treated as a system of 7 electrons by using the same basis set for s, p, and d functions. Among the 21 electrons explicitly considered for SiN (14 electrons for Si and 7 for N) 10 inner electrons were frozen in subsequent calculations so that 11 valence electrons were explicitly treated. The active space contains  $7\sigma(\text{Si}: 3s, 3p_0, 4s; \text{N}: 1s, 2s, 2p_0, 3s)$  and  $2\pi(\text{Si}: 3p_{\pm 1}; \text{N}: 2p_{\pm 1})$  orbitals which correspond to 11 active molecular orbitals distributed into irreducible representation  $a_1, b_1, b_2$  and  $a_2$  in the following way:  $7a_1, 2b_1, 2b_2, 0$ , noted [7, 2, 2, 0]. All computations were performed in the  $C_{2v}$  point group. The 14 doublet and 16 quartet low-lying electronic states of the molecule SiN were generated using the MRSDCI calculation for 61 internuclear distances in the range  $1\text{\AA} \leq R_e \leq 3\text{\AA}$  in the representation  $^{2s+1}\Lambda^{(+/-)}$  where we assumed that, the SiN molecule is mainly ionic around the equilibrium position. These potential energy curves are given in Figs (4.1-4.4).

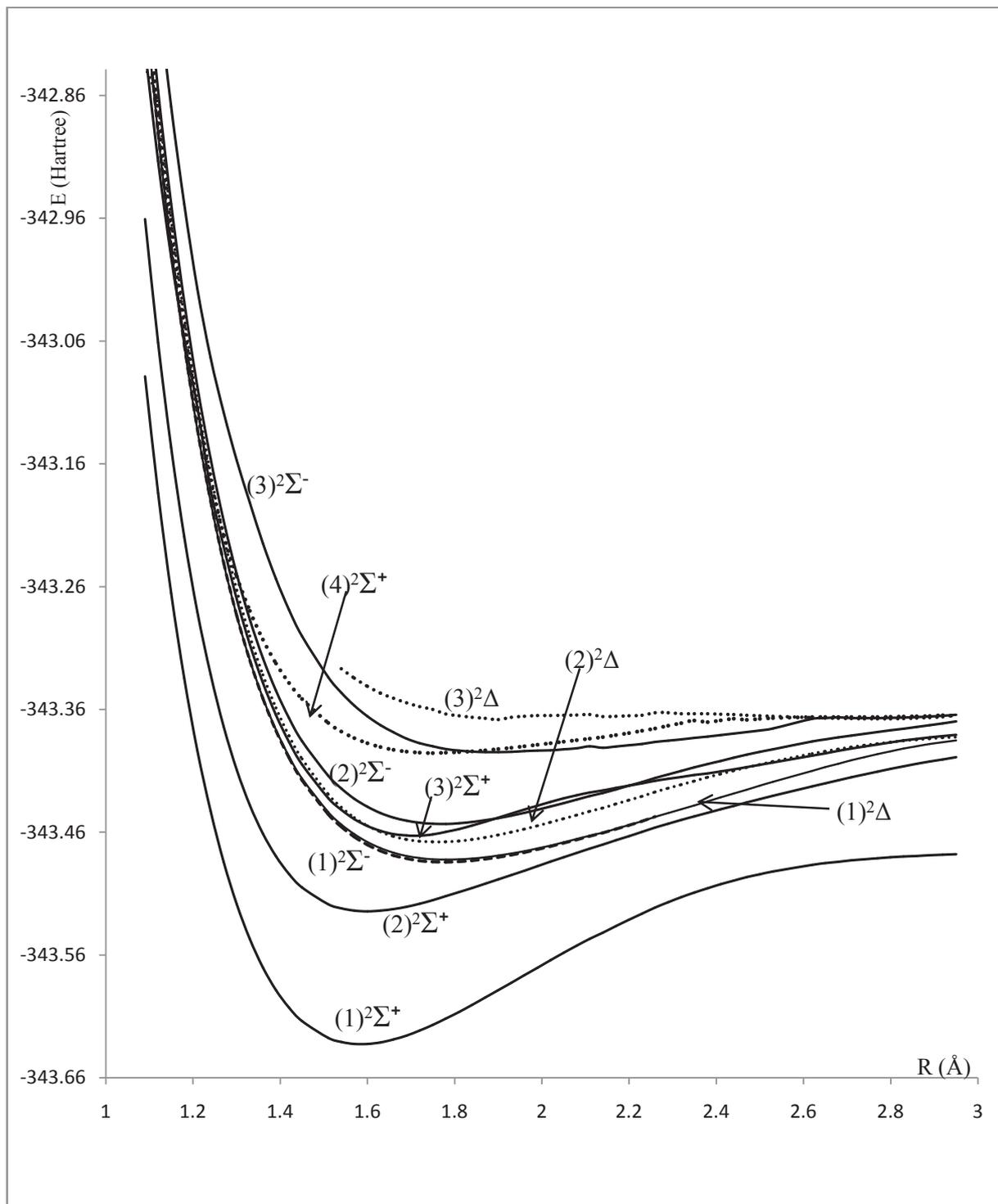


Fig. 4.1: Potential energy curves of the states  $^2\Sigma^\pm$  and  $^2\Delta$  of the molecule SiN

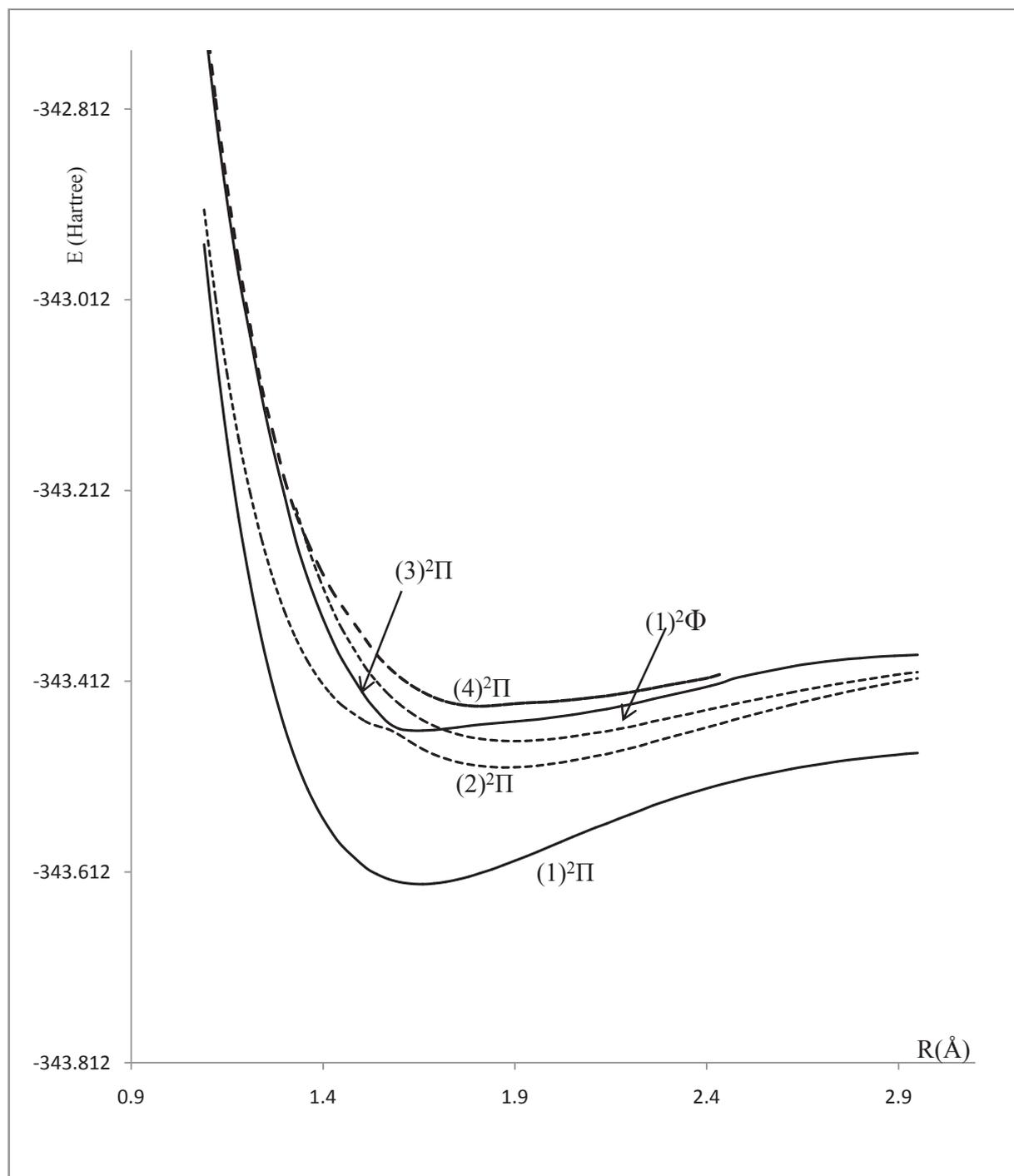


Fig.4.2: Potential energy curves of the states  $^2\Pi$  and  $^2\Phi$  of the molecule SiN

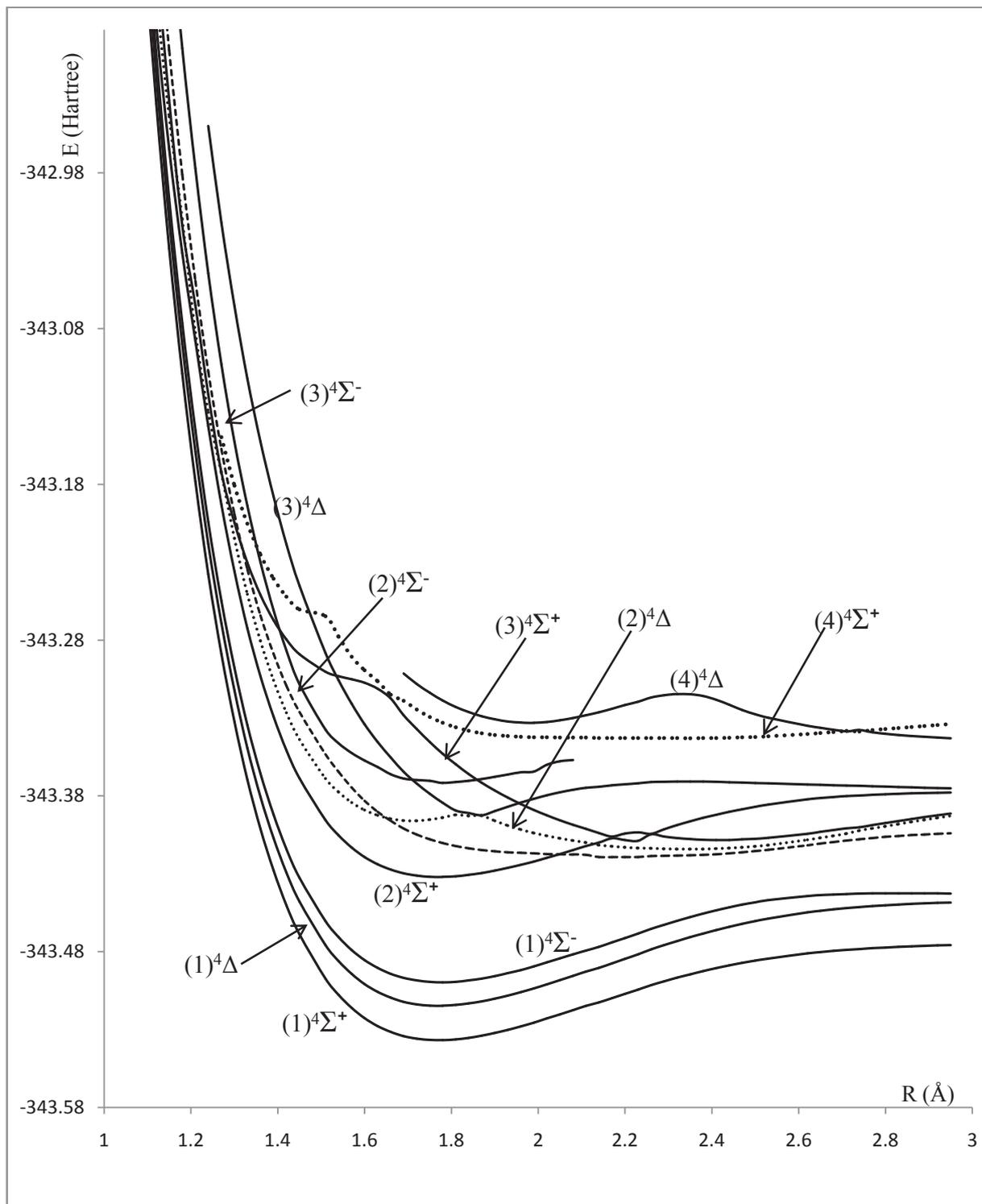


Fig.4.3: Potential energy curves of the states  $^4\Sigma^\pm$  and  $^4\Delta$  of the molecule SiN

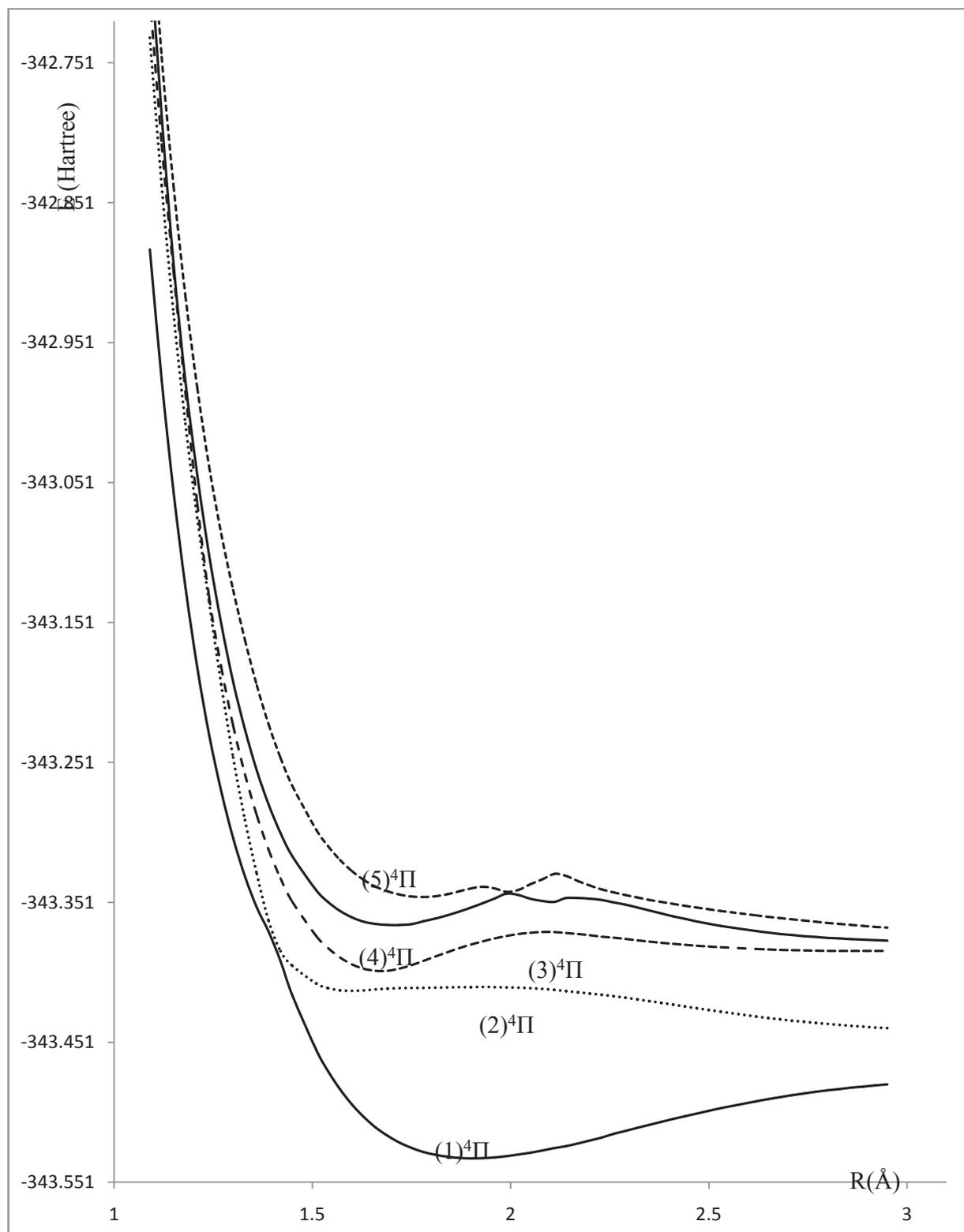


Fig. 4.4: Potential energy curves of the states  $4\Pi$  of the molecule SiN

In the considered range of R, some crossings and avoided crossings occur between the potential energy curves of different symmetries at large values of the internuclear distance. The positions of these crossings and avoided crossings are given in Table (4.1, 4.2).

Table 4.1: Positions of the crossings between the different electronic states of the molecule SiN

state 1	state 2	Crossing between (n <sub>1</sub> ) state1/(n <sub>2</sub> ) state2	R <sub>c</sub> (Å)
$^2\Sigma^+$	$^2\Delta$	3/2	1.60
		3/2	2.47
		3/2	2.77
		4/3	2.53
$^2\Sigma^+$	$^2\Sigma^-$	3/2	1.87
		3/2	2.17
		4/3	1.84
		4/2	1.30
		4/3	2.62
$^2\Pi$	$^2\Phi$	3/1	1.69
		4/1	1.33
$^4\Sigma^+$	$^4\Delta$	2/2	2.11
		3/3	1.93
		3/3	1.51
		4/3	1.45
		3/2	1.18
		4/4	2.71
$^4\Sigma^+$	$^4\Sigma^-$	2/2	2.05
		2/3	1.84
		3/3	1.30
		4/3	1.33
		3/2	1.30
$^4\Sigma^-$	$^4\Delta$	3/3	1.72

Table 4.2: The avoided crossing between different electronic states

State(1)/state(2)	$R_{AC}(\text{\AA})$	$\Delta E_{AC}(\text{cm}^{-1})$
(2) $^2\Pi$ /(3) $^2\Pi$	1.57	1502.54
(1) $^4\Pi$ /(2) $^4\Pi$	1.39	1710.32
(4) $^4\Pi$ /(5) $^4\Pi$	1.99	298.85
(2) $^4\Pi$ /(3) $^4\Pi$	1.24	746.45
(2) $^4\Pi$ /(3) $^4\Pi$	1.66	2922.87
(2) $^4\Delta$ /(3) $^4\Delta$	1.84	402.46
(2) $^4\Sigma$ /(3) $^4\Sigma$	2.14	1356.353
(2) $^4\Sigma$ /(3) $^4\Sigma$	2.23	1201.18
(3) $^4\Sigma$ /(4) $^4\Sigma$	1.63	1069.41

$R_{AC}$  and  $\Delta E_{AC}$  are respectively the internuclear distance and the energy difference at the avoided crossing between the two corresponding states

The energy separation between the ground and the highest doublet electronic states and the lowest and the highest excited quartet electronic state are respectively  $58169.84 \text{ cm}^{-1}$  and  $65431.82 \text{ cm}^{-1}$ . For the investigated bound electronic states the transition energy with respect to the energy minimum for the ground state  $T_e$ , the equilibrium internuclear distance  $R_e$ , the harmonic frequency  $\omega_e$  and the rotational constant  $B_e$  have been calculated. These values are given in Table 4.3.

Table 4.3: Spectroscopic constants of the molecule SiN

$^{2S+1}\Lambda^{(\pm)}$ states	$T_e$ ( $\text{cm}^{-1}$ )	$\Delta T_e/T_e$ %	$R_e$ ( $\text{\AA}$ )	$\Delta R_e/R_e$ %	$B_e$ ( $\text{cm}^{-1}$ )	$\Delta B_e/B_e$ %	$\omega_e$ ( $\text{cm}^{-1}$ )	$\Delta\omega_e/\omega_e$ %
$X^2\Sigma^+$	0.0 <sup>(a)</sup>		1.585 <sup>(a)</sup>		0.717 <sup>(a)</sup>		1115.77 <sup>(a)</sup>	
	0.0 <sup>(b)</sup>		1.572 <sup>(b)</sup>	0.82	0.73 <sup>(b)</sup>	1.78	1155 <sup>(b)</sup>	3.39
	0.0 <sup>(c)</sup>		1.593 <sup>(c)</sup>	0.50			1124 <sup>(c)</sup>	0.73
	0.0 <sup>(d)</sup>		1.566 <sup>(d)</sup>	1.21				
	0.0 <sup>(e)</sup>		1.582 <sup>(e)</sup>	0.18				
	0.0 <sup>(f)</sup>		1.568 <sup>(f)</sup>	1.08			1167 <sup>(f)</sup>	4.38
	0.0 <sup>(g)</sup>		1.568 <sup>(g)</sup>	1.08			1189 <sup>(g)</sup>	6.15
	0.0 <sup>(h)</sup>						1151 <sup>(h)</sup>	3.06
	0.0 <sup>(i)</sup>		1.578 <sup>(i)</sup>	0.44			1162 <sup>(i)</sup>	3.97
	0.0 <sup>(j)</sup>		1.589 <sup>(j)</sup>	0.25				
	0.0 <sup>(k)</sup>		1.571 <sup>(k)</sup>	0.89	0.731 <sup>(k)</sup>	1.91	1151.36 <sup>(k)</sup>	3.09
	0.0 <sup>(l)</sup>		1.572 <sup>(l)</sup>	0.82	0.73 <sup>(l)</sup>	1.78		
	0.0 <sup>(m)</sup>						1151.3 <sup>(m)</sup>	3.09
	0.0 <sup>(n)</sup>						1151.2 <sup>(n)</sup>	3.07
0.0 <sup>(s)</sup>			1.58 <sup>(s)</sup>	0.31	0.722 <sup>(s)</sup>	0.69	1152 <sup>(s)</sup>	3.14
(1) $^2\Pi$	1999.3 <sup>(a)</sup>		1.654 <sup>(a)</sup>		0.658 <sup>(a)</sup>		1004.02 <sup>(a)</sup>	
	2053 <sup>(b)</sup>	2.60	1.639 <sup>(b)</sup>	0.91	0.672 <sup>(b)</sup>	2.08	1044 <sup>(b)</sup>	3.82
	4785 <sup>(e)</sup>	58.20	1.646 <sup>(e)</sup>	0.48				

Chapter four: Theoretical calculation of the electronic structure of the molecule SiN molecule

	633 <sup>(f)</sup>		1.64 <sup>(f)</sup> 1.693 <sup>(i)</sup> 1.635 <sup>(k)</sup>	0.85 2.30 1.16			1046 <sup>(f)</sup> 1044.41 <sup>(k)</sup> 1031.65 <sup>(m)</sup> 1031.94 <sup>(n)</sup>	4.01 3.86 2.67 2.70
	2032.15 <sup>(m)</sup> 2031.37 <sup>(n)</sup> 2032.4 <sup>(p)</sup> 2099 <sup>(s)</sup>	1.61 1.57 1.62 4.74	1.641 <sup>(p)</sup> 1.65 <sup>(s)</sup>	0.79 0.24	0.675 <sup>(k)</sup> 0.67 <sup>(n)</sup> 0.67 <sup>(p)</sup> 0.66 <sup>(s)</sup>	2.51 1.79 1.79 0.30	1025 <sup>(s)</sup>	
(1) <sup>4</sup> Σ <sup>+</sup>	20724.4 <sup>(a)</sup> 18551 <sup>(r)</sup> 22195 <sup>(s)</sup>	11.71 6.62	1.770 <sup>(a)</sup> 1.783 <sup>(r)</sup> 1.756 <sup>(s)</sup>	0.72 0.79	0.575 <sup>(a)</sup> 0.585 <sup>(s)</sup>	1.70	745.88 <sup>(a)</sup> 799 <sup>(s)</sup>	6.64
(1) <sup>4</sup> Π	21892.42 <sup>(a)</sup> 20890 <sup>(r)</sup> 22809 <sup>(s)</sup>	4.79 4.01	1.900 <sup>(a)</sup> 1.892 <sup>(r)</sup> 1.893 <sup>(s)</sup>	0.422 0.36	0.496 <sup>(a)</sup> 0.504 <sup>(s)</sup>	1.58	605.92 <sup>(a)</sup> 639 <sup>(s)</sup>	5.17
(2) <sup>2</sup> Σ <sup>+</sup>	23745.1 <sup>(a)</sup> 24122 <sup>(c)</sup> 24299.21 <sup>(k)</sup> 24299.19 <sup>(m)</sup> 24861 <sup>(s)</sup>	1.56 2.28 2.28 4.48	1.599 <sup>(a)</sup> 1.612 <sup>(c)</sup> 1.579 <sup>(k)</sup> 1.59 <sup>(s)</sup>	0.80 1.26 0.56	0.705 <sup>(a)</sup> 0.723 <sup>(k)</sup> 0.714 <sup>(s)</sup>	2.48 1.26	952.25 <sup>(a)</sup> 958 <sup>(c)</sup> 1031.03 <sup>(k)</sup> 1031.02 <sup>(m)</sup> 1025 <sup>(s)</sup>	0.6 7.64 7.64 7.09
(1) <sup>4</sup> Δ	25567.0 <sup>(a)</sup> 24197 <sup>(r)</sup> 27172 <sup>(s)</sup>	5.66 5.9	1.770 <sup>(a)</sup> 1.78 <sup>(r)</sup> 1.757 <sup>(s)</sup>	0.56 0.74	0.575 <sup>(a)</sup> 0.584	1.54	746.10 <sup>(a)</sup> 779 <sup>(s)</sup>	4.22
(1) <sup>4</sup> Σ <sup>-</sup>	28878.3 <sup>(a)</sup> 27020 <sup>(r)</sup> 30236 <sup>(s)</sup>	6.87 4.49	1.770 <sup>(a)</sup> 1.784 <sup>(r)</sup> 1.763 <sup>(s)</sup>	0.78 0.39	0.571 <sup>(a)</sup> 0.581 <sup>(s)</sup>	1.72	715.08 <sup>(a)</sup> 760 <sup>(s)</sup>	5.91
(2) <sup>2</sup> Π	28887.6 <sup>(a)</sup> 27865.63+a <sup>(k)</sup> 28859.55 <sup>(m)</sup> 28859.55 <sup>(q)</sup> 29652 <sup>(s)</sup>	0.10 0.10 2.57	1.875 <sup>(a)</sup> 1.857 <sup>(k)</sup> 1.869 <sup>(s)</sup>	0.969 0.32	0.512 <sup>(a)</sup> 0.523 <sup>(k)</sup> 0.517 <sup>(s)</sup>	2.1 0.97	680.08 <sup>(a)</sup> 699.33 <sup>(k)</sup> 699.32 <sup>(m)</sup> 699.32 <sup>(q)</sup> 705 <sup>(s)</sup>	2.75 2.75 2.75 3.53
(1) <sup>2</sup> Σ <sup>-</sup>	32547.9 <sup>(a)</sup> 33847 <sup>(s)</sup>	3.84	1.776 <sup>(a)</sup> 1.768 <sup>(s)</sup>	0.45	0.571 <sup>(a)</sup> 0.577 <sup>(s)</sup>	1.04	711.93 <sup>(a)</sup> 755 <sup>(s)</sup>	5.82
(1) <sup>2</sup> Δ	32978.4 <sup>(a)</sup> 34489 <sup>(s)</sup>	4.38	1.780 <sup>(a)</sup> 1.776 <sup>(s)</sup>	0.22	0.568 <sup>(a)</sup> 0.572 <sup>(s)</sup>	0.69	693.76 <sup>(a)</sup> 739 <sup>(s)</sup>	6.12
(1) <sup>2</sup> Φ	34943.4 <sup>(a)</sup> 38752 <sup>(s)</sup>	9.82	1.897 <sup>(a)</sup> 1.724 <sup>(s)</sup>	10.03	0.5 <sup>(a)</sup> 0.607 <sup>(s)</sup>	17.62	639.7 <sup>(a)</sup> 1247 <sup>(s)</sup>	48.7
(2) <sup>2</sup> Δ	36144.8 <sup>(a)</sup> 37592 <sup>(s)</sup>	3.84	1.760 <sup>(a)</sup> 1.753 <sup>(s)</sup>	0.39	0.582 <sup>(a)</sup> 0.587 <sup>(s)</sup>	0.85	763.69 <sup>(a)</sup> 797 <sup>(s)</sup>	4.17
(3) <sup>2</sup> Σ <sup>+</sup>	37258.8 <sup>(a)</sup> 38713 <sup>(s)</sup>	3.75	1.700 <sup>(a)</sup> 1.71 <sup>(s)</sup>	0.58	0.62 <sup>(a)</sup> 0.617 <sup>(s)</sup>	0.48	993.30 <sup>(a)</sup> 941 <sup>(s)</sup>	5.55
(2) <sup>2</sup> Σ <sup>-</sup>	39378.1 <sup>(a)</sup>		1.770 <sup>(a)</sup>		0.575 <sup>(a)</sup>		743.93 <sup>(a)</sup>	
(4) <sup>2</sup> Π	42949.4 <sup>(a)</sup> 44861 <sup>(s)</sup>	4.26	1.806 <sup>(a)</sup> 1.801 <sup>(s)</sup>	0.27	0.552 <sup>(a)</sup> 0.566 <sup>(s)</sup>	2.47	913.38 <sup>(a)</sup> 989 <sup>(s)</sup>	7.64
(2) <sup>4</sup> Σ <sup>+</sup>	(F)43718.1 <sup>(a)</sup> (S)48916.7 <sup>(a)</sup> 44895 <sup>(s)</sup>	2.62	1.769 <sup>(a)</sup> 2.41 <sup>(a)</sup> 1.759 <sup>(a3)</sup>	0.56	0.576 <sup>(a)</sup> 0.309 <sup>(a)</sup> 0.583 <sup>(s)</sup>	1.20	700.37 <sup>(a)</sup> 453.21 <sup>(a)</sup> 738 <sup>(s)</sup>	5.09
(2) <sup>4</sup> Σ <sup>-</sup>	46511.2 <sup>(a)</sup>		2.190 <sup>(a)</sup>		0.372 <sup>(a)</sup>		463.65 <sup>(a)</sup>	
(2) <sup>4</sup> Π	48149.6 <sup>(a)</sup> 49282 <sup>(s)</sup>	2.29	1.599 <sup>(a)</sup> 1.59 <sup>(s)</sup>	0.56	0.703 <sup>(a)</sup> 0.714 <sup>(s)</sup>	1.54	803.39 <sup>(a)</sup> 968 <sup>(s)</sup>	17.0
(2) <sup>4</sup> Δ	47638.1 <sup>(a)</sup> 50063 <sup>(s)</sup>	4.84	2.340 <sup>(a)</sup> 2.35 <sup>(s)</sup>	0.42	0.326 <sup>(a)</sup> 0.326 <sup>(s)</sup>	0.00	330.23 <sup>(a)</sup> 358 <sup>(s)</sup>	7.75
(3) <sup>4</sup> Π	51277.7 <sup>(a)</sup> 53266 <sup>(s)</sup>	3.73	1.673 <sup>(a)</sup> 1.695 <sup>(s)</sup>	1.00	0.644 <sup>(a)</sup> 0.628 <sup>(s)</sup>	2.54	1139.63 <sup>(a)</sup> 1134 <sup>(s)</sup>	0.49
(4) <sup>2</sup> Σ <sup>+</sup>	52051.9 <sup>(a)</sup>		1.750 <sup>(a)</sup>		0.587 <sup>(a)</sup>		613.01 <sup>(a)</sup>	
(3) <sup>2</sup> Σ <sup>-</sup>	52208.2 <sup>(a)</sup>		1.877 <sup>(a)</sup>		0.509 <sup>(a)</sup>		584.33 <sup>(a)</sup>	
(3) <sup>4</sup> Σ <sup>-</sup>	57066.5 <sup>(a)</sup>		1.785 <sup>(a)</sup>		0.564 <sup>(a)</sup>		644.88 <sup>(a)</sup>	
(3) <sup>2</sup> Δ	58169.5 <sup>(a)</sup>		1.870 <sup>(a)</sup>		0.509 <sup>(a)</sup>		831.98 <sup>(a)</sup>	
(4) <sup>4</sup> Π	58464.5 <sup>(a)</sup>		1.699 <sup>(a)</sup>		0.624 <sup>(a)</sup>		857.13 <sup>(a)</sup>	
(5) <sup>4</sup> Π	62861.3 <sup>(a)</sup> 64362 <sup>(s)</sup>	2.33	1.776 <sup>(a)</sup> 1.766 <sup>(s)</sup>	0.56	0.57 0.578 <sup>(s)</sup>	1.38	928.82 <sup>(a)</sup> 879 <sup>(s)</sup>	5.66

$(4)^4\Sigma^+$	63275.3 <sup>(a)</sup>		2.340 <sup>(a)</sup>		0.349 <sup>(a)</sup>		46.97 <sup>(a)</sup>
$(4)^4\Delta$	65431.8 <sup>(a)</sup>		1.978 <sup>(a)</sup>		0.460 <sup>(a)</sup>		737.46 <sup>(a)</sup>

a1)the first entry is for the present work, b)Ref.[22], c)Ref. [29], d)Ref. [14], e)Ref.[13], f) Ref. [18] , g)Ref.[21], h)Ref.[16], i)Ref.[20], j)Ref.[17], k) Ref.[3], l)Ref.[4], m)Ref.[9], n)Ref.[10], o) Ref.[12] , p)Ref.[8], q)Ref.[5], r)Ref.[15], s)Ref. [32], (F) and (S) represent the first and the second minima respectively.

### 4.3 Results and discussion

By comparing our calculating values with those obtained experimentally for the 4 states  $X^2\Sigma^+$ ,  $(1)^2\Pi$ ,  $(2)^2\Sigma^+$ , and  $(2)^2\Pi$ , available in literature, one can find an excellent agreements for  $T_e$ ,  $R_e$ ,  $B_e$  with the relative differences 0.1%(Refs. [5,9]  $(2)^2\Pi$ )  $\leq \Delta T_e/T_e \leq 2.28\%$  (Refs. [3,9]  $(2)^2\Sigma^+$ ), 0.79%(Ref. [8]  $(1)^2\Pi$ )  $\leq \Delta R_e/R_e \leq 1.26\%$ (Ref. [3]  $(2)^2\Sigma^+$ ), 1.78%(Refs. [4,10]  $X^2\Sigma^+$ )  $\leq \Delta B_e/B_e \leq 2.48\%$ (Ref. [3]  $(2)^2\Sigma^+$ ) respectively and a good agreement for the value of  $\omega_e$  with the relative difference 2.67%(Refs. [10]  $(1)^2\Pi$ )  $\leq \Delta \omega_e/\omega_e \leq 7.64\%$ (Refs. [3,9]  $(2)^2\Sigma^+$ ). The comparison of these constants, calculated in the present work, with the theoretical values published in literature shows also good agreements with the relative differences 1.56%(Ref. [29]  $(2)^2\Sigma^+$ )  $\leq \Delta T_e/T_e \leq 9.82\%$ (Ref. [32]  $(1)^2\Phi$ ), 0.18%(Ref. [13]  $X^2\Sigma^+$ )  $\leq \Delta R_e/R_e \leq 10.03\%$ (Ref. [32]  $(1)^2\Phi$ ), 0.00%(Ref. [32]  $(2)^4\Delta$ )  $\leq \Delta B_e/B_e \leq 2.47\%$ (Ref. [32]  $(4)^2\Pi$ ) and 1.56%(Ref. [29]  $(2)^2\Sigma^+$ )  $\leq \Delta \omega_e/\omega_e \leq 9.82\%$ (Ref. [32]  $(1)^2\Phi$ ) except the values of  $T_e$  given in Refs. [13, 18] for the states  $(1)^2\Pi$  and  $(1)^4\Sigma$  and the values  $B_e$  and  $\omega_e$  for the state  $(1)^2\Phi$  calculated by Cai *et al.* [32] at cMRCI level. From this very good agreement with the experimental and theoretical data in literature, we can pretend the accuracy of the results concerning the new investigated electronic states in the present work which can be confirmed by new experiments on this molecule.

The electric dipole moment is a fundamental property; it is used for the description of numerous physical phenomena. The expectation value of this operator is

sensitive to the relevant valence electrons. The calculated values of the dipole moments for the considered lowest-lying electronic states of the molecule SiN, as a function of the internuclear distance, are given in Figures (4.5-4.8).

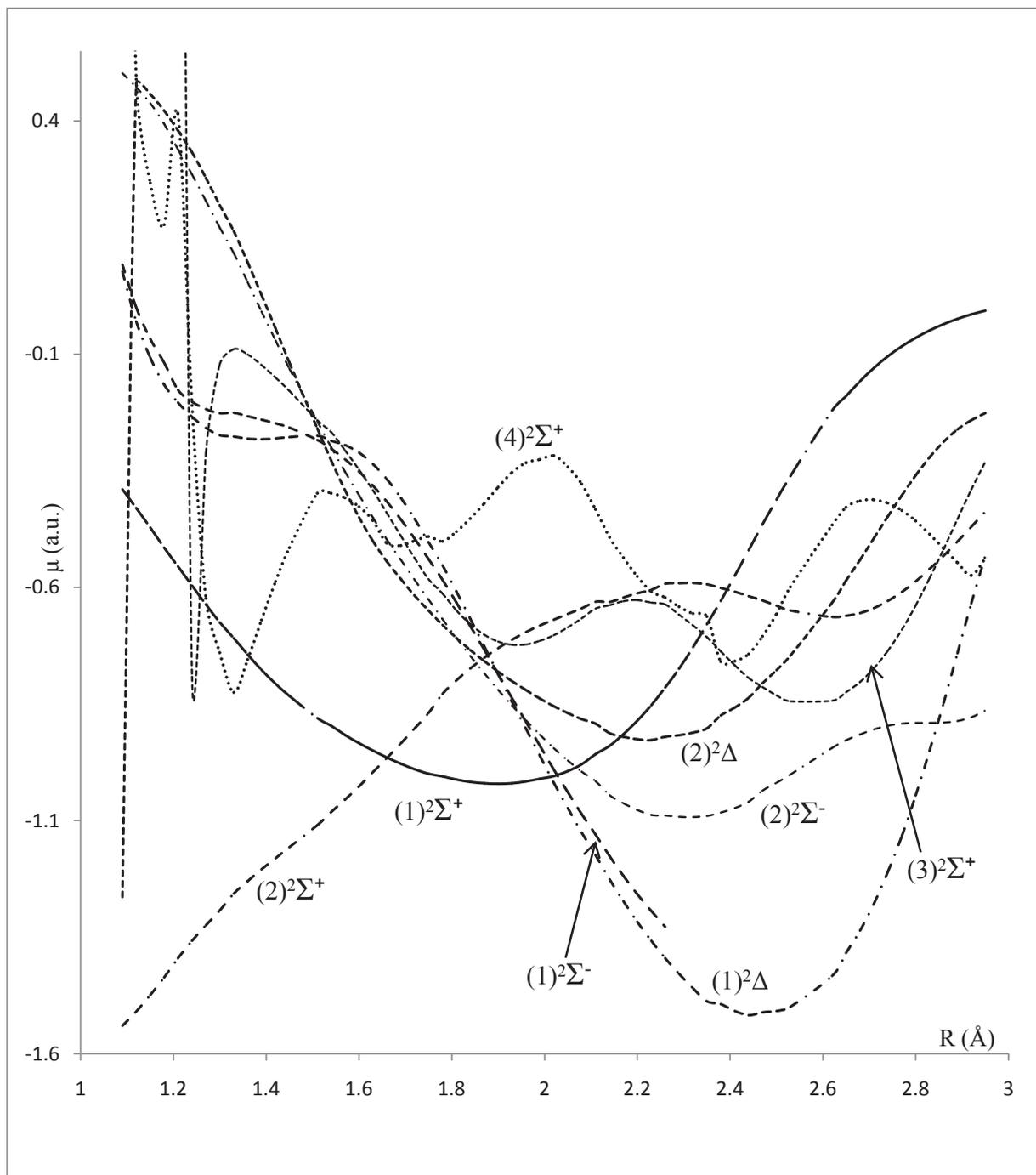


Fig.4.5: Static dipole moment curves of state  ${}^2\Sigma^{\pm}$  and  ${}^2\Delta$  of the molecule SiN

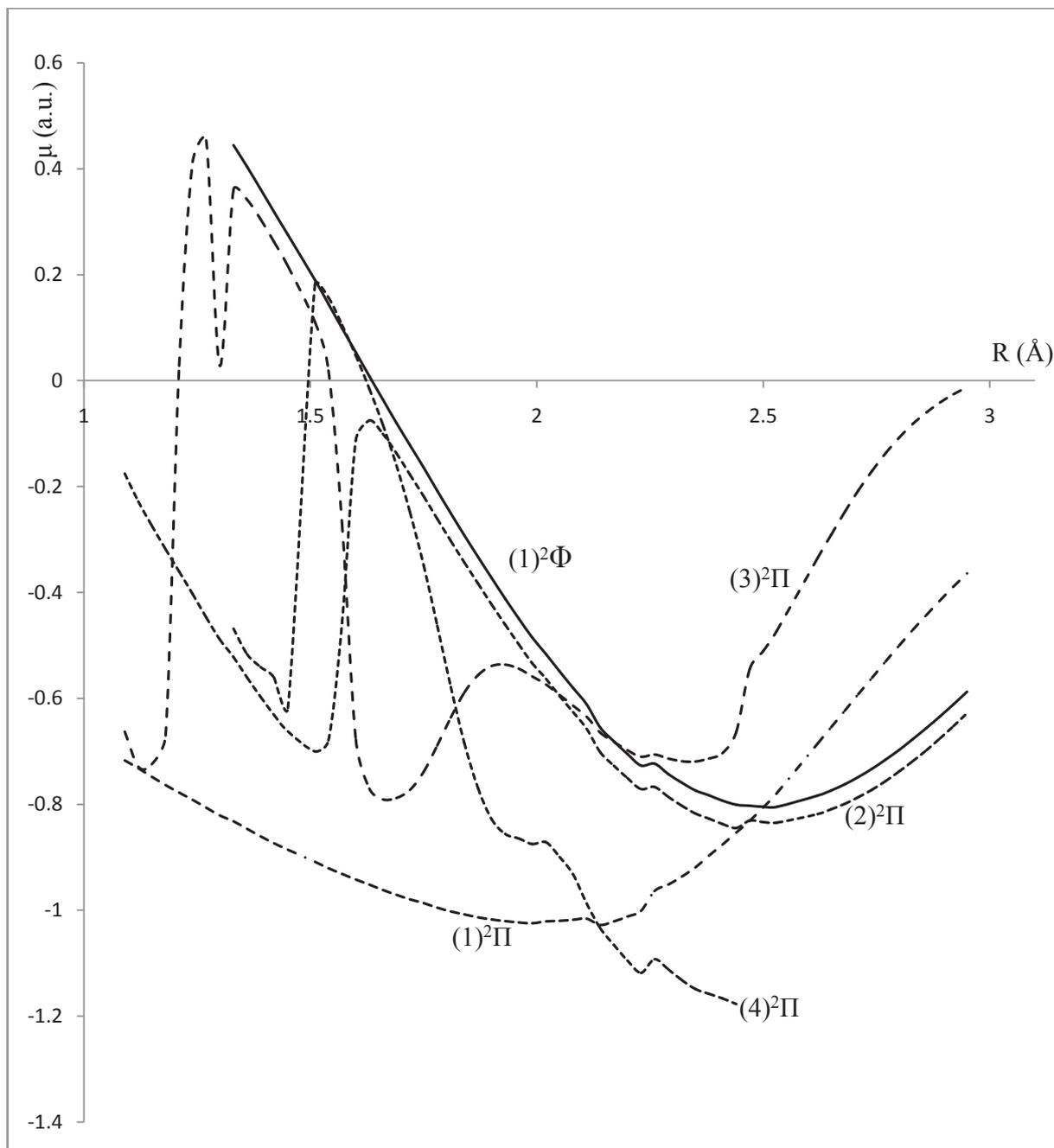


Fig.4.6: Static dipole moment curves of the states  ${}^2\Pi$  and  ${}^2\Phi$  of the molecule SiN

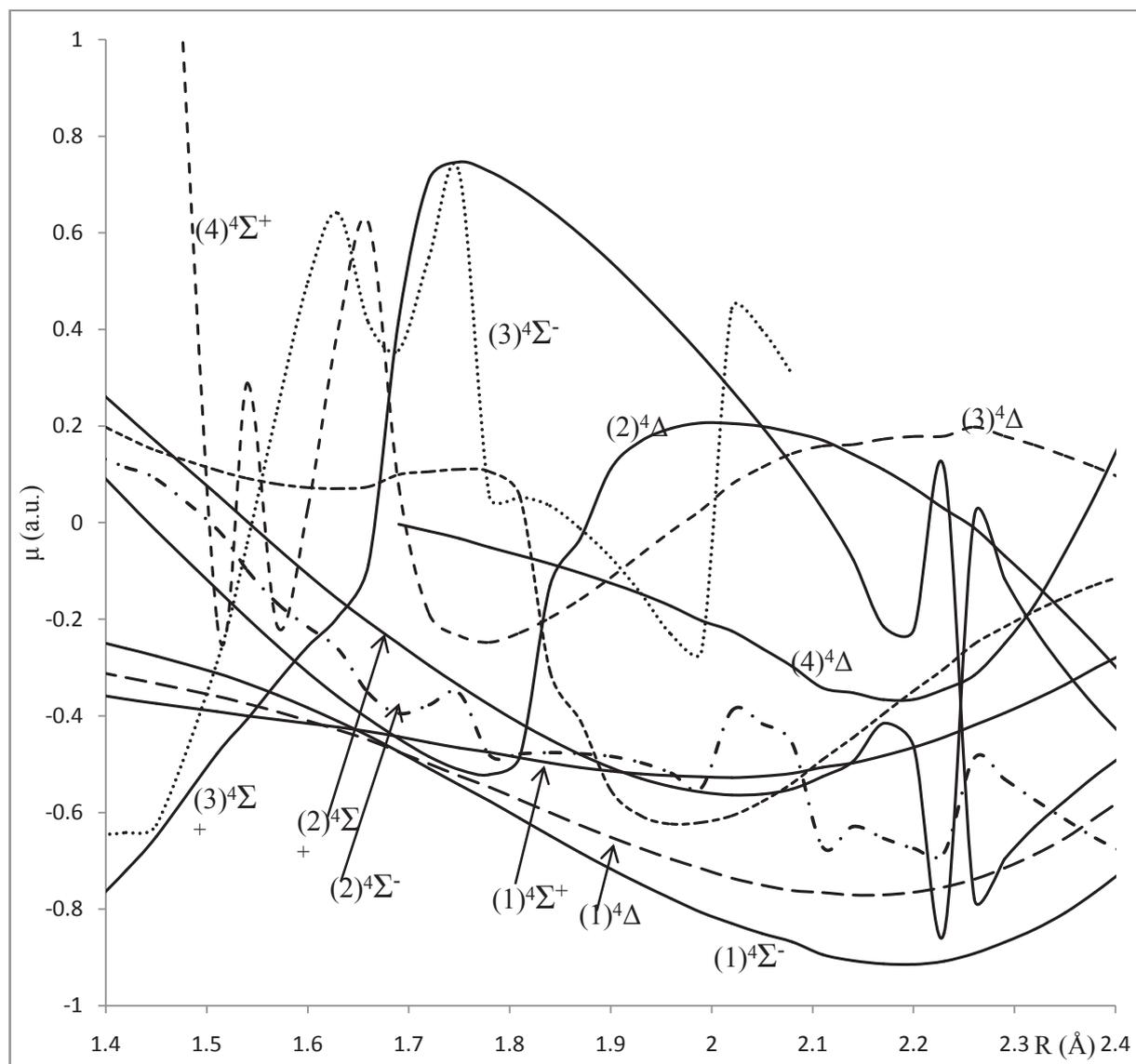


Fig. 4.7: Static dipole moment curves of the states  ${}^4\Sigma^\pm$  and  ${}^4\Delta$  of the molecule SiN

By comparing these curves to the potential energy curves (Figs.4.1- 4.4), one can notice the agreement between the positions of the avoided crossings of the PECs (Table 4.2) and the crossings of dipole moment curves. This agreement may confirm the validity and the accuracy of the calculation of the studied excited electronic states.

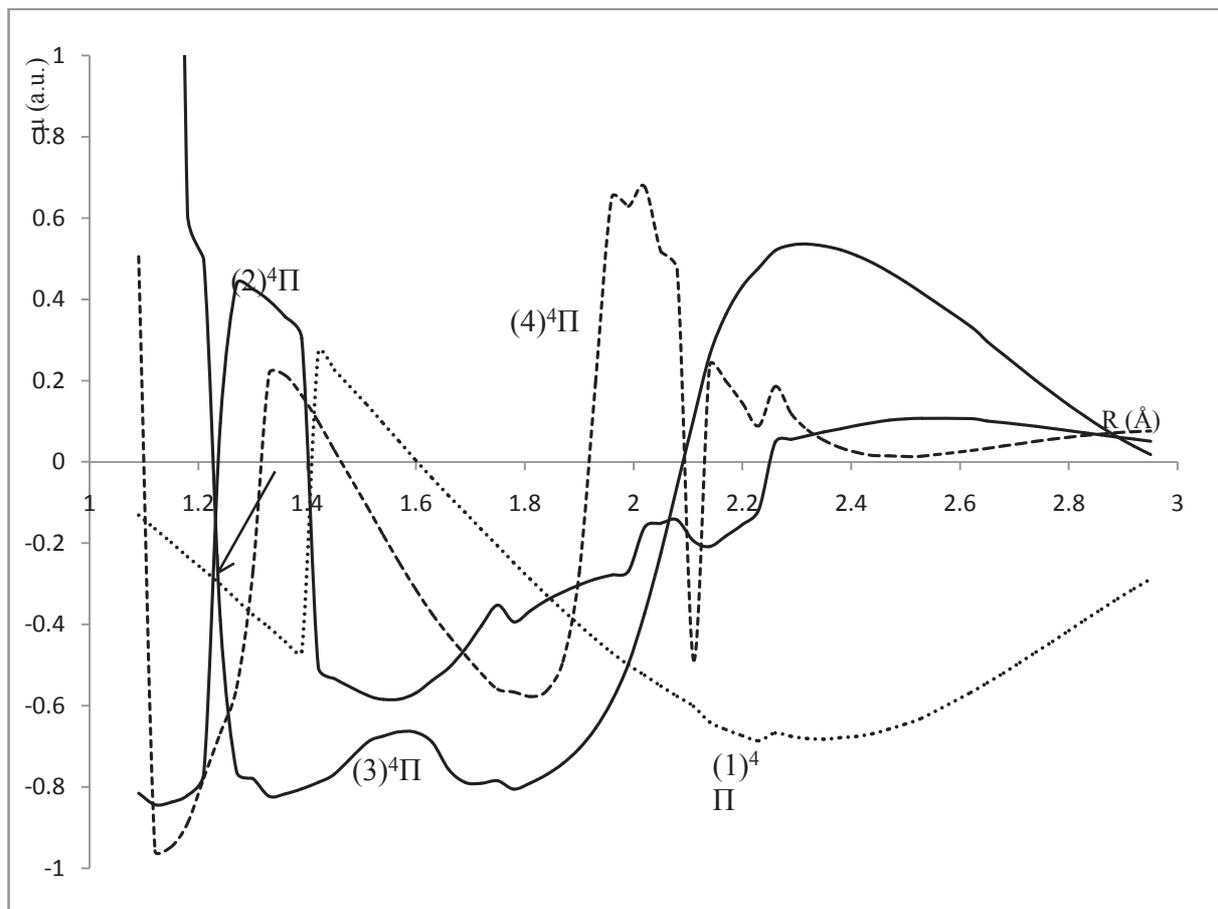


Fig.4.8: Static dipole moment curves of the states  ${}^4\Pi$  of the molecule SiN

## 4.4 Conclusion

An *ab initio* calculation of 30 doublet and quartet lowest electronic states in the  ${}^{2s+1}\Lambda^{(\pm)}$  representation up to  $70000\text{ cm}^{-1}$  has been performed via CASSCF/MRCI methods. The static dipole moment  $\mu$ , the potential energy curves and the spectroscopic constants  $T_e$ ,  $R_e$ ,  $B_e$ , and  $\omega_e$  have been calculated for these electronic states. The comparison of our results with the theoretical and experimental data available in the literature demonstrated a very good agreement which confirms the validity and the accuracy of the investigated electronic states.

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## Theoretical Calculation of the Low-Lying Electronic States of the Molecule LaH

### 5.1 Introduction

The transition metal monohydrides and monohalides have been extensively studied over several decades because they are of considerable interest in various fields such as astrophysics, catalytic chemistry, high-temperature chemistry and surface material [1–3]. The nature of transition metal–H bonding and the role of the metal d orbital in this bonding should be understood. In particular, components of diatomic molecules of La atom are of great importance as test cases for modeling the role of the d electron in the chemical bond on account of their simpler open d shell electronic configurations. These hydrides possess a large number of densely packed low-lying electronic states of different spatial and spin symmetries. The theoretical and experimental studies of these molecules in literature are much more limited. In 1976 Bernard and Bacis [4] assigned the transitions  ${}^3\Phi - {}^3\Delta$ ,  ${}^1\Sigma - {}^1\Pi$ , and  ${}^1\Delta - {}^1\Pi$  for several observed bands with a lower state  ${}^1\Pi$  without observing any transitions having a  ${}^1\Sigma^+$ . Based on some erroneous ab initio calculations on ScH, they suspected that LaH probably had a  ${}^3\Delta$  ground state, but they were not sure about the nature of their finding. A complete active space MCSCF calculations of the energies and spectroscopic properties  $T_e$ ,  $R_e$ ,  $\omega_e$ ,  $\mu_e$ , and  $D_e$  of many low-lying electronic states of LaH molecule have been performed by Das and Balasubramanian [5]. They recognized that the transitions observed by Bernard and Bacis [4] was incorrect and tried to reassign them as  $B^1\Pi - X^1\Sigma^+$ ,  $C^1\Pi - X^1\Sigma^+$  and  $b^3\Delta - a^3\Pi$ . In this calculation they predict  ${}^1\Sigma^+$  state as ground state and  ${}^3\Delta$  as low-lying excited electronic state. After comparing their results with YH [7] and LaF molecules [8–10], this assumption was confirmed experimentally by Ram and

Bernarth [6], and they observed two new electronic transitions  $A^1\Pi - X^1\Sigma^+$  and  $d^3\Phi - a^3\Delta$ . In order to confirm theoretically the nature of the ground and the other results in literature, and investigate new higher excited electronic states, we present in this work an ab initio calculation for the molecule LaH.

The present work is the second theoretical calculation for the electronic states below the  $19000\text{ cm}^{-1}$  in literature. An ab initio investigation of the low-lying electronic states of LaH molecule has been performed via CASSCF/MRCI method. The potential energy curves (PECs) and the spectroscopic constants have been obtained for the 24 lowest-lying electronic states. Taking advantages of the electronic structure of these electronic states and by using the canonical functions approach [11], the vibrational eigenvalues  $E_v$ , the rotational constant  $B_v$ , and the abscissas of the turning points  $R_{\min}$  and  $R_{\max}$  were calculated for several vibrational levels up to  $v=43$ .

## 5.2 Computational approach

The potential energy curves of the low-lying 24 electronic states of the LaH molecule are investigated via CASSCF method. Multireference CI calculations (single and double excitations with Davidson corrections), in which the entire CASSCF configuration space was used as reference, were performed to account the correlation effects. MRCI calculations have been done by using the computational chemistry program MOLPRO [12] taking advantage of the graphical user interface GABEDIT [13]. This software is intended for high level accuracy correlated ab initio calculations. MOLPRO has been run on a PC-computer with LUNIX-type operating systems. Lanthanum species is treated with 46 effective core potential and the remaining 11 electrons are considered as

valence electrons using the ECP46MHF [14] basis set for the s, p, d functions. The hydrogen atom is treated in its only electron scheme by using the aug-cc-pVQZ [15] basis set for s, p, d and f functions.

With the 12 electrons explicitly considered for the LaH molecule and in the  $C_{2v}$  symmetry the calculation has been performed with 2, 6, 8 and 10 valence electrons; the corresponding active orbitals with the distribution into the irreducible representation  $a_1$ ,  $b_1$ ,  $b_2$  and  $a_2$  are respectively

$5\sigma(La:6s,6p_0,5d_0;H:2s,2p_0)$ ,  $3\pi(La:5d_{\pm 1},6p_{\pm 1};H:2p_{\pm 1})$ ,  $1\delta(La:5d_{\pm 2})$  noted [6, 3, 3, 1],  $6\sigma(La:5s,6s,5d_0;H:1s,2s,2p_0)$ ,  $2\pi(La:5d_{\pm 1};H:2p_{\pm 1})$ ,  $1\delta(La:5d_{\pm 2})$  noted [7, 2, 2, 1],  $5\sigma(La:5p_0,6s,5d_0;H:2s,2p_0)$ ,  $3\pi(La:5p_{\pm 1},5d_{\pm 1};H:2p_{\pm 1})$ ,  $1\delta(La:5d_{\pm 2})$  noted [6, 3, 3, 1], and  $6\sigma(La:5p_0,6s,5d_0;H:1s,2s,2p_0)$ ,  $3\pi(La:5p_{\pm 1},5d_{\pm 1};H:2p_{\pm 1})$ ,  $1\delta(La:5d_{\pm 2})$  noted [7, 3, 3, 1]. One can notice that the values of the relative energy with respect to the ground state  $T_e$  of the different electronic states depends on the number of valence electrons used in the theoretical calculation (Table 1 in supplementary material). In the present work we found that the 10 valence electrons is the best choice to obtain the good agreement with the fragmented values of  $T_e$ , for the different electronic states, in literature. The potential energy curves for the 9 singlet and 14 triplet electronic states in the representation  $^{2s+1}\Lambda^{(\pm)}$  in the range  $0.83\text{\AA} \leq R \leq 8.42\text{\AA}$  are given in Figs. (5.1-5.3)

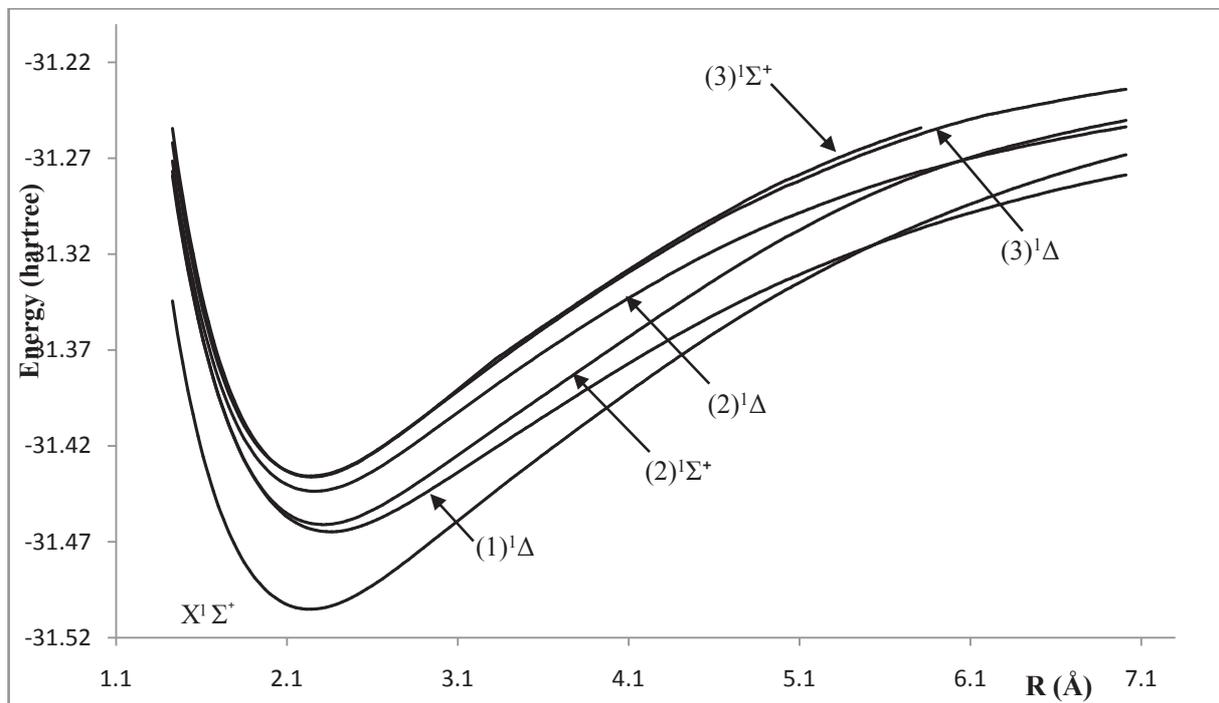


Fig.5.1: Potential energy curves for  $1\Sigma^+$  and  $1\Delta$  states of the molecule LaH.

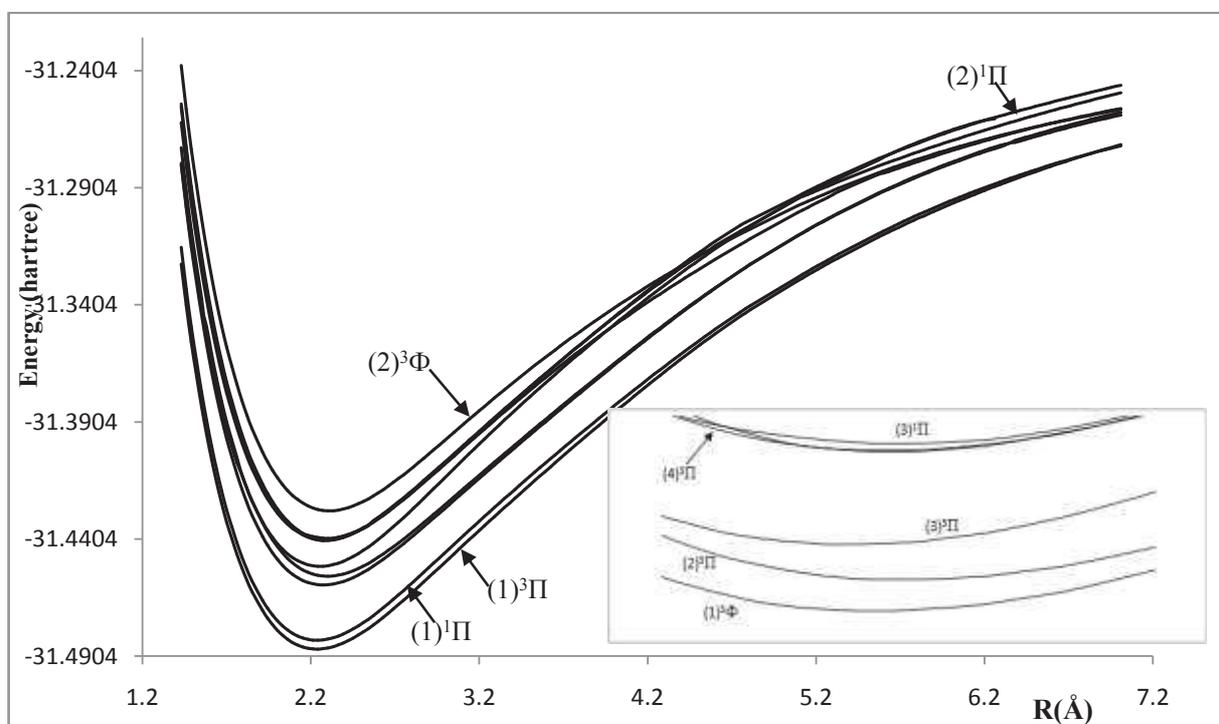
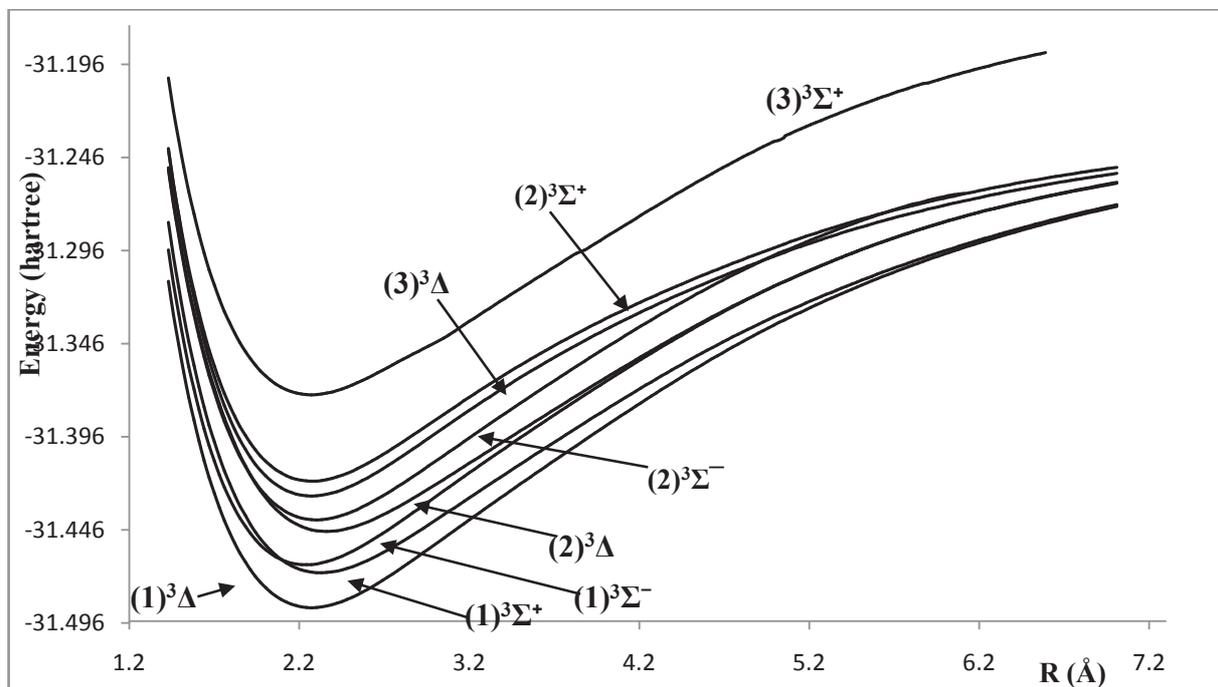


Fig.5.2: Potential energy curves for  $^1\Pi$ ,  $^3\Pi$  and  $^3\Phi$  states of the molecule LaH.Fig.5.3: Potential energy curves for  $^3\Sigma^+$  and  $^3\Delta$  states of the molecule LaH.

Using the number of valence electrons equal 10. In this range of  $R$ , some crossings and avoided crossings of abscissas  $R_c$  and  $R_{ac}$  respectively occur between the potential energy curves of different symmetries at large values of the internuclear distance (Table 5.1).

Table 5.1: Positions of the crossings and avoided crossings between the different electronic states of the molecule LaH.

state 1	state 2	Crossing between ( $n_1$ ) state1/( $n_2$ ) state2	Avoided crossing between ( $n_1$ ) state1/( $n_2$ ) state2	$R_c$ ( $\text{\AA}$ )	$R_{ac}$ ( $\text{\AA}$ )	$\Delta E_{ac}$ $\text{cm}^{-1}$
$^1\Sigma$	$^1\Delta$	1/1		5.91		
		2/2		1.58		
		2/2		1.76		
		2/2		5.54		
$^1\Delta$	$^1\Sigma$	3/3		2.24		

$^3\Pi$	$^1\Pi$	3/2		6.05		
		3/2		2.75		
$^1\Pi$	$^3\Phi$	3/2		5.57		
$^3\Pi$	$^3\Phi$	4/2		3.56		
		3/2		6.11		
$^3\Sigma$	$^3\Delta$	2/3		1.38		
		2/3		6.19		
		2/2		1.95		
		2/2		1.40		
$^3\Sigma$	$^3\Sigma$		1/2		3.0219	18.5521

$R_{ac}$  and  $\Delta E_{ac}$  are respectively the internuclear distance and the energy difference at the avoided crossing between the two corresponding electronic states.

The calculated values of  $R_c$ ,  $R_{ac}$  and the energy gap at avoided crossings  $E_{ac}$  are given in Table 1. Such crossings or avoided crossings can dramatically alter the stability of the considered molecule. The equilibrium bond distances  $R_e$ , the harmonic vibrational frequencies  $\omega_e$ , the relative energy separations  $T_e$ , and the rotational constants  $B_e$ , have been obtained by fitting the calculated energy values of the different investigated electronic states into a polynomial in  $R$  around the internuclear distance at equilibrium  $R_e$ . Using the values of 10 valence electrons for the investigated electronic states, the calculated energy  $T_e$ , the spectroscopic constants  $\omega_e$ ,  $B_e$  and  $R_e$  are given in Table 5.2 along with the theoretical values [5, 19-23, 25, 28] and the fragmented experimental data [6, 24, 26-27] in literature.

Table 5.2: Spectroscopic constants for the electronic states of the molecule LaH.

State	$T_e$ (cm $^{-1}$ )	$R_e$ (Å)	$\omega_e$ (cm $^{-1}$ )	$B_e$ (cm $^{-1}$ )
$X^1\Sigma^+$	0.0	2.235 <sup>(a1)</sup>	1353.26 <sup>(a1)</sup>	3.37 <sup>(a)</sup>
		2.031969(20) <sup>(b)</sup>		4.080534(80) <sup>(b)</sup>
		2.005 <sup>(c)</sup>	1418(2) <sup>(n)</sup>	
		2.027 <sup>(d1)</sup>	1416 <sup>(c)</sup>	
		2.016 <sup>(d2)</sup>	1446 <sup>(d1)</sup>	
		2.11 <sup>(e1)</sup>	1456 <sup>(d2)</sup>	
		2.08 <sup>(e2)</sup>	1350 <sup>(e1)</sup>	
		2.05 <sup>(e3)</sup>	1380 <sup>(e2)</sup>	
		2.032 <sup>(f)</sup>	1420 <sup>(e3)</sup>	
			1390 <sup>(f)</sup>	

		2.064 <sup>(j1)</sup> 2.057 <sup>(j2)</sup> 2.045 <sup>(j3)</sup> 2.05 <sup>(g1)</sup> 2.06 <sup>(g2)</sup> 2.00 <sup>(g3)</sup> 2.00 <sup>(g4)</sup> 2.00 <sup>(g5)</sup> 2.06 <sup>(o1)</sup> 2.07 <sup>(o2)</sup> 2.09 <sup>(o3)</sup> 2.08 <sup>(o4)</sup> 2.08 <sup>(k)</sup>	1421.1 <sup>(j1)</sup> 1443.1 <sup>(j2)</sup> 1448.2 <sup>(j3)</sup> 1516 <sup>(g1)</sup> 1510 <sup>(g2)</sup> 1521 <sup>(g3)</sup>	
(1) <sup>3</sup> Π	3880.3 <sup>(a1)</sup> 3307.3 <sup>(a2)</sup> 5147 <sup>(k)</sup>	2.235 <sup>(a1)</sup> 2.12 <sup>(k)</sup>	1341.37 <sup>(a1)</sup> 1341 <sup>(k)</sup>	3.37 <sup>(a1)</sup>
(1) <sup>3</sup> Δ	3916.3 <sup>(a1)</sup> 4121.7 <sup>(a2)</sup>  3987.2 <sup>(j2)</sup>  2805 <sup>(k)</sup>	2.272 <sup>(a1)</sup>  2.09 <sup>(b)</sup> 2.109 <sup>(j1)</sup> 2.106 <sup>(j2)</sup> 2.116 <sup>(j3)</sup> 2.13 <sup>(k)</sup>	1314.98 <sup>(a1)</sup>  1355 <sup>(n)</sup>  1342.1 <sup>(j1)</sup> 1356.9 <sup>(j2)</sup> 1322.9 <sup>(j3)</sup> 1352 <sup>(k)</sup>	3.25 <sup>(a1)</sup>
(1) <sup>1</sup> Π	4711.5 <sup>(a1)</sup> 4174.3 <sup>(a2)</sup> 4533.6 <sup>(n)</sup>  6226 <sup>(k)</sup>	2.235 <sup>(a1)</sup>  2.074276 <sup>(b)</sup> 2.13 <sup>(k)</sup>	1356.74 <sup>(a1)</sup>   1309 <sup>(k)</sup>	3.36 <sup>(a1)</sup>  3.915776 <sup>(b)</sup>
(1) <sup>1</sup> Δ	8032.9 <sup>(a1)</sup> 7960.7 <sup>(a2)</sup> 6510 <sup>(k)</sup>	2.326 <sup>(a1)</sup> 2.16 <sup>(k)</sup>	1272.64 <sup>(a1)</sup> 1299 <sup>(k)</sup>	3.11 <sup>(a1)</sup>
(2) <sup>1</sup> Δ	8863.8 <sup>(a1)</sup> 9393.8 <sup>(a2)</sup> 17427 <sup>(k)</sup>	2.18 <sup>(k)</sup>	1234 <sup>(k)</sup>	
(1) <sup>3</sup> Σ <sup>+</sup>	8969.1 <sup>(a1)</sup> 8049.2 <sup>(a2)</sup>  11794 <sup>(k)</sup>	2.236 <sup>(a1)</sup>  2.156 <sup>(j1)</sup> 2.153 <sup>(j2)</sup> 2.166 <sup>(j2)</sup> 2.20 <sup>(k)</sup>	1338.11 <sup>(a1)</sup>  1258.3 <sup>(j1)</sup> 1272.5 <sup>(j2)</sup> 1244.1 <sup>(j3)</sup> 1203 <sup>(k)</sup>	3.36 <sup>(a1)</sup>
(2) <sup>1</sup> Σ <sup>+</sup>	9688.2 <sup>(a1)</sup> 9963.4 <sup>(a2)</sup> 9508 <sup>(m)</sup> 13025 <sup>(k)</sup>	2.310 <sup>(a1)</sup>  2.20 <sup>(k)</sup>	1288.97 <sup>(a1)</sup>  1230 <sup>(k)</sup>	3.15 <sup>(a1)</sup>
(2) <sup>3</sup> Π	9894.9 <sup>(a1)</sup> 9534.0 <sup>(a2)</sup> 11956 <sup>(k)</sup>	2.272 <sup>(a1)</sup> 2.19 <sup>(k)</sup>	1329.48 <sup>(a1)</sup> 1228 <sup>(k)</sup>	3.26 <sup>(a1)</sup>
(1) <sup>3</sup> Φ	10709.6 <sup>(a1)</sup> 10415.2 <sup>(a2)</sup>  10612 <sup>(k)</sup>	2.297 <sup>(a1)</sup>  2.14 <sup>(b)</sup> 2.19 <sup>(k)</sup>	1297.59 <sup>(a1)</sup>  1240 <sup>(k)</sup>	3.19 <sup>(a1)</sup>
(3) <sup>3</sup> Π	11638.2 <sup>(a1)</sup> 11561.1 <sup>(a2)</sup> 15880 <sup>(k)</sup>	2.253 <sup>(a1)</sup> 2.09 <sup>(k)</sup>	1363.12 <sup>(a1)</sup> 1377 <sup>(k)</sup>	3.31 <sup>(a1)</sup>

Chapter five: Theoretical calculation of the low-lying Electronic states of the molecule LaH

(2) <sup>3</sup> Δ	12902.3 <sup>(a1)</sup> 13128.4 <sup>(a2)</sup> 14020 <sup>(k)</sup>	2.361 <sup>(a1)</sup>  2.24 <sup>(k)</sup>	1255.60 <sup>(a1)</sup>  1166 <sup>(k)</sup>	3.02 <sup>(a1)</sup>
(3) <sup>1</sup> Δ	13502.3 <sup>(a1)</sup> 12741.36 <sup>(a2)</sup> 20109 <sup>(k)</sup>	2.261 <sup>(a1)</sup>  2.20 <sup>(k)</sup>	1316.43 <sup>(a1)</sup>  1226 <sup>(k)</sup>	3.29 <sup>(a1)</sup>
(2) <sup>1</sup> Π	14050.2 <sup>(a1)</sup> 13997.3 <sup>(a2)</sup> 15729 <sup>(k)</sup>	2.280 <sup>(a1)</sup>  2.16 <sup>(k)</sup>	1696.53 <sup>(a1)</sup>  1293 <sup>(k)</sup>	3.27 <sup>(a1)</sup>
(4) <sup>3</sup> Π	14081.8 <sup>(a1)</sup> 13768.3 <sup>(a2)</sup>	2.281 <sup>(a1)</sup>	1348.00 <sup>(a1)</sup>	3.24 <sup>(a1)</sup>
(3) <sup>1</sup> Π	14259.8 <sup>(a1)</sup> 14220.8 <sup>(a2)</sup> 20170 <sup>(k)</sup>	2.29 <sup>(a1)</sup>	1460.44 <sup>(a1)</sup>	3.13 <sup>(a1)</sup>
(1) <sup>3</sup> Σ <sup>-</sup>	14268.1 <sup>(a1)</sup>  15622.7 <sup>(p)</sup> 12035 <sup>(k)</sup>	2.303 <sup>(a1)</sup>  2.18 <sup>(k)</sup>	1316.93 <sup>(a1)</sup>  1247 <sup>(k)</sup>	3.18 <sup>(a1)</sup>
(4) <sup>1</sup> Δ	15138.2 <sup>(a1)</sup> 14618 <sup>(a2)</sup> 20109 <sup>(k)</sup>	2.243 <sup>(a1)</sup>  2.20 <sup>(k)</sup>	1394.48 <sup>(a1)</sup>  1226 <sup>(k)</sup>	3.34 <sup>(a1)</sup>
(2) <sup>3</sup> Φ	16844.3 <sup>(a1)</sup> 17110.2 <sup>(a2)</sup>	2.309 <sup>(a1)</sup>	1311.22 <sup>(a1)</sup>	3.15 <sup>(a1)</sup>
(3) <sup>3</sup> Δ	17075.0 <sup>(a1)</sup> 16550.3 <sup>(a2)</sup> 23256 <sup>(k)</sup>	2.271 <sup>(a1)</sup>  2.10 <sup>(k)</sup>	1334.13 <sup>(a1)</sup>  1364 <sup>(k)</sup>	3.26 <sup>(a1)</sup>
(2) <sup>3</sup> Σ <sup>+</sup>	18816.3 <sup>(a1)</sup> 18256.1 <sup>(a2)</sup>	2.273 <sup>(a1)</sup>	1328.65 <sup>(a1)</sup>	3.26 <sup>(a1)</sup>

a1 and a2 represent the calculated values of the present work using 10 and 8 valence electrons respectively, <sup>b</sup>Ref.[6], <sup>c</sup>Ref.[19], <sup>d1,d2</sup>Ref.[20], <sup>e1,e2,e3</sup>Ref<sup>Theo</sup>.[21], <sup>f</sup>Ref.[22], <sup>g</sup>Ref.[23], <sup>j</sup>Ref.[25], <sup>k</sup>Ref.[5], <sup>m</sup>Ref.[26], <sup>n</sup>Ref.[27], <sup>o</sup>Ref.[28].

From the calculated values of  $\omega_e$  for the ground and excited states we can approximate our calculated values of  $T_e$  with the experimental values  $T_{v=0}(\text{ground}) - T_{v=0}(\text{excited state})$ . By comparing our calculated values of  $T_e$  to those of Mukund *et al.* [27], obtained experimentally, we can find that the first excited state in the present work is  $(1)^3\Pi$  instead of  $a^3\Delta$ ; but the average value of  $T_e$  for  $b^3\Pi_{0-}$ ,  $b^3\Pi_{0+}$  and  $b^3\Pi_1$  [27] can be approximated to our calculated value with relative difference of 6.5% while the theoretical value of Das and Balasubramanian [5] are higher than our calculated value by  $1267 \text{ cm}^{-1}$  by examining Table 5.3.

States	$T_e \text{ (cm}^{-1}\text{)}$				
	2 Valence electrons	6 Valence Electrons	8 Valence electrons	10 Valence electrons	8 Valence electrons with f
$X^1\Sigma^+$	0.0	0.0	0.0	0.0	0.00
$(1)^3\Pi$	2589.62 <sup>(a1)</sup>	2748.35 <sup>(a2)</sup>	3307.33 <sup>(a3)</sup>	3880.29 <sup>(a4)</sup>	2795.29
$(1)^3\Delta$	2432.65 <sup>(a1)</sup>	2412.90 <sup>(a2)</sup>	4121.69 <sup>(a3)</sup>	3916.29 <sup>(a4)</sup>	3085.55
$(1)^1\Pi$	2972.96 <sup>(a1)</sup>	3321.83 <sup>(a2)</sup>	4174.26 <sup>(a3)</sup>	4711.53 <sup>(a4)</sup>	3600.97
$(1)^1\Delta$	5967.24 <sup>(a1)</sup>	6242.21 <sup>(a2)</sup>	7960.73 <sup>(a3)</sup>	8032.89 <sup>(a4)</sup>	8403.79
$(1)^3\Sigma^+$	7564.48 <sup>(a1)</sup>	7709.67 <sup>(a2)</sup>	8049.22 <sup>(a3)</sup>	8969.14 <sup>(a4)</sup>	10891.47
$(2)^1\Delta$	6935.60 <sup>(a1)</sup>	7067.81 <sup>(a2)</sup>	9393.82 <sup>(a3)</sup>	8863.84 <sup>(a4)</sup>	12620.82
$(2)^1\Sigma^+$	9467.14 <sup>(a1)</sup>	8988.36 <sup>(a2)</sup>	9963.40 <sup>(a3)</sup>	9688.15 <sup>(a4)</sup>	11624.89
$(2)^3\Pi$	6446.32 <sup>(a1)</sup>	7028.24 <sup>(a2)</sup>	9533.97 <sup>(a3)</sup>	9894.85 <sup>(a4)</sup>	8395.49
$(1)^3\Phi$	8108.20 <sup>(a1)</sup>	8163.15 <sup>(a2)</sup>	10415.22 <sup>(a3)</sup>	10709.65 <sup>(a4)</sup>	9819.06
$(3)^3\Pi$	11585.25 <sup>(a1)</sup>	11058.72 <sup>(a2)</sup>	11561.05 <sup>(a3)</sup>	11638.18 <sup>(a4)</sup>	12039.99
$(2)^3\Delta$	10574.89 <sup>(a1)</sup>	10429.85 <sup>(a2)</sup>	13128.43 <sup>(a3)</sup>	12902.27 <sup>(a4)</sup>	14560.32
$(3)^1\Delta$	11429.62 <sup>(a1)</sup>	11315.37 <sup>(a2)</sup>	12741.36 <sup>(a3)</sup>	13502.33 <sup>(a4)</sup>	13821.59
$(2)^1\Pi$	11969.40 <sup>(a1)</sup>	11836.84 <sup>(a2)</sup>	13997.29 <sup>(a3)</sup>	14050.23 <sup>(a4)</sup>	13005.94
$(4)^3\Pi$	12671.48 <sup>(a1)</sup>	12009.97 <sup>(a2)</sup>	13768.28 <sup>(a3)</sup>	14081.84 <sup>(a4)</sup>	15016.25
$(3)^1\Pi$	14414.29 <sup>(a1)</sup>	12615.40 <sup>(a2)</sup>	14220.78 <sup>(a3)</sup>	14259.83 <sup>(a4)</sup>	16632.99
$(2)^3\Sigma^-$	11861.31 <sup>(a1)</sup>	11310.25 <sup>(a2)</sup>	14391.29 <sup>(a3)</sup>	14268.08 <sup>(a4)</sup>	13020.36
$(4)^1\Delta$	13048.59 <sup>(a1)</sup>	12516.57 <sup>(a2)</sup>	14618.66 <sup>(a3)</sup>	15138.24 <sup>(a4)</sup>	14721.86
$(2)^3\Phi$	15536.32 <sup>(a1)</sup>	14446.12 <sup>(a2)</sup>	17110.18 <sup>(a3)</sup>	16844.33 <sup>(a4)</sup>	17697.89
$(3)^3\Delta$	15632.46 <sup>(a1)</sup>	15263.90 <sup>(a2)</sup>	16550.25 <sup>(a3)</sup>	17074.98 <sup>(a4)</sup>	17578.94
$(2)^3\Sigma^+$	17497.65 <sup>(a1)</sup>	17007.76 <sup>(a2)</sup>	18256.12 <sup>(a3)</sup>	18816.25 <sup>(a4)</sup>	19024.14
$(3)^3\Sigma^+$	30323.49 <sup>(a1)</sup>	28967.78 <sup>(a2)</sup>			30165.73

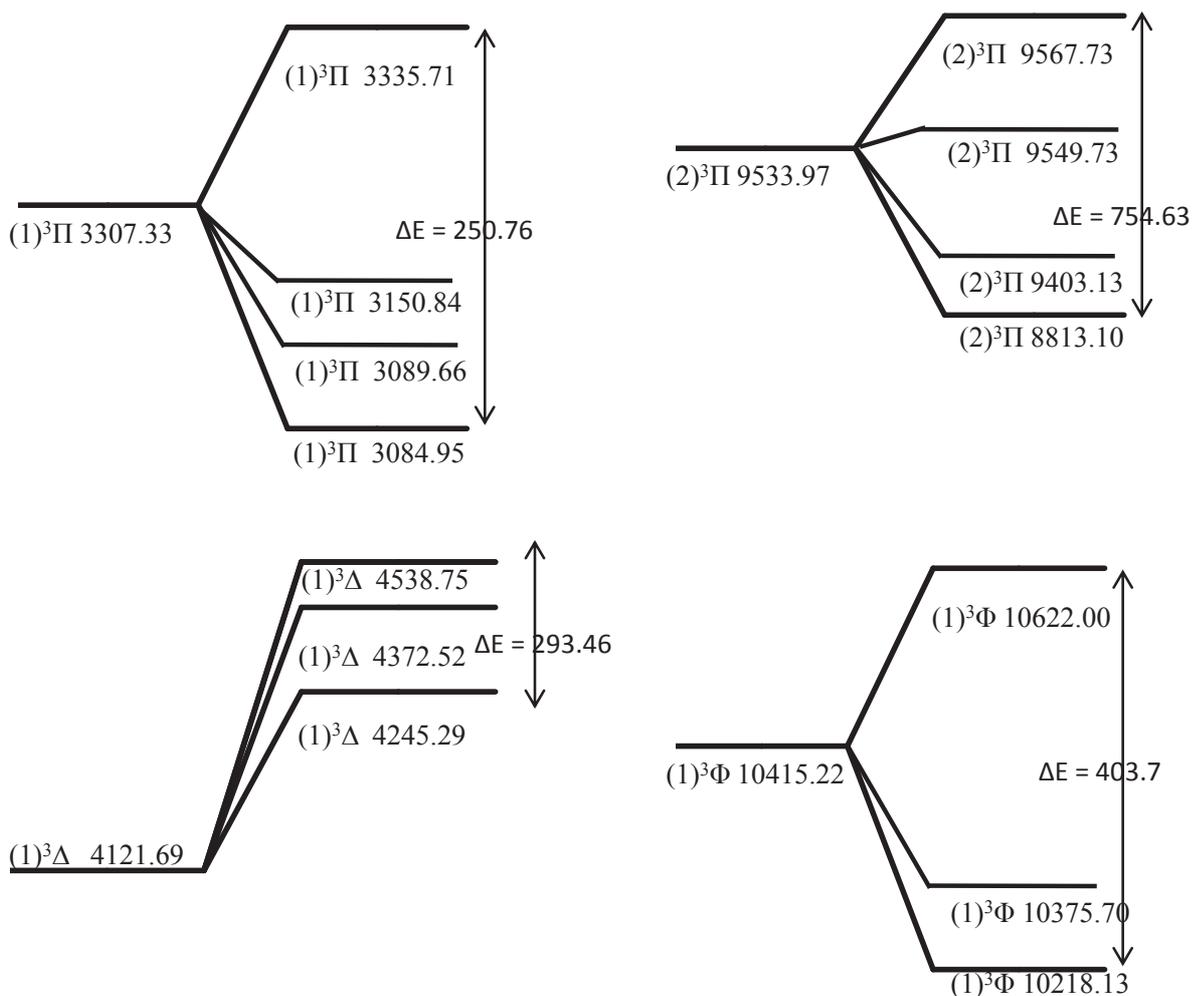
Table 5.3. Calculated values of the transition energy with respect to the ground state obtained by using different valence electrons

One can find that the first excited state is  $^1\Delta$  by adopting the small number of valence electrons 2 and 6, but for the higher valence electron 8, and 10 we find that the ground state is  $^3\Pi$ . Since the first excited state of Mukund *et al.* [27] is the  $a^3\Delta$  our calculated value of  $T_e$  for this state is higher than those of Mukund *et al.* [27] and Das and Balasubramanian [5] but it is in excellent agreement with that given by Wang *et al.* [25] based on the MP2/6-311++G(d,p)/SDD calculation. For the electronic state  $(1)^1\Pi$ , our calculated value of  $T_e$  is in good agreement with that given in Ref. [27] with relative difference 3.9% but it is lower than that of Ref. [5] by  $1515\text{ cm}^{-1}$ , while our calculated value of  $T_e$  for the  $(1)^1\Delta$  is higher than that of Mukund *et al.* [27] by about  $2000\text{ cm}^{-1}$ . Our calculated values of  $8863.8\text{ cm}^{-1} \leq T_e < 19000\text{ cm}^{-1}$  are smaller than those calculated by Das and Balasubramanian [5] except the values of the two electronic states  $(1)^3\Phi$  and  $(1)^3\Sigma^-$  with relative difference varies between 0.9% and 49% which may be explained by the small distribution of the three electrons in the active space and one electron in the external space in all possible ways [5]. In the same range of  $T_e$  our calculated values are in very good agreement with the experimental data [26] for the state  $(2)^1\Sigma^+$  with relative difference of 1.9% and acceptable agreement for the state  $(1)^3\Sigma^-$  with relative difference 8.7% [24]. By comparing our calculated value for the transition energy  $T_e[(1)^3\Phi] - T_e[(1)^3\Delta] = 6793\text{ cm}^{-1}$  to the average value of the experimental partial transitions  $d^3\Phi_i - a^3\Delta_i$  [6] one can find an acceptable agreement with relative difference 10% which is better than that given by Das and Balasubramanian [5] which is equal 27%. Yarlagadda *et al.* [24] assigned to the states D1 and E1 in the transitions  $(0, 0) D1 - X^1\Sigma^+$  and  $(0, 0) E1 - X^1\Sigma^+$  the state

$^1\Pi$ , our calculated value of  $T_e [(3)^1\Pi] = 14259.8\text{cm}^{-1}$  while that of Ref.[5] equal to  $20170\text{cm}^{-1}$ . The  $18509\text{cm}^{-1}$  band observed experimentally [24, 29] is assigned to the transition  $0^+ - a^3\Delta_1$  by Ram and Bernath [6] while Yarlagadda *et al.* [24] could not assign this band to this transition. In the present work the transitions  $(1)^1\Sigma^+ - (3)^3\Delta$  and  $(1)^1\Sigma^+ - (2)^3\Sigma^+$  are calculated respectively as  $17075.0\text{cm}^{-1}$  and  $18816.3\text{cm}^{-1}$  while the first transition is found to be  $23256\text{cm}^{-1}$  by Das and Balasubramanian [5]. The comparison of our calculated values of  $\omega_e$  with those obtained experimentally [27] for the ground  $X^1\Sigma^+$  and  $(1)^3\Delta$  states shows a good accuracy with relative differences 4.6% and 2.9% respectively. While the comparison with those obtained theoretically for all the investigated electronic states shows a very good agreement with relative difference  $0.0\% \leq \Delta\omega_e/\omega_e \leq 12.4\%$ . Our calculated values of  $R_e$  for the 4 electronic states  $X^1\Sigma^+$ ,  $(1)^3\Delta$ ,  $(1)^1\Pi$ ,  $(1)^3\Phi$  are larger than those obtained experimentally by Ram and Bernath [6] with the relative differences 9.0%, 8.0%, 7.2% and 6.8% respectively. The comparison of our values of  $R_e$ , for the different investigated electronic states, with those obtained theoretically in literature shows also the good agreement with an average difference of  $0.10\text{cm}^{-1}$ . The agreement becomes less by comparing our calculating value of  $B_e$  with the experimental data [6] for the 2 states  $X^1\Sigma^+$  and  $(1)^1\Pi$  with relative difference 17.4% and 14.4% respectively. We noticed that the use of different values of the valence electrons has poor influence on the values of rotational constants  $B_e$  for the different electronic states.

### 5.3 Spin-Orbit effect

By taking into consideration the spin orbit effect of the molecule LaH we give in figure (5.4) the energy splitting of the electronic states  $(1, 2)^3\Pi$ ,  $(1)^3\Delta$ ,  $(1)^3\Phi$  and  $(1)^3\Sigma^+$ .



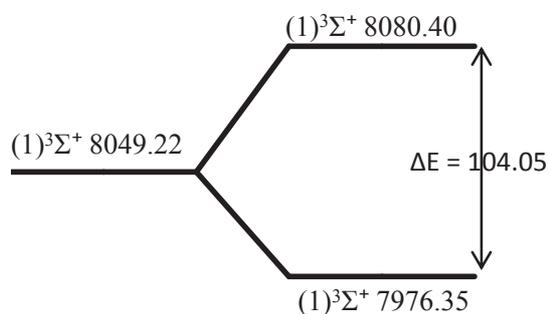


Fig 5.4: Spin-orbit splitting occurring in the electronic states of the LaH molecule in  $\text{cm}^{-1}$ .

For these states one can notice that the largest energy splitting is for the  $(2)^3\Pi$  and the corresponding spectroscopic constants in the  $\Omega$ -representation are given in Table 5.4. There is no comparison of these values with other results since they are given here for the first time.

Table 5.4: transition energies  $T_e$ , equilibrium internuclear distances  $R_e$ , and harmonic frequencies  $\omega_e$  for  $\Omega$ -states of the molecule LaH using 8valence electrons.

Symmetry	States	$T_e$ (cm <sup>-1</sup> )	$R_e$ (Å)	$\omega_e$ (cm <sup>-1</sup> )
$\Omega=0^+$	$X^1\Sigma^+$	0.0	2.215	1357.43
	$[(1)^3\Pi]$	3084.95	2.22	1239.51
	$[(2)^1\Sigma^+]$	9963.40	2.296	1285.16
	$[(2)^3\Pi]$	9533.72	2.274	1516.17
$\Omega=0^-$	$[(1)^3\Pi]$	3089.66	2.225	1361.64
	$[(1)^3\Sigma^+]$	7976.35	2.277	1840.47
	$[(2)^3\Pi]$	9567.73	2.276	1453.34
$\Omega=1$	$[(1)^3\Pi]$	3150.84	2.214	1294.28
	$[(1)^3\Delta]$	4245.29	2.246	1388.33
	$[(1)^1\Pi]$	4174.26	2.217	1358.89
	$[(1)^3\Sigma^+]$	8080.40	2.272	1647.50
	$[(2)^3\Pi]$	9403.13	2.3	5726.32
$\Omega=2$	$[(1)^3\Pi]$	3335.71	2.221	1324.80
	$[(1)^3\Delta]$	4372.52	2.227	1392.31
	$[(1)^1\Delta]$	7960.73	2.329	1228.79
	$[(2)^1\Delta]$	9393.82	2.239	1321.04
	$[(2)^3\Pi]$	8813.10	2.267	1238.39
	$[(1)^3\Phi]$	10218.13	2.277	1403.06
$\Omega=3$	$[(1)^3\Delta]$	4538.75	2.254	1231.91
	$[(1)^3\Phi]$	10375.70	2.288	1268.50
$\Omega=4$	$[(1)^3\Phi]$	10622.00	2.291	1237.20

## 5.4 Vibration-rotation calculation

The vibration rotation calculation is performed by using the cubic spline interpolation between each two constructive points of the potential energy curves obtained from the ab initio calculation. Then, we use the canonical functions approach [11, 16-18] to calculate the eigenvalue  $E_v$ , and the rotational constant  $B_v$  for the different investigated vibrational levels  $v$ . By using the calculated values of  $E_v$  the abscissas of the turning point  $R_{\min}$  and  $R_{\max}$  have been determined for different vibrational levels for fifteen low-lying electronic states of LaH molecule ( $X^1\Sigma^+$ ,  $(1)^1\Delta$ ,  $(2)^1\Delta$ ,  $(3)^1\Delta$ ,  $(2)^1\Sigma$ ,  $(1)^1\Pi$ ,  $(2)^1\Pi$ ,  $(1)^3\Delta$ ,  $(2)^3\Sigma$ ,  $(2)^3\Delta$ ,  $(3)^3\Delta$ ,  $(1)^3\Pi$ ,  $(2)^3\Pi$ ,  $(1)^3\Phi$ ,  $(1)^3\Sigma$ ). These constants for the electronics states  $X^1\Sigma^+$  and  $(1)^3\Delta$  are reported in Tables 4 as example. The data for the other electronic states are given in Appendix IV. The comparison of these values calculated for  $X^1\Sigma^+$  with the experimental data, obtained from the pure rotational spectra of LaH [6], shows a barley acceptable agreement with relative difference  $\Delta B_v/B_v$  equal 16% and 15% respectively for  $v = 0$  and  $v = 1$ .

Table (5.4): Values of the eigenvalues  $E_v$ , the rotational constants  $B_v$  and the abscissa of the turning points  $R_{\min}$  and  $R_{\max}$  for the different vibrational levels of  $(1)^1\Sigma^+$ ,  $(1)^3\Delta$  states of the LaH molecule.

$(1)^1\Sigma^+$					$(1)^3\Delta$				
$v$	$E_v$ $\text{cm}^{-1}$	$B_v$ $\text{cm}^{-1}$	$R_{\min}$ $\text{Å}$	$R_{\max}$ $\text{Å}$	$v$	$E_v$ $\text{cm}^{-1}$	$B_v$ $\text{cm}^{-1}$	$R_{\min}$ $\text{Å}$	$R_{\max}$ $\text{Å}$
0	671.37*	3.389 4.041 <sup>(b)</sup> 4.041837 <sup>(b)</sup>	2.074	2.391	655.042	3.262	2.115	2.115	2.436
1	1995.89	3.350 3.964 <sup>(b)</sup>	1.975	2.529	1943.959	3.218	2.016	2.016	2.578
2	3293.412	3.308	1.912	2.634	3201.588	3.172	1.955	1.955	2.686
3	4563.31	3.263	1.825	2.726	4430.715	3.126	1.905	1.905	2.78
4	5805.309	3.216	1.825	2.810	5631.745	3.077	1.865	1.865	2.868
5	7019.436	3.167	1.791	2.891	6802.586	3.027	1.832	1.832	2.951
6	8205.703	3.116	1.762	2.969	7945.941	2.976	1.802	1.802	3.032
7	9364.49	3.065	1.736	3.045	9060.734	2.924	1.776	1.776	3.111

8	10496.58	3.013	1.712	3.120	10148.96	2.872	1.753	1.753	3.188
9	11603.17	2.962	1.691	3.193	11210.82	2.823	1.732	1.732	3.264
10	12684.85	2.910	1.672	3.266	12249.41	2.774	1.712	1.712	3.339
11	13741.65	2.859	1.654	3.339	13265.63	2.727	1.694	1.694	3.412
12	14774.79	2.809	1.638	3.411	14259.95	2.68	1.678	1.678	3.485
13	15786.12	2.761	1.622	3.482	15234.5	2.635	1.662	1.662	3.557
14	16776.52	2.713	1.608	3.553	16189.99	2.592	1.648	1.648	3.629
15	17746.97	2.667	1.595	3.623	17127.56	2.55	1.634	1.634	3.669
16	18698.88	2.623	1.582	3.692	18048.54	2.51	1.621	1.621	3.769
17	19632.91	2.580	1.570	3.762	18953.23	2.471	1.609	1.609	3.838
18	20550.19	2.539	1.559	3.830	19842.68	2.433	1.598	1.598	3.907
19	21451.29	2.498	1.548	3.898	20717.41	2.396	1.587	1.587	3.975
20	22337.08	2.46	1.538	3.966	21577.77	2.36	1.577	1.577	4.043
21	23207.92	2.421	1.529	4.034	22423.95	2.324	1.567	1.567	4.111
22	24064.51	2.384	1.520	4.101	23256.53	2.288	1.557	1.557	4.179
23	24907.05	2.348	1.511	4.168	24075.45	2.253	1.548	1.548	4.246
24	25736.07	2.312	1.502	4.235	24880.77	2.219	1.54	1.54	4.314
25	26551.73	2.277	1.494	4.302	25672.4	2.183	1.531	1.531	4.382
26	27354.3	2.242	1.487	4.368	26450.09	2.148	1.523	1.523	4.451
27	28143.95	2.207	1.479	4.435	27213.82	2.113	1.518	1.518	4.52
28	28920.85	2.174	1.472	4.503	27963.69	2.078	1.509	1.509	4.59
29	29685.38	2.141	1.465	4.570	28699.53	2.043	1.502	1.502	4.66
30	30437.66	2.108	1.459	4.637	29421.34	2.008	1.495	1.495	4.732
31	31177.91	2.076	1.459	4.705	30129.33	1.973	1.488	1.488	4.803
32	31906.5	2.043	1.446	4.772	30823.48	1.939	1.482	1.482	4.876
33	32623.63	2.014	1.440	4.840	31504.65	1.907	1.476	1.476	4.95
34	33329.76	1.985	1.435	4.908	32174.16	1.878	1.471	1.471	5.024
35	34025.67	1.957	1.429	4.976	32834.37	1.854	1.465	1.465	5.089
36	34712.51	1.933	1.424	5.041	33486.31	1.829	1.46	1.46	5.161
37	35391.8	1.911	1.419	5.104	34126.63	1.793	1.454	1.454	5.237
38	36063.72	1.886	1.413	5.172					
39	36725.3	1.854	1.409	5.241					
40	37373.05	1.82	1.404	5.309					
41	38009.73	1.797	1.399	5.378					
42	38640.17	1.776	1.395	5.447					
43	39260.72	1.744	1.391	5.516					

\*First entry is for the present work, <sup>b</sup>Ref [6], <sup>h</sup>Ref [24].

## 5.5 Conclusion

In the present work, an ab initio investigation for 24 low-lying molecular states of LaH molecule has been performed via CAS-SCF/MRCI method.

Multireference CI calculations (single and double excitations + Davidson corrections) in which the entire CAS-SCF configuration space was used as the reference were performed to account the correlation effects. This calculation has been done in 4 different ways using 2, 6, 8, and 10 valence electrons. The potential energy curves along with the spectroscopic constants  $T_e$ ,  $r_e$ ,  $\omega_e$  and  $B_e$  have been obtained for the investigated electronic states of the molecule LaH. The number of valence electrons used in the calculation has an influence on the calculated values of  $T_e$  for the different electronic states. One can consider this influence is the responsible of the discrepancy between our calculated values of  $T_e$  and those of Das and Balasubramanian [5] for some electronic states while the comparison with other theoretical calculation [25] shows an excellent agreement. Taking advantage of the electronic structure of the investigated electronic states of LaH molecule and by using the canonical functions approach, the vibrational eigenvalues  $E_v$ , the rotational constant  $B_v$ , and the abscissas of the turning points  $R_{\min}$  and  $R_{\max}$  were calculated for the 22 low-lying electronic states. The comparison of our calculated data in the present work for the molecule LaH with those obtained theoretically and experimentally in literature shows an overall good agreement except the values of  $T_e$  investigated in Ref. [6] for some electronic states.

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## Conclusion and Perspective

Ab initio calculations provide us with a valuable tool that helps people understand problems with the use of a computer and allow one to investigate the molecular structure and properties of atoms, molecules and solids. Computational studies can in general be carried out in order to find a starting point for laboratory experiments, or to assist in understanding experimental data. Thus computational studies can explore new properties and guide new experimental works. Heavy polar diatomic molecules form suitable candidates for computational investigations, particularly due to their rich inner electronic structures and due to their importance in several areas of science, as astrophysics, chemistry, ultracold interactions, and molecular quantum computing. In the present work, we perform *ab initio* calculations for the electronic structure of the Boron-nitrides, silicon nitride and Lanthanum monohydride (BN, SiN and LaH). The potential energy curves (PEC) for the ground and excited electronic states were constructed as a function of the internuclear distance  $R$ . Then by fitting the calculated potential energy curves in to a polynomial in  $R$  several spectroscopic constants were calculated, such as the transition energy  $T_e$  relative to the ground state, the harmonic vibrational frequencies  $\omega_e$ , the equilibrium internuclear distances  $R_e$ , and the rotational constants  $B_e$  and  $D_e$ . Relativistic spin orbit effects were included by the method of effective core potentials (ECP) and then based on the calculated PECs vibro-rotational calculations were performed for the vibrational and rotational energy levels of LaH molecule. Our calculations yielded accurate spectroscopic constants along with several physical and chemical properties that are within a few percent of the experimental values. Many other properties have

been also computed that weren't available in literature on the electronic structures of these molecules.

Our Perspective is to study in same way the molecule TiN and ZnO, therefore to calculate the potential energy curves (PEC) for the ground and excited electronic states. Then the spectroscopic constants, such as the transition energy  $T_e$  relative to the ground state, the harmonic vibrational frequencies  $\omega_e$ , the equilibrium internuclear distances  $R_e$ , and the rotational constants  $B_e$  and  $D_e$ . And To perform the Relativistic spin orbit effects by the method of effective core potentials (ECP) of (BN, SiN, TiN and ZnO). Then based on the calculated PECs we will do vibro-rotational calculations to calculate the vibrational and rotational energy levels of BN molecule (SiN, TiN and ZnO).

In other hand we will try to perform another theoretical calculation in the molecule (BN, SiN, TiN and ZnO) in the density functional theory DFT by using the WIEN2K program and we will try to link these calculations to our theoretical calculations in MOLPRO and we propose through this project to develop ceramic oxides and non-oxides in IEMM using an original method of preparation of thin films and nanostructures 1D and then to study the optical properties (i.e. absorbance and fluorescence) of the materials obtained in order to go back to their electronic structures.

This original method, "Atomic Layer Deposition (ALD)," allows "atom by atom" deposition of inorganic materials and can be used for the synthesis of ultra-thin layers (<100 nm). Initially employed for the synthesis of catalysts, this technique can also be applied to synthesis of materials of different types and morphologies such as oxide ceramics, non-oxide ceramics and metals.

Thus, we propose to control the morphology of these structures by combining ALD with replication techniques like chemical or physical template (i.e. alumina

membranes, membranes of polycarbonate, polystyrene spheres, and nanowires synthesized by electrospinning). Also, specific morphologies can be obtained (ie training nanotubes, concentric nanotubes, nanowires or hollow spheres of controlled porosity).

The chemical and physical characterization of materials obtained would correlate the optical properties (i.e. absorbance and fluorescence) and the change of electronic structures with the morphology of the nanostructures obtained (0D, 1D and 2D) and to better understands the effect of quantum confinement on these properties.

## APPENDIX I

MOLPRO INPUT DATA FILE FOR THE CALCULATION OF THE  
ELECTRONIC ENERGIES AND DIPOLE MOMENTS OF ALL THE  
42 STATES OF **BN** MOLECULE

```
***,Input file generated by gabedit;
Memory,4000000;
Gprint,basis;                ! Print basis information
Gprint,orbital;             ! Print orbitals in SCF and MCSCF

geomtyp=xyz
geometry={ANGSTROM;
2 ! number of atoms
GeomXYZ
B, 0.0, 0.0, 0.0
N, 0.0, 0.0, 1.334
}
basis={
s,B,cc-pVTZ;c
p,B,cc-pVTZ;c
d,B,cc-pVTZ;c
f,B,cc-pVTZ;c
s,N,cc-pVTZ;c
p,N,cc-pVTZ;c
d,N,cc-pVTZ;c
}
hf;
wf,12,1,0;
orbprint,1000;

multi;
occ,7,2,2,0;
closed,3,0,0,0;
core,0,0,0,0;

wf,12,1,0;state,9;
wf,12,2,0;state,4;
wf,12,3,0;state,4;
wf,12,4,0;state,5;

wf,12,1,2;state,8;
wf,12,2,2;state,5;
wf,12,3,2;state,5;
wf,12,4,2;state,5;

r0 = 1.21
step = 0.03
do i=1,7

r = r0 + (i-1)*step

dist(i) = r

geomtyp=xyz
geometry={ANGSTROM;
2 ! number of atoms
GeomXYZ
```

```
B,    0.0, 0.0, 0.0
N,    0.0, 0.0, r
}

multi;
occ,7,2,2,0;
closed,3,0,0,0;
core,0,0,0,0;

wf,12,1,0;state,9;
wf,12,2,0;state,4;
wf,12,3,0;state,4;
wf,12,4,0;state,5;

wf,12,1,2;state,8;
wf,12,2,2;state,5;
wf,12,3,2;state,5;
wf,12,4,2;state,5;

TRAN2,LXX,LYY,LZZ;
s_Lz_1_1(i)= sqrt(abs(LZLZ(1)))
s_Lz_1_2(i)= sqrt(abs(LZLZ(2)))
s_Lz_1_3(i)= sqrt(abs(LZLZ(3)))
s_Lz_1_4(i)= sqrt(abs(LZLZ(4)))
s_Lz_1_5(i)= sqrt(abs(LZLZ(5)))
s_Lz_1_6(i)= sqrt(abs(LZLZ(6)))
s_Lz_1_7(i)= sqrt(abs(LZLZ(7)))
s_Lz_1_8(i)= sqrt(abs(LZLZ(8)))
s_Lz_1_9(i)= sqrt(abs(LZLZ(9)))

s_Lz_2_1(i)= sqrt(abs(LZLZ(10)))
s_Lz_2_2(i)= sqrt(abs(LZLZ(11)))
s_Lz_2_3(i)= sqrt(abs(LZLZ(12)))
s_Lz_2_4(i)= sqrt(abs(LZLZ(13)))

s_Lz_3_1(i)= sqrt(abs(LZLZ(14)))
s_Lz_3_2(i)= sqrt(abs(LZLZ(15)))
s_Lz_3_3(i)= sqrt(abs(LZLZ(16)))
s_Lz_3_4(i)= sqrt(abs(LZLZ(17)))

s_Lz_4_1(i)= sqrt(abs(LZLZ(18)))
s_Lz_4_2(i)= sqrt(abs(LZLZ(19)))
s_Lz_4_3(i)= sqrt(abs(LZLZ(20)))
s_Lz_4_4(i)= sqrt(abs(LZLZ(21)))
s_Lz_4_5(i)= sqrt(abs(LZLZ(22)))

! triplet states
```

```
t_Lz_1_1(i)= sqrt(abs(LZLZ(23)))
t_Lz_1_2(i)= sqrt(abs(LZLZ(24)))
t_Lz_1_3(i)= sqrt(abs(LZLZ(25)))
t_Lz_1_4(i)= sqrt(abs(LZLZ(26)))
t_Lz_1_5(i)= sqrt(abs(LZLZ(27)))
t_Lz_1_6(i)= sqrt(abs(LZLZ(28)))
t_Lz_1_7(i)= sqrt(abs(LZLZ(29)))
t_Lz_1_8(i)= sqrt(abs(LZLZ(30)))
```

```
t_Lz_2_1(i)= sqrt(abs(LZLZ(31)))
t_Lz_2_2(i)= sqrt(abs(LZLZ(32)))
t_Lz_2_3(i)= sqrt(abs(LZLZ(33)))
t_Lz_2_4(i)= sqrt(abs(LZLZ(34)))
t_Lz_2_5(i)= sqrt(abs(LZLZ(35)))
```

```
t_Lz_3_1(i)= sqrt(abs(LZLZ(36)))
t_Lz_3_2(i)= sqrt(abs(LZLZ(37)))
t_Lz_3_3(i)= sqrt(abs(LZLZ(38)))
t_Lz_3_4(i)= sqrt(abs(LZLZ(39)))
t_Lz_3_5(i)= sqrt(abs(LZLZ(40)))
```

```
t_Lz_4_1(i)= sqrt(abs(LZLZ(41)))
t_Lz_4_2(i)= sqrt(abs(LZLZ(42)))
t_Lz_4_3(i)= sqrt(abs(LZLZ(43)))
t_Lz_4_4(i)= sqrt(abs(LZLZ(44)))
t_Lz_4_5(i)= sqrt(abs(LZLZ(45)))
```

```
!CI calculation
ci;
maxiti,maxiter,250,2500;
occ,7,2,2,0;
closed,3,0,0,0;
core,2,0,0,0;
wf,12,1,0;state,9;option,nstati=12;
```

```
s_e_sym1_1(i)= energd(1)
s_e_sym1_2(i)= energd(2)
s_e_sym1_3(i)= energd(3)
s_e_sym1_4(i)= energd(4)
s_e_sym1_5(i)= energd(5)
s_e_sym1_6(i)= energd(6)
s_e_sym1_7(i)= energd(7)
s_e_sym1_8(i)= energd(8)
s_e_sym1_9(i)= energd(9)
```

```
s_d_sym1_1(i)= DMZ(1)
s_d_sym1_2(i)= DMZ(2)
s_d_sym1_3(i)= DMZ(3)
s_d_sym1_4(i)= DMZ(4)
```

```
s_d_sym1_5(i)= DMZ(5)
s_d_sym1_6(i)= DMZ(6)
s_d_sym1_7(i)= DMZ(7)
s_d_sym1_8(i)= DMZ(8)
s_d_sym1_9(i)= DMZ(9)
```

```
table,dist,s_Lz_1_1,s_e_sym1_1,s_d_sym1_1
DIGITS,,8
table,dist,s_Lz_1_2,s_e_sym1_2,s_d_sym1_2
DIGITS,,8
table,dist,s_Lz_1_3,s_e_sym1_3,s_d_sym1_3
DIGITS,,8
table,dist,s_Lz_1_4,s_e_sym1_4,s_d_sym1_4
DIGITS,,8
table,dist,s_Lz_1_5,s_e_sym1_5,s_d_sym1_5
DIGITS,,8
table,dist,s_Lz_1_6,s_e_sym1_6,s_d_sym1_6
DIGITS,,8
table,dist,s_Lz_1_7,s_e_sym1_7,s_d_sym1_7
DIGITS,,8
table,dist,s_Lz_1_8,s_e_sym1_8,s_d_sym1_8
DIGITS,,8
table,dist,s_Lz_1_9,s_e_sym1_9,s_d_sym1_9
DIGITS,,8
```

```
ci;
maxiti,maxiter,250,2500;
occ,7,2,2,0;
closed,3,0,0,0;
core,2,0,0,0;
wf,12,2,0;state,4;option,nstati=12;
```

```
s_e_sym2_1(i)= energd(1)
s_e_sym2_2(i)= energd(2)
s_e_sym2_3(i)= energd(3)
s_e_sym2_4(i)= energd(4)
```

```
s_d_sym2_1(i)= DMZ(1)
s_d_sym2_2(i)= DMZ(2)
s_d_sym2_3(i)= DMZ(3)
s_d_sym2_4(i)= DMZ(4)
```

```
table,dist,s_Lz_2_1,s_e_sym2_1,s_d_sym2_1
DIGITS,,8
table,dist,s_Lz_2_2,s_e_sym2_2,s_d_sym2_2
DIGITS,,8
```

```
table,dist,s_Lz_2_3,s_e_sym2_3,s_d_sym2_3
DIGITS,,8
table,dist,s_Lz_2_4,s_e_sym2_4,s_d_sym2_4
DIGITS,,8
```

```
ci;
maxiti,maxiter,250,2500;
occ,7,2,2,0;
closed,3,0,0,0;
core,2,0,0,0;
wf,12,4,0;state,5;option,nstati=12;
```

```
s_e_sym4_1(i)= energd(1)
s_e_sym4_2(i)= energd(2)
s_e_sym4_3(i)= energd(3)
s_e_sym4_4(i)= energd(4)
s_e_sym4_5(i)= energd(5)
```

```
s_d_sym4_1(i)= DMZ(1)
s_d_sym4_2(i)= DMZ(2)
s_d_sym4_3(i)= DMZ(3)
s_d_sym4_4(i)= DMZ(4)
s_d_sym4_5(i)= DMZ(5)
```

```
table,dist,s_Lz_4_1,s_e_sym4_1,s_d_sym4_1
DIGITS,,8
table,dist,s_Lz_4_2,s_e_sym4_2,s_d_sym4_2
DIGITS,,8
table,dist,s_Lz_4_3,s_e_sym4_3,s_d_sym4_3
DIGITS,,8
table,dist,s_Lz_4_4,s_e_sym4_4,s_d_sym4_4
DIGITS,,8
table,dist,s_Lz_4_5,s_e_sym4_5,s_d_sym4_5
DIGITS,,8
```

```
ci;
maxiti,maxiter,250,2500;
occ,7,2,2,0;
closed,3,0,0,0;
core,2,0,0,0;
wf,12,1,2;state,8;option,nstati=12;
```

```
t_e_sym1_1(i)= energd(1)
t_e_sym1_2(i)= energd(2)
t_e_sym1_3(i)= energd(3)
t_e_sym1_4(i)= energd(4)
t_e_sym1_5(i)= energd(5)
```

```
t_e_sym1_6(i)= energd(6)
t_e_sym1_7(i)= energd(7)
t_e_sym1_8(i)= energd(8)

t_d_sym1_1(i)= DMZ(1)
t_d_sym1_2(i)= DMZ(2)
t_d_sym1_3(i)= DMZ(3)
t_d_sym1_4(i)= DMZ(4)
t_d_sym1_5(i)= DMZ(5)
t_d_sym1_6(i)= DMZ(6)
t_d_sym1_7(i)= DMZ(7)
t_d_sym1_8(i)= DMZ(8)

table,dist,t_Lz_1_1,t_e_sym1_1,t_d_sym1_1
DIGITS,,8
table,dist,t_Lz_1_2,t_e_sym1_2,t_d_sym1_2
DIGITS,,8
table,dist,t_Lz_1_3,t_e_sym1_3,t_d_sym1_3
DIGITS,,8
table,dist,t_Lz_1_4,t_e_sym1_4,t_d_sym1_4
DIGITS,,8
table,dist,t_Lz_1_5,t_e_sym1_5,t_d_sym1_5
DIGITS,,8
table,dist,t_Lz_1_6,t_e_sym1_6,t_d_sym1_6
DIGITS,,8
table,dist,t_Lz_1_7,t_e_sym1_7,t_d_sym1_7
DIGITS,,8
table,dist,t_Lz_1_8,t_e_sym1_8,t_d_sym1_8
DIGITS,,8

ci;
maxiti,maxiter,250,2500;
occ,7,2,2,0;
closed,3,0,0,0;
core,2,0,0,0;
wf,12,2,2;state,5;option,nstati=12;

t_e_sym2_1(i)= energd(1)
t_e_sym2_2(i)= energd(2)
t_e_sym2_3(i)= energd(3)
t_e_sym2_4(i)= energd(4)
t_e_sym2_5(i)= energd(5)

t_d_sym2_1(i)= DMZ(1)
t_d_sym2_2(i)= DMZ(2)
t_d_sym2_3(i)= DMZ(3)
t_d_sym2_4(i)= DMZ(4)
t_d_sym2_5(i)= DMZ(5)

table,dist,t_Lz_2_1,t_e_sym2_1,t_d_sym2_1
DIGITS,,8
table,dist,t_Lz_2_2,t_e_sym2_2,t_d_sym2_2
```

```

DIGITS,,8
table,dist,t_Lz_2_3,t_e_sym2_3,t_d_sym2_3
DIGITS,,8
table,dist,t_Lz_2_4,t_e_sym2_4,t_d_sym2_4
DIGITS,,8
table,dist,t_Lz_2_5,t_e_sym2_5,t_d_sym2_5
DIGITS,,8

ci;
maxiti,maxiter,250,2500;
occ,7,2,2,0;
closed,3,0,0,0;
core,2,0,0,0;
wf,12,4,2;state,5;option,nstati=12;

t_e_sym4_1(i)= energd(1)
t_e_sym4_2(i)= energd(2)
t_e_sym4_3(i)= energd(3)
t_e_sym4_4(i)= energd(4)
t_e_sym4_5(i)= energd(5)

t_d_sym4_1(i)= DMZ(1)
t_d_sym4_2(i)= DMZ(2)
t_d_sym4_3(i)= DMZ(3)
t_d_sym4_4(i)= DMZ(4)
t_d_sym4_5(i)= DMZ(5)

table,dist,t_Lz_4_1,t_e_sym4_1,t_d_sym4_1
DIGITS,,8
table,dist,t_Lz_4_2,t_e_sym4_2,t_d_sym4_2
DIGITS,,8
table,dist,t_Lz_4_3,t_e_sym4_3,t_d_sym4_3
DIGITS,,8
table,dist,t_Lz_4_4,t_e_sym4_4,t_d_sym4_4
DIGITS,,8
table,dist,t_Lz_4_5,t_e_sym4_5,t_d_sym4_5
DIGITS,,8

enddo
!=====
table,dist,s_Lz_1_1,s_e_sym1_1,s_d_sym1_1
DIGITS,,8
table,dist,s_Lz_1_2,s_e_sym1_2,s_d_sym1_2
DIGITS,,8
table,dist,s_Lz_1_3,s_e_sym1_3,s_d_sym1_3

```

---

```
DIGITS,,8
table,dist,s_Lz_1_4,s_e_sym1_4,s_d_sym1_4
DIGITS,,8
table,dist,s_Lz_1_5,s_e_sym1_5,s_d_sym1_5
DIGITS,,8
table,dist,s_Lz_1_6,s_e_sym1_6,s_d_sym1_6
DIGITS,,8
table,dist,s_Lz_1_7,s_e_sym1_7,s_d_sym1_7
DIGITS,,8
table,dist,s_Lz_1_8,s_e_sym1_8,s_d_sym1_8
DIGITS,,8
table,dist,s_Lz_1_9,s_e_sym1_9,s_d_sym1_9
DIGITS,,8

table,dist,s_Lz_2_1,s_e_sym2_1,s_d_sym2_1
DIGITS,,8
table,dist,s_Lz_2_2,s_e_sym2_2,s_d_sym2_2
DIGITS,,8
table,dist,s_Lz_2_3,s_e_sym2_3,s_d_sym2_3
DIGITS,,8
table,dist,s_Lz_2_4,s_e_sym2_4,s_d_sym2_4
DIGITS,,8

table,dist,s_Lz_4_1,s_e_sym4_1,s_d_sym4_1
DIGITS,,8
table,dist,s_Lz_4_2,s_e_sym4_2,s_d_sym4_2
DIGITS,,8
table,dist,s_Lz_4_3,s_e_sym4_3,s_d_sym4_3
DIGITS,,8
table,dist,s_Lz_4_4,s_e_sym4_4,s_d_sym4_4
DIGITS,,8
table,dist,s_Lz_4_5,s_e_sym4_5,s_d_sym4_5
DIGITS,,8

table,dist,t_Lz_1_1,t_e_sym1_1,t_d_sym1_1
DIGITS,,8
table,dist,t_Lz_1_2,t_e_sym1_2,t_d_sym1_2
DIGITS,,8
table,dist,t_Lz_1_3,t_e_sym1_3,t_d_sym1_3
DIGITS,,8
table,dist,t_Lz_1_4,t_e_sym1_4,t_d_sym1_4
DIGITS,,8
table,dist,t_Lz_1_5,t_e_sym1_5,t_d_sym1_5
DIGITS,,8
table,dist,t_Lz_1_6,t_e_sym1_6,t_d_sym1_6
DIGITS,,8
table,dist,t_Lz_1_7,t_e_sym1_7,t_d_sym1_7
DIGITS,,8
```

---

```
table,dist,t_Lz_1_8,t_e_sym1_8,t_d_sym1_8
DIGITS,,8
```

```
table,dist,t_Lz_2_1,t_e_sym2_1,t_d_sym2_1
DIGITS,,8
table,dist,t_Lz_2_2,t_e_sym2_2,t_d_sym2_2
DIGITS,,8
table,dist,t_Lz_2_3,t_e_sym2_3,t_d_sym2_3
DIGITS,,8
table,dist,t_Lz_2_4,t_e_sym2_4,t_d_sym2_4
DIGITS,,8
table,dist,t_Lz_2_5,t_e_sym2_5,t_d_sym2_5
DIGITS,,8
```

```
table,dist,t_Lz_4_1,t_e_sym4_1,t_d_sym4_1
DIGITS,,8
table,dist,t_Lz_4_2,t_e_sym4_2,t_d_sym4_2
DIGITS,,8
table,dist,t_Lz_4_3,t_e_sym4_3,t_d_sym4_3
DIGITS,,8
table,dist,t_Lz_4_4,t_e_sym4_4,t_d_sym4_4
DIGITS,,8
table,dist,t_Lz_4_5,t_e_sym4_5,t_d_sym4_5
DIGITS,,8
```

```
put,molden,BN-ci-cc-pvtz-1.molden
```

## APPENDIX II

MOLPRO INPUT DATA FILE FOR THE CALCULATION OF THE  
ELECTRONIC ENERGIES AND DIPOLE MOMENTS OF ALL THE  
28 STATES OF SiN MOLECULE

```
***,Input file generated by gabedit;
Memory,400000000;
Gprint,basis;                ! Print basis information
Gprint,orbital;              ! Print orbitals in SCF and MCSCF

geomtyp=xyz
geometry={ANGSTROM;
2 ! number of atoms
GeomXYZ
Si,  0.0,  0.0,  0.0
N,   0.0,  0.0,  1.5730
}
basis={
s,Si,aug-cc-pV5Z;c
p,Si,aug-cc-pV5Z;c
d,Si,aug-cc-pV5Z;c
f,Si,aug-cc-pV5Z;c
s,N,aug-cc-pV5Z;c
p,N,aug-cc-pV5Z;c
d,N,aug-cc-pV5Z;c
}
hf;
orbprint,1500;
wf,21,1,1;

multi;
occ,10,3,3,0;
closed,5,1,1,0;
core,0,0,0,0;

wf,21,1,1;state,8;
wf,21,2,1;state,5;
wf,21,3,1;state,5;
wf,21,4,1;state,5;

wf,21,1,3;state,8;
wf,21,2,3;state,5;
wf,21,3,3;state,5;
wf,21,4,3;state,5;

r0 = 1.84
step = 0.03
do i=1,14

r = r0 + (i-1)*step

dist(i) = r
```

```
geomtyp=xyz
geometry={ANGSTROM;
2 ! number of atoms
GeomXYZ
Si, 0.0, 0.0, 0.0
N, 0.0, 0.0, r
}

multi;
occ,10,3,3,0;
closed,5,1,1,0;
core,0,0,0,0;

wf,21,1,1;state,8;
wf,21,2,1;state,5;
wf,21,3,1;state,5;
wf,21,4,1;state,5;

wf,21,1,3;state,8;
wf,21,2,3;state,5;
wf,21,3,3;state,5;
wf,21,4,3;state,5;

TRAN2,LXX,LYY,LZZ;
d_Lz_1_1(i)=sqrt(abs(LZLZ(1)))
d_Lz_1_2(i)=sqrt(abs(LZLZ(2)))
d_Lz_1_3(i)=sqrt(abs(LZLZ(3)))
d_Lz_1_4(i)=sqrt(abs(LZLZ(4)))
d_Lz_1_5(i)=sqrt(abs(LZLZ(5)))
d_Lz_1_6(i)=sqrt(abs(LZLZ(6)))
d_Lz_1_7(i)=sqrt(abs(LZLZ(7)))
d_Lz_1_8(i)=sqrt(abs(LZLZ(8)))

d_Lz_2_1(i)=sqrt(abs(LZLZ(9)))
d_Lz_2_2(i)=sqrt(abs(LZLZ(10)))
d_Lz_2_3(i)=sqrt(abs(LZLZ(11)))
d_Lz_2_4(i)=sqrt(abs(LZLZ(12)))
d_Lz_2_5(i)=sqrt(abs(LZLZ(13)))

d_Lz_3_1(i)=sqrt(abs(LZLZ(14)))
d_Lz_3_2(i)=sqrt(abs(LZLZ(15)))
d_Lz_3_3(i)=sqrt(abs(LZLZ(16)))
d_Lz_3_4(i)=sqrt(abs(LZLZ(17)))
d_Lz_3_5(i)=sqrt(abs(LZLZ(18)))

d_Lz_4_1(i)=sqrt(abs(LZLZ(19)))
d_Lz_4_2(i)=sqrt(abs(LZLZ(20)))
d_Lz_4_3(i)=sqrt(abs(LZLZ(21)))
d_Lz_4_4(i)=sqrt(abs(LZLZ(22)))
d_Lz_4_5(i)=sqrt(abs(LZLZ(23)))
```

```
! quartet states
q_Lz_1_1(i)= sqrt(abs(LZLZ(24)))
q_Lz_1_2(i)= sqrt(abs(LZLZ(25)))
q_Lz_1_3(i)= sqrt(abs(LZLZ(26)))
q_Lz_1_4(i)= sqrt(abs(LZLZ(27)))
q_Lz_1_5(i)= sqrt(abs(LZLZ(28)))
q_Lz_1_6(i)= sqrt(abs(LZLZ(29)))
q_Lz_1_7(i)= sqrt(abs(LZLZ(30)))
q_Lz_1_8(i)= sqrt(abs(LZLZ(31)))

q_Lz_2_1(i)= sqrt(abs(LZLZ(32)))
q_Lz_2_2(i)= sqrt(abs(LZLZ(33)))
q_Lz_2_3(i)= sqrt(abs(LZLZ(34)))
q_Lz_2_4(i)= sqrt(abs(LZLZ(35)))
q_Lz_2_5(i)= sqrt(abs(LZLZ(36)))

q_Lz_3_1(i)= sqrt(abs(LZLZ(37)))
q_Lz_3_2(i)= sqrt(abs(LZLZ(38)))
q_Lz_3_3(i)= sqrt(abs(LZLZ(39)))
q_Lz_3_4(i)= sqrt(abs(LZLZ(40)))
q_Lz_3_5(i)= sqrt(abs(LZLZ(41)))

q_Lz_4_1(i)= sqrt(abs(LZLZ(42)))
q_Lz_4_2(i)= sqrt(abs(LZLZ(43)))
q_Lz_4_3(i)= sqrt(abs(LZLZ(44)))
q_Lz_4_4(i)= sqrt(abs(LZLZ(45)))
q_Lz_4_5(i)= sqrt(abs(LZLZ(46)))

!CI calculation
ci;
maxiti,maxiter,150,1500;
occ,10,3,3,0;
closed,5,1,1,0;
core,3,1,1,0;
wf,21,1,1;state,8;option,nstati=20;

d_e_sym1_1(i)= energd(1)
d_e_sym1_2(i)= energd(2)
d_e_sym1_3(i)= energd(3)
d_e_sym1_4(i)= energd(4)
d_e_sym1_5(i)= energd(5)
d_e_sym1_6(i)= energd(6)
d_e_sym1_7(i)= energd(7)
d_e_sym1_8(i)= energd(8)
```

```
d_d_sym1_1(i)= DMZ(1)
d_d_sym1_2(i)= DMZ(2)
d_d_sym1_3(i)= DMZ(3)
d_d_sym1_4(i)= DMZ(4)
d_d_sym1_5(i)= DMZ(5)
d_d_sym1_6(i)= DMZ(6)
d_d_sym1_7(i)= DMZ(7)
d_d_sym1_8(i)= DMZ(8)
```

```
table,dist,d_Lz_1_1,d_e_sym1_1,d_d_sym1_1
DIGITS,,8
table,dist,d_Lz_1_2,d_e_sym1_2,d_d_sym1_2
DIGITS,,8
table,dist,d_Lz_1_3,d_e_sym1_3,d_d_sym1_3
DIGITS,,8
table,dist,d_Lz_1_4,d_e_sym1_4,d_d_sym1_4
DIGITS,,8
table,dist,d_Lz_1_5,d_e_sym1_5,d_d_sym1_5
DIGITS,,8
table,dist,d_Lz_1_6,d_e_sym1_6,d_d_sym1_6
DIGITS,,8
table,dist,d_Lz_1_7,d_e_sym1_7,d_d_sym1_7
DIGITS,,8
table,dist,d_Lz_1_8,d_e_sym1_8,d_d_sym1_8
DIGITS,,8
```

```
ci;
maxiti,maxiter,150,1500;
occ,10,3,3,0;
closed,5,1,1,0;
core,3,1,1,0;
wf,21,2,1;state,5;option,nstati=20;
```

```
d_e_sym2_1(i)= energd(1)
d_e_sym2_2(i)= energd(2)
d_e_sym2_3(i)= energd(3)
d_e_sym2_4(i)= energd(4)
d_e_sym2_5(i)= energd(5)
```

```
d_d_sym2_1(i)= DMZ(1)
d_d_sym2_2(i)= DMZ(2)
d_d_sym2_3(i)= DMZ(3)
d_d_sym2_4(i)= DMZ(4)
d_d_sym2_5(i)= DMZ(5)
```

```
table,dist,d_Lz_2_1,d_e_sym2_1,d_d_sym2_1
DIGITS,,8
```

```
table,dist,d_Lz_2_2,d_e_sym2_2,d_d_sym2_2
DIGITS,,8
table,dist,d_Lz_2_3,d_e_sym2_3,d_d_sym2_3
DIGITS,,8
table,dist,d_Lz_2_4,d_e_sym2_4,d_d_sym2_4
DIGITS,,8
table,dist,d_Lz_2_5,d_e_sym2_5,d_d_sym2_5
DIGITS,,8
```

```
ci;
maxiti,maxiter,150,1500;
occ,10,3,3,0;
closed,5,1,1,0;
core,3,1,1,0;
wf,21,4,1;state,5;option,nstati=20;
```

```
d_e_sym4_1(i)= energd(1)
d_e_sym4_2(i)= energd(2)
d_e_sym4_3(i)= energd(3)
d_e_sym4_4(i)= energd(4)
d_e_sym4_5(i)= energd(5)
```

```
d_d_sym4_1(i)= DMZ(1)
d_d_sym4_2(i)= DMZ(2)
d_d_sym4_3(i)= DMZ(3)
d_d_sym4_4(i)= DMZ(4)
d_d_sym4_5(i)= DMZ(5)
```

```
table,dist,d_Lz_4_1,d_e_sym4_1,d_d_sym4_1
DIGITS,,8
table,dist,d_Lz_4_2,d_e_sym4_2,d_d_sym4_2
DIGITS,,8
table,dist,d_Lz_4_3,d_e_sym4_3,d_d_sym4_3
DIGITS,,8
table,dist,d_Lz_4_4,d_e_sym4_4,d_d_sym4_4
DIGITS,,8
table,dist,d_Lz_4_5,d_e_sym4_5,d_d_sym4_5
DIGITS,,8
```

```
ci;
maxiti,maxiter,150,1500;
occ,10,3,3,0;
closed,5,1,1,0;
core,3,1,1,0;
wf,21,1,3;state,8;option,nstati=20;
```

```
q_e_sym1_1(i)= energd(1)
q_e_sym1_2(i)= energd(2)
q_e_sym1_3(i)= energd(3)
q_e_sym1_4(i)= energd(4)
q_e_sym1_5(i)= energd(5)
q_e_sym1_6(i)= energd(6)
q_e_sym1_7(i)= energd(7)
q_e_sym1_8(i)= energd(8)
```

```
q_d_sym1_1(i)= DMZ(1)
q_d_sym1_2(i)= DMZ(2)
q_d_sym1_3(i)= DMZ(3)
q_d_sym1_4(i)= DMZ(4)
q_d_sym1_5(i)= DMZ(5)
q_d_sym1_6(i)= DMZ(6)
q_d_sym1_7(i)= DMZ(7)
q_d_sym1_8(i)= DMZ(8)
```

```
table,dist,q_Lz_1_1,q_e_sym1_1,q_d_sym1_1
DIGITS,,8
table,dist,q_Lz_1_2,q_e_sym1_2,q_d_sym1_2
DIGITS,,8
table,dist,q_Lz_1_3,q_e_sym1_3,q_d_sym1_3
DIGITS,,8
table,dist,q_Lz_1_4,q_e_sym1_4,q_d_sym1_4
DIGITS,,8
table,dist,q_Lz_1_5,q_e_sym1_5,q_d_sym1_5
DIGITS,,8
table,dist,q_Lz_1_6,q_e_sym1_6,q_d_sym1_6
DIGITS,,8
table,dist,q_Lz_1_7,q_e_sym1_7,q_d_sym1_7
DIGITS,,8
table,dist,q_Lz_1_8,q_e_sym1_8,q_d_sym1_8
DIGITS,,8
```

```
ci;
maxiti,maxiter,150,1500;
occ,10,3,3,0;
closed,5,1,1,0;
core,3,1,1,0;
wf,21,2,3;state,5;option,nstati=20;
```

```
q_e_sym2_1(i)= energd(1)
q_e_sym2_2(i)= energd(2)
q_e_sym2_3(i)= energd(3)
q_e_sym2_4(i)= energd(4)
q_e_sym2_5(i)= energd(5)
```

```
q_d_sym2_1(i)= DMZ(1)
q_d_sym2_2(i)= DMZ(2)
q_d_sym2_3(i)= DMZ(3)
q_d_sym2_4(i)= DMZ(4)
```

```
q_d_sym2_5(i) = DMZ(5)

table,dist,q_Lz_2_1,q_e_sym2_1,q_d_sym2_1
DIGITS,,8
table,dist,q_Lz_2_2,q_e_sym2_2,q_d_sym2_2
DIGITS,,8
table,dist,q_Lz_2_3,q_e_sym2_3,q_d_sym2_3
DIGITS,,8
table,dist,q_Lz_2_4,q_e_sym2_4,q_d_sym2_4
DIGITS,,8
table,dist,q_Lz_2_5,q_e_sym2_5,q_d_sym2_5
DIGITS,,8

ci;
maxiti,maxiter,150,1500;
occ,10,3,3,0;
closed,5,1,1,0;
core,3,1,1,0;
wf,21,4,3;state,5;option,nstati=20;

q_e_sym4_1(i) = energd(1)
q_e_sym4_2(i) = energd(2)
q_e_sym4_3(i) = energd(3)
q_e_sym4_4(i) = energd(4)
q_e_sym4_5(i) = energd(5)

q_d_sym4_1(i) = DMZ(1)
q_d_sym4_2(i) = DMZ(2)
q_d_sym4_3(i) = DMZ(3)
q_d_sym4_4(i) = DMZ(4)
q_d_sym4_5(i) = DMZ(5)

table,dist,q_Lz_4_1,q_e_sym4_1,q_d_sym4_1
DIGITS,,8
table,dist,q_Lz_4_2,q_e_sym4_2,q_d_sym4_2
DIGITS,,8
table,dist,q_Lz_4_3,q_e_sym4_3,q_d_sym4_3
DIGITS,,8
table,dist,q_Lz_4_4,q_e_sym4_4,q_d_sym4_4
DIGITS,,8
table,dist,q_Lz_4_5,q_e_sym4_5,q_d_sym4_5
DIGITS,,8
```

```
enddo
!=====
table,dist,d_Lz_1_1,d_e_sym1_1,d_d_sym1_1
DIGITS,,8
table,dist,d_Lz_1_2,d_e_sym1_2,d_d_sym1_2
DIGITS,,8
table,dist,d_Lz_1_3,d_e_sym1_3,d_d_sym1_3
DIGITS,,8
table,dist,d_Lz_1_4,d_e_sym1_4,d_d_sym1_4
DIGITS,,8
table,dist,d_Lz_1_5,d_e_sym1_5,d_d_sym1_5
DIGITS,,8
table,dist,d_Lz_1_6,d_e_sym1_6,d_d_sym1_6
DIGITS,,8
table,dist,d_Lz_1_7,d_e_sym1_7,d_d_sym1_7
DIGITS,,8
table,dist,d_Lz_1_8,d_e_sym1_8,d_d_sym1_8
DIGITS,,8

table,dist,d_Lz_2_1,d_e_sym2_1,d_d_sym2_1
DIGITS,,8
table,dist,d_Lz_2_2,d_e_sym2_2,d_d_sym2_2
DIGITS,,8
table,dist,d_Lz_2_3,d_e_sym2_3,d_d_sym2_3
DIGITS,,8
table,dist,d_Lz_2_4,d_e_sym2_4,d_d_sym2_4
DIGITS,,8
table,dist,d_Lz_2_5,d_e_sym2_5,d_d_sym2_5
DIGITS,,8

table,dist,d_Lz_4_1,d_e_sym4_1,d_d_sym4_1
DIGITS,,8
table,dist,d_Lz_4_2,d_e_sym4_2,d_d_sym4_2
DIGITS,,8
table,dist,d_Lz_4_3,d_e_sym4_3,d_d_sym4_3
DIGITS,,8
table,dist,d_Lz_4_4,d_e_sym4_4,d_d_sym4_4
DIGITS,,8
table,dist,d_Lz_4_5,d_e_sym4_5,d_d_sym4_5
DIGITS,,8

table,dist,q_Lz_1_1,q_e_sym1_1,q_d_sym1_1
DIGITS,,8
table,dist,q_Lz_1_2,q_e_sym1_2,q_d_sym1_2
DIGITS,,8
table,dist,q_Lz_1_3,q_e_sym1_3,q_d_sym1_3
DIGITS,,8
```

---

```
table,dist,q_Lz_1_4,q_e_sym1_4,q_d_sym1_4
DIGITS,,8
table,dist,q_Lz_1_5,q_e_sym1_5,q_d_sym1_5
DIGITS,,8
table,dist,q_Lz_1_6,q_e_sym1_6,q_d_sym1_6
DIGITS,,8
table,dist,q_Lz_1_7,q_e_sym1_7,q_d_sym1_7
DIGITS,,8
table,dist,q_Lz_1_8,q_e_sym1_8,q_d_sym1_8
DIGITS,,8
```

```
table,dist,q_Lz_2_1,q_e_sym2_1,q_d_sym2_1
DIGITS,,8
table,dist,q_Lz_2_2,q_e_sym2_2,q_d_sym2_2
DIGITS,,8
table,dist,q_Lz_2_3,q_e_sym2_3,q_d_sym2_3
DIGITS,,8
table,dist,q_Lz_2_4,q_e_sym2_4,q_d_sym2_4
DIGITS,,8
table,dist,q_Lz_2_5,q_e_sym2_5,q_d_sym2_5
DIGITS,,8
```

```
table,dist,q_Lz_4_1,q_e_sym4_1,q_d_sym4_1
DIGITS,,8
table,dist,q_Lz_4_2,q_e_sym4_2,q_d_sym4_2
DIGITS,,8
table,dist,q_Lz_4_3,q_e_sym4_3,q_d_sym4_3
DIGITS,,8
table,dist,q_Lz_4_4,q_e_sym4_4,q_d_sym4_4
DIGITS,,8
table,dist,q_Lz_4_5,q_e_sym4_5,q_d_sym4_5
DIGITS,,8
```

```
put,molden,SiN-ci-1.molden
```

## APPENDIX III

MOLPRO INPUT DATA FILE FOR THE CALCULATION OF THE  
ELECTRONIC ENERGIES AND DIPOLE MOMENTS OF ALL THE  
24 STATES OF **LaH** MOLECULE WITH SPIN-ORBIT

```
***,Input file generated by gabedit;
Memory,120000000;
Gprint,basis;                ! Print basis information
Gprint,orbital;             ! Print orbitals in SCF and MCSCF

geomtyp=xyz
geometry={ANGSTROM;
2 ! number of atoms
GeomXYZ
La, 0.0, 0.0, 0.0
H, 0.0, 0.0, 2.031969
}
basis={
! LANTHANUM (9s,9p,5d) -> [4s,4p,3d]
s,LA,0.917300000E+01,0.312000000E+01,0.210400000E+01,0.132000000E+01,0
.496000000E+00,0.618200000E+00,0.454600000E-01,0.177500000E-
01,0.200400000E+00
c,1.5,-0.548330000E-01, 0.676604000E+00,-0.103442900E+01,-
0.518907000E+00, 0.163160300E+01
c,6.7,-0.107095000E+00, 0.103344800E+01
c,8.8, 0.100000000E+01
c,9.9, 0.100000000E+01
p,LA,0.917300000E+01,0.312000000E+01,0.210400000E+01,0.132000000E+01,0
.496000000E+00,0.618200000E+00,0.454600000E-01,0.177500000E-
01,0.200400000E+00
c,1.5,-0.979800000E-02, 0.231262000E+00,-0.601215000E+00,
0.195189000E+00, 0.107613700E+01
c,6.7,-0.518690000E-01, 0.100810800E+01
c,8.8, 0.100000000E+01
c,9.9, 0.100000000E+01
d,LA,0.123800000E+01,0.606100000E+00,0.251800000E+00,0.978700000E-
01,0.353600000E-01
c,1.3,-0.537970000E-01, 0.380144000E+00, 0.720349000E+00
c,4.4, 0.100000000E+01
c,5.5, 0.100000000E+01

!f,LA,0.124797100E+03,0.439427000E+02,0.192668000E+02,0.848930000E+01,
0.376720000E+01,0.159020000E+01,0.609800000E+00,0.197300000E+0
!c,1.5,0.001466,0.013540,0.065590,0.156947,0.286961
!c,6.6,1.000000
!c,7.7,1.000000
!c,8.8,1.000000

! Effective Core Potentials
! -----
ECP,la,46,5,3;

! h potential
1
1, 1.0000000,0.00000000;
```

---

```
! s-h potential
4
0, 22.2973900,8.85347000;
1, 1.42345000,-2.8566500;
2, 1.64320000,-68.417780;
2, 1.85122000,110.124630;

! p-h potential
4
0, 1.77635000,2.98675000;
1, 1.42345000,-2.8566500;
2, 3.98941000,-35.518150;
2, 2.47524000,53.6542300;

! d-h potential
3
0, 1.52169000,1.67298000;
1, 1.42345000,-2.8566500;
2, 1.52182000,18.4662500;

! f-h potential
3
1, 1.42345000,-2.8566500;
1, 2.67762000,-4.6443000;
1, 10.0660800,-14.431010;

! g-h potential
1
1, 1.42345000,-2.8566500;

! p-so potential
4
0, 1.77635000,0.3188456;
1, 1.42345000,-0.3049568;
2, 3.98941000,-3.7917409;
2, 2.47524000,5.7278634;

! d-so potential
3
0, 1.52169000,0.0234087;
1, 1.42345000,-0.0399702;
2, 1.52182000,0.2583833;

! f-so potential
3
1, 1.42345000,0.0015168;
1, 2.67762000,0.0027235;
1, 10.0660800,0.0084629;
```

```
QZ;c
s,H,aug-cc-pVQZ;c
p,H,aug-cc-pVQZ;c
d,H,aug-cc-pVQZ;c
f,H,aug-cc-pVQZ;c
}
r=2.0319
int;lat,1e-20,,,40.0;
hf;
wf,12,1,0;
orbprint,3000;

multi;
occ,8,3,3,1;
closed,3,1,1,0;
core,0,0,0,0;

wf,12,1,0;state,6;
wf,12,2,0;state,3;
wf,12,3,0;state,3;
wf,12,4,0;state,3;

wf,12,1,2;state,6;
wf,12,2,2;state,6;
wf,12,3,2;state,6;
wf,12,4,2;state,5;

NatOrb;
Orbital,7100.2;

r0 = 1.8519
step = 0.03
do i=1,22

r = r0 + (i-1)*step

dist(i) = r

geomtyp=xyz
geometry={ANGSTROM;
2 ! number of atoms
GeomXYZ
La, 0.0, 0.0, 0.0
H, 0.0, 0.0, r
}
int;lat,1e-20,,,40.0;
hf;
wf,12,1,0;
orbprint,3000;
```

```
multi;
start,7100.2
occ,8,3,3,1;
closed,3,1,1,0;
core,0,0,0,0;

wf,12,1,0;state,6;
wf,12,2,0;state,3;
wf,12,3,0;state,3;
wf,12,4,0;state,3;

wf,12,1,2;state,6;
wf,12,2,2;state,6;
wf,12,3,2;state,6;
wf,12,4,2;state,5;

TRAN2,LXX,LYY,LZZ;
s_Lz_1_1(i)= sqrt(abs(LZLZ(1)))
s_Lz_1_2(i)= sqrt(abs(LZLZ(2)))
s_Lz_1_3(i)= sqrt(abs(LZLZ(3)))
s_Lz_1_4(i)= sqrt(abs(LZLZ(4)))
s_Lz_1_5(i)= sqrt(abs(LZLZ(5)))
s_Lz_1_6(i)= sqrt(abs(LZLZ(6)))

s_Lz_2_1(i)= sqrt(abs(LZLZ(7)))
s_Lz_2_2(i)= sqrt(abs(LZLZ(8)))
s_Lz_2_3(i)= sqrt(abs(LZLZ(9)))

s_Lz_3_1(i)= sqrt(abs(LZLZ(10)))
s_Lz_3_2(i)= sqrt(abs(LZLZ(11)))
s_Lz_3_3(i)= sqrt(abs(LZLZ(12)))

s_Lz_4_1(i)= sqrt(abs(LZLZ(13)))
s_Lz_4_2(i)= sqrt(abs(LZLZ(14)))
s_Lz_4_3(i)= sqrt(abs(LZLZ(15)))

! triplet states
t_Lz_1_1(i)= sqrt(abs(LZLZ(16)))
t_Lz_1_2(i)= sqrt(abs(LZLZ(17)))
t_Lz_1_3(i)= sqrt(abs(LZLZ(18)))
t_Lz_1_4(i)= sqrt(abs(LZLZ(19)))
t_Lz_1_5(i)= sqrt(abs(LZLZ(20)))
t_Lz_1_6(i)= sqrt(abs(LZLZ(21)))

t_Lz_2_1(i)= sqrt(abs(LZLZ(22)))
t_Lz_2_2(i)= sqrt(abs(LZLZ(23)))
```

```
t_Lz_2_3(i)= sqrt(abs(LZLZ(24)))
t_Lz_2_4(i)= sqrt(abs(LZLZ(25)))
t_Lz_2_5(i)= sqrt(abs(LZLZ(26)))
t_Lz_2_6(i)= sqrt(abs(LZLZ(27)))

t_Lz_3_1(i)= sqrt(abs(LZLZ(28)))
t_Lz_3_2(i)= sqrt(abs(LZLZ(29)))
t_Lz_3_3(i)= sqrt(abs(LZLZ(30)))
t_Lz_3_4(i)= sqrt(abs(LZLZ(31)))
t_Lz_3_5(i)= sqrt(abs(LZLZ(32)))
t_Lz_3_6(i)= sqrt(abs(LZLZ(33)))

t_Lz_4_1(i)= sqrt(abs(LZLZ(34)))
t_Lz_4_2(i)= sqrt(abs(LZLZ(35)))
t_Lz_4_3(i)= sqrt(abs(LZLZ(36)))
t_Lz_4_4(i)= sqrt(abs(LZLZ(37)))
t_Lz_4_5(i)= sqrt(abs(LZLZ(38)))

!CI calculation
ci;
maxiti,maxiter,50,500;
occ,8,3,3,1;
closed,3,1,1,0;
core,2,0,0,0;
wf,12,1,0;state,6;option,nstati=12;

s_e_sym1_1(i)= energd(1)
s_e_sym1_2(i)= energd(2)
s_e_sym1_3(i)= energd(3)
s_e_sym1_4(i)= energd(4)
s_e_sym1_5(i)= energd(5)
s_e_sym1_6(i)= energd(6)

E1=s_e_sym1_1(i)
E2=s_e_sym1_2(i)
E3=s_e_sym1_3(i)
E4=s_e_sym1_4(i)
E5=s_e_sym1_5(i)
E6=s_e_sym1_6(i)

s_d_sym1_1(i)= DMZ(1)
s_d_sym1_2(i)= DMZ(2)
s_d_sym1_3(i)= DMZ(3)
s_d_sym1_4(i)= DMZ(4)
s_d_sym1_5(i)= DMZ(5)
s_d_sym1_6(i)= DMZ(6)

table,dist,s_Lz_1_1,s_e_sym1_1,s_d_sym1_1
DIGITS,,8
```

```
table,dist,s_Lz_1_2,s_e_sym1_2,s_d_sym1_2
DIGITS,,8
table,dist,s_Lz_1_3,s_e_sym1_3,s_d_sym1_3
DIGITS,,8
table,dist,s_Lz_1_4,s_e_sym1_4,s_d_sym1_4
DIGITS,,8
table,dist,s_Lz_1_5,s_e_sym1_5,s_d_sym1_5
DIGITS,,8
table,dist,s_Lz_1_6,s_e_sym1_6,s_d_sym1_6
DIGITS,,8

ci;
maxiti,maxiter,50,500;
occ,8,3,3,1;
closed,3,1,1,0;
core,2,0,0,0;
wf,12,2,0;state,3;option,nstati=12;

s_e_sym2_1(i)= energd(1)
s_e_sym2_2(i)= energd(2)
s_e_sym2_3(i)= energd(3)

E7=s_e_sym2_1(i)
E8=s_e_sym2_2(i)
E9=s_e_sym2_3(i)

s_d_sym2_1(i)= DMZ(1)
s_d_sym2_2(i)= DMZ(2)
s_d_sym2_3(i)= DMZ(3)

table,dist,s_Lz_2_1,s_e_sym2_1,s_d_sym2_1
DIGITS,,8
table,dist,s_Lz_2_2,s_e_sym2_2,s_d_sym2_2
DIGITS,,8
table,dist,s_Lz_2_3,s_e_sym2_3,s_d_sym2_3
DIGITS,,8

!The energy of singlet_symmetry_3 is equal to singlet_symmetry_2
E10=E7
E11=E8
E12=E9

!The enrgy of singlet_symmetry_4 for delta is equal to
singlet_symmetry_1 for delta
E13=E2
E14=E4
E15=E6
```

```
ci;
occ,8,3,3,1;
closed,3,1,1,0;
core,2,0,0,0;
wf,12,1,2;state,6;option,nstati=12;

t_e_sym1_1(i)= energd(1)
t_e_sym1_2(i)= energd(2)
t_e_sym1_3(i)= energd(3)
t_e_sym1_4(i)= energd(4)
t_e_sym1_5(i)= energd(5)
t_e_sym1_6(i)= energd(6)

E16=t_e_sym1_1(i)
E17=t_e_sym1_2(i)
E18=t_e_sym1_3(i)
E19=t_e_sym1_4(i)
E20=t_e_sym1_5(i)
E21=t_e_sym1_6(i)

t_d_sym1_1(i)= DMZ(1)
t_d_sym1_2(i)= DMZ(2)
t_d_sym1_3(i)= DMZ(3)
t_d_sym1_4(i)= DMZ(4)
t_d_sym1_5(i)= DMZ(5)
t_d_sym1_6(i)= DMZ(6)

table,dist,t_Lz_1_1,t_e_sym1_1,t_d_sym1_1
DIGITS,,8
table,dist,t_Lz_1_2,t_e_sym1_2,t_d_sym1_2
DIGITS,,8
table,dist,t_Lz_1_3,t_e_sym1_3,t_d_sym1_3
DIGITS,,8
table,dist,t_Lz_1_4,t_e_sym1_4,t_d_sym1_4
DIGITS,,8
table,dist,t_Lz_1_5,t_e_sym1_5,t_d_sym1_5
DIGITS,,8
table,dist,t_Lz_1_6,t_e_sym1_6,t_d_sym1_6
DIGITS,,8

ci;
occ,8,3,3,1;
closed,3,1,1,0;
core,2,0,0,0;
wf,12,2,2;state,6;option,nstati=12;
```

```
t_e_sym2_1(i)= energd(1)
t_e_sym2_2(i)= energd(2)
t_e_sym2_3(i)= energd(3)
t_e_sym2_4(i)= energd(4)
t_e_sym2_5(i)= energd(5)
t_e_sym2_6(i)= energd(6)
```

```
E22=t_e_sym2_1(i)
E23=t_e_sym2_2(i)
E24=t_e_sym2_3(i)
E25=t_e_sym2_4(i)
E26=t_e_sym2_5(i)
E27=t_e_sym2_6(i)
```

```
t_d_sym2_1(i)= DMZ(1)
t_d_sym2_2(i)= DMZ(2)
t_d_sym2_3(i)= DMZ(3)
t_d_sym2_4(i)= DMZ(4)
t_d_sym2_5(i)= DMZ(5)
t_d_sym2_6(i)= DMZ(6)
```

```
table,dist,t_Lz_2_1,t_e_sym2_1,t_d_sym2_1
DIGITS,,8
table,dist,t_Lz_2_2,t_e_sym2_2,t_d_sym2_2
DIGITS,,8
table,dist,t_Lz_2_3,t_e_sym2_3,t_d_sym2_3
DIGITS,,8
table,dist,t_Lz_2_4,t_e_sym2_4,t_d_sym2_4
DIGITS,,8
table,dist,t_Lz_2_5,t_e_sym2_5,t_d_sym2_5
DIGITS,,8
table,dist,t_Lz_2_6,t_e_sym2_6,t_d_sym2_6
DIGITS,,8
```

```
!The energy of triplet_symmetry_3 is equal to triplet_symmetry_2
E28=E22
E29=E23
E30=E24
E31=E25
E32=E26
E33=E27
```

```
ci;
occ,8,3,3,1;
closed,3,1,1,0;
core,2,0,0,0;
wf,12,4,2;state,5;option,nstati=12;
```

```
t_e_sym4_1(i)= energd(1)
t_e_sym4_2(i)= energd(2)
t_e_sym4_3(i)= energd(3)
t_e_sym4_4(i)= energd(4)
t_e_sym4_5(i)= energd(5)
```

```
E34=E16
E35=t_e_sym4_2(i)
E36=E18
E37=t_e_sym4_4(i)
E38=E20
```

```
t_d_sym4_1(i)= DMZ(1)
t_d_sym4_2(i)= DMZ(2)
t_d_sym4_3(i)= DMZ(3)
t_d_sym4_4(i)= DMZ(4)
t_d_sym4_5(i)= DMZ(5)
```

```
table,dist,t_Lz_4_1,t_e_sym4_1,t_d_sym4_1
DIGITS,,8
table,dist,t_Lz_4_2,t_e_sym4_2,t_d_sym4_2
DIGITS,,8
table,dist,t_Lz_4_3,t_e_sym4_3,t_d_sym4_3
DIGITS,,8
table,dist,t_Lz_4_4,t_e_sym4_4,t_d_sym4_4
DIGITS,,8
table,dist,t_Lz_4_5,t_e_sym4_5,t_d_sym4_5
DIGITS,,8
```

```
! CI without excitation
```

```
ci;
maxiti,maxiter,50,500;
occ,8,3,3,1;
closed,3,1,1,0;
core,2,0,0,0;
wf,12,1,0;state,6;option,nstati=12;noexc;save,5100.2;
```

```
ci;
maxiti,maxiter,50,500;
occ,8,3,3,1;
closed,3,1,1,0;
core,2,0,0,0;
wf,12,2,0;state,3;option,nstati=12;noexc;save,5200.2;
```

```
ci;
maxiti,maxiter,50,500;
occ,8,3,3,1;
```

```
closed,3,1,1,0;  
core,2,0,0,0;  
wf,12,3,0;state,3;option,nstati=12;noexc;save,5300.2;
```

```
ci;  
maxiti,maxiter,50,500;  
occ,8,3,3,1;  
closed,3,1,1,0;  
core,2,0,0,0;  
wf,12,4,0;state,3;option,nstati=12;noexc;save,5400.2;
```

```
ci;  
occ,8,3,3,1;  
closed,3,1,1,0;  
core,2,0,0,0;  
wf,12,1,2;state,6;option,nstati=12;noexc;save,6100.2;
```

```
ci;  
occ,8,3,3,1;  
closed,3,1,1,0;  
core,2,0,0,0;  
wf,12,2,2;state,6;option,nstati=12;noexc;save,6200.2;
```

```
ci;  
occ,8,3,3,1;  
closed,3,1,1,0;  
core,2,0,0,0;  
wf,12,3,2;state,6;option,nstati=12;noexc;save,6300.2;
```

```
ci;  
occ,8,3,3,1;  
closed,3,1,1,0;  
core,2,0,0,0;  
wf,12,4,2;state,5;option,nstati=12;noexc;save,6400.2;
```

```
hlsdiag=[E1,E2,E3,E4,E5,E6,E7,E8,E9,E10,E11,E12,E13,E14,E15,E16,E17,E18,E19,E20,E21,E22,E23,E24,E25,E26,E27,E28,E29,E30,E31,E32,E33,E34,E35,E36,E37,E38]  
ci;options,hlstrans=0;print,HLS=1,VLS=1;hlsmat,ecp,5100.2,5200.2,5300.2,5400.2,6100.2,6200.2,6300.2,6400.2;
```

```
eso_1(i) = energy(1)  
eso_2(i) = energy(2)  
eso_3(i) = energy(3)  
eso_4(i) = energy(4)  
eso_5(i) = energy(5)  
eso_6(i) = energy(6)  
eso_7(i) = energy(7)  
eso_8(i) = energy(8)  
eso_9(i) = energy(9)
```

eso\_10(i) = energy(10)  
eso\_11(i) = energy(11)  
eso\_12(i) = energy(12)  
eso\_13(i) = energy(13)  
eso\_14(i) = energy(14)  
eso\_15(i) = energy(15)  
eso\_16(i) = energy(16)  
eso\_17(i) = energy(17)  
eso\_18(i) = energy(18)  
eso\_19(i) = energy(19)  
eso\_20(i) = energy(20)  
eso\_21(i) = energy(21)  
eso\_22(i) = energy(22)  
eso\_23(i) = energy(23)  
eso\_24(i) = energy(24)  
eso\_25(i) = energy(25)  
eso\_26(i) = energy(26)  
eso\_27(i) = energy(27)  
eso\_28(i) = energy(28)  
eso\_29(i) = energy(29)  
eso\_30(i) = energy(30)  
eso\_31(i) = energy(31)  
eso\_32(i) = energy(32)  
eso\_33(i) = energy(33)  
eso\_34(i) = energy(34)  
eso\_35(i) = energy(35)  
eso\_36(i) = energy(36)  
eso\_37(i) = energy(37)  
eso\_38(i) = energy(38)  
eso\_39(i) = energy(39)  
eso\_40(i) = energy(40)  
eso\_41(i) = energy(41)  
eso\_42(i) = energy(42)  
eso\_43(i) = energy(43)  
eso\_44(i) = energy(44)  
eso\_45(i) = energy(45)  
eso\_46(i) = energy(46)  
eso\_47(i) = energy(47)  
eso\_48(i) = energy(48)  
eso\_49(i) = energy(49)  
eso\_50(i) = energy(50)  
eso\_51(i) = energy(51)  
eso\_52(i) = energy(52)  
eso\_53(i) = energy(53)  
eso\_54(i) = energy(54)  
eso\_55(i) = energy(55)  
eso\_56(i) = energy(56)  
eso\_57(i) = energy(57)  
eso\_58(i) = energy(58)  
eso\_59(i) = energy(59)

dso\_1(i) = DMZ(1)

dso\_2(i) = DMZ(2)  
dso\_3(i) = DMZ(3)  
dso\_4(i) = DMZ(4)  
dso\_5(i) = DMZ(5)  
dso\_6(i) = DMZ(6)  
dso\_7(i) = DMZ(7)  
dso\_8(i) = DMZ(8)  
dso\_9(i) = DMZ(9)  
dso\_10(i) = DMZ(10)  
dso\_11(i) = DMZ(11)  
dso\_12(i) = DMZ(12)  
dso\_13(i) = DMZ(13)  
dso\_14(i) = DMZ(14)  
dso\_15(i) = DMZ(15)  
dso\_16(i) = DMZ(16)  
dso\_17(i) = DMZ(17)  
dso\_18(i) = DMZ(18)  
dso\_19(i) = DMZ(19)  
dso\_20(i) = DMZ(20)  
dso\_21(i) = DMZ(21)  
dso\_22(i) = DMZ(22)  
dso\_23(i) = DMZ(23)  
dso\_24(i) = DMZ(24)  
dso\_25(i) = DMZ(25)  
dso\_26(i) = DMZ(26)  
dso\_27(i) = DMZ(27)  
dso\_28(i) = DMZ(28)  
dso\_29(i) = DMZ(29)  
dso\_30(i) = DMZ(30)  
dso\_31(i) = DMZ(31)  
dso\_32(i) = DMZ(32)  
dso\_33(i) = DMZ(33)  
dso\_34(i) = DMZ(34)  
dso\_35(i) = DMZ(35)  
dso\_36(i) = DMZ(36)  
dso\_37(i) = DMZ(37)  
dso\_38(i) = DMZ(38)  
dso\_39(i) = DMZ(39)  
dso\_40(i) = DMZ(40)  
dso\_41(i) = DMZ(41)  
dso\_42(i) = DMZ(42)  
dso\_43(i) = DMZ(43)  
dso\_44(i) = DMZ(44)  
dso\_45(i) = DMZ(45)  
dso\_46(i) = DMZ(46)  
dso\_47(i) = DMZ(47)  
dso\_48(i) = DMZ(48)  
dso\_49(i) = DMZ(49)  
dso\_50(i) = DMZ(50)  
dso\_51(i) = DMZ(51)  
dso\_52(i) = DMZ(52)  
dso\_53(i) = DMZ(53)

---

dso\_54(i) = DMZ(54)  
dso\_55(i) = DMZ(55)  
dso\_56(i) = DMZ(56)  
dso\_57(i) = DMZ(57)  
dso\_58(i) = DMZ(58)  
dso\_59(i) = DMZ(59)

table,dist,eso\_1,dso\_1  
DIGITS,,8  
table,dist,eso\_2,dso\_2  
DIGITS,,8  
table,dist,eso\_3,dso\_3  
DIGITS,,8  
table,dist,eso\_4,dso\_4  
DIGITS,,8  
table,dist,eso\_5,dso\_5  
DIGITS,,8  
table,dist,eso\_6,dso\_6  
DIGITS,,8  
table,dist,eso\_7,dso\_7  
DIGITS,,8  
table,dist,eso\_8,dso\_8  
DIGITS,,8  
table,dist,eso\_9,dso\_9  
DIGITS,,8  
table,dist,eso\_10,dso\_10  
DIGITS,,8  
table,dist,eso\_11,dso\_11  
DIGITS,,8  
table,dist,eso\_12,dso\_12  
DIGITS,,8  
table,dist,eso\_13,dso\_13  
DIGITS,,8  
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APPENDIX IV  
ROVIBRATIONALS RESULTES

Table (5): Values of the eigenvalues  $E_v$ , the rotational constants  $B_v$  and the abscissa of the turning points  $R_{\min}$  and  $R_{\max}$  for the different vibrational levels of  $(2)^1\Sigma$  state of the LaH molecule.

$v$	$E_v (cm^{-1})$	$B_v (cm^{-1})$	$D_v \times 10^5 (cm^{-1})$	$R_{\min} (\text{Å})$	$R_{\max} (\text{Å})$
0	631.447	3.128	7.761	2.16	2.487
1	1878.524	3.087	7.946	2.06	2.63
2	3096.175	3.042	8.216	1.996	2.741
3	4280.933	2.995	8.236	1.947	2.898
4	5437.345	2.949	8.39	1.906	2.927
5	6564.963	2.901	8.383	1.872	3.013
6	7665.826	2.855	8.426	1.842	3.094
7	8740.932	2.808	8.303	1.815	3.173
8	9792.486	2.763	8.426	1.791	3.251
9	10820.04	2.717	8.221	1.769	3.328
10	11825.8	2.673	8.133	1.749	3.402
11	12811.47	2.632	7.983	1.73	3.476
12	13778.56	2.591	7.791	1.713	3.548
13	14728.45	2.553	7.699	1.696	3.619
14	15662.25	2.517	7.501	1.681	3.689
15	16581.1	2.481	7.281	1.667	3.757
16	17486.22	2.447	7.254	1.653	3.825
17	18377.97	2.415	7.014	1.64	3.892
18	19257.34	2.383	6.839	1.628	3.958
19	20124.91	2.352	6.808	1.616	4.023
20	20980.89	2.322	6.694	1.605	4.088
21	21825.49	2.292	6.472	1.595	4.152
22	22659.09	2.262	6.507	1.584	4.217
23	23481.32	2.233	6.436	1.575	4.281
24	24292.4	2.204	6.217	1.565	4.344
25	25093.01	2.176	6.01	1.556	4.407
26	25883.57	2.148	6.142	1.548	4.471
27	26663.12	2.119	6.231	1.54	4.535
28	27431.04	2.09	5.905	1.532	4.599
29	28188.21	2.061	5.951	1.524	4.663
30	28933.91	2.03	6.057	1.517	4.728
31	29667.5	2.001	5.882	1.51	4.794
32	30389.37	1.97	6.058	1.503	4.86
33	31098.34	1.938	5.916	1.496	4.928
34	31794.35	1.906	6.106	1.49	4.997
35	32476.1	1.87	6.171	1.484	5.071
36	33143.1	1.836	6.072	1.478	5.141
37	33796.04	1.804	5.412	1.473	5.213
38	34437.49	1.776	5.415	1.467	5.287
39	35067.03	1.742	6.092	1.462	5.362
40	35681.23	1.705	6.132	1.457	5.439
41	36280.25	1.673	5.287	1.452	5.517
42	36866.73	1.639	6.226	1.448	5.598

Table(6): Values of the eigenvalues  $E_v$ , the rotational constants  $B_v$  and the abscissa of the turning points  $R_{\min}$  and  $R_{\max}$  for the different vibrational levels of  $(1)^1\Delta$  state of the LaH molecule.

$v$	$E_v (cm^{-1})$	$B_v (cm^{-1})$	$D_v \times 10^5 (cm^{-1})$	$R_{\min} (\text{Å})$	$R_{\max} (\text{Å})$
0	609.238	3.047	7.783	2.188	2.52
1	1806.27	3.006	8.043	2.08	2.688
2	2972.106	2.963	8.239	2.02	2.781
3	4108.22	2.919	8.428	1.969	2.88
4	5214.984	2.874	8.493	1.928	2.971
5	6294.555	2.829	8.63	1.892	3.058
6	7346.743	2.782	8.778	1.861	3.142
7	8370.889	2.733	8.701	1.834	3.225
8	9369.786	2.688	8.443	1.809	3.305
9	10347.19	2.644	8.567	1.786	3.384
10	11302.19	2.599	8.36	1.766	3.461
11	12236.83	2.556	8.28	1.746	3.53
12	13151.97	2.514	8.077	1.729	3.613
13	14048.98	2.473	8.073	1.712	3.688
14	14928.03	2.433	7.769	1.697	3.762
15	15790.59	2.393	7.833	1.683	3.836
16	16636.34	2.355	7.592	1.669	3.909
17	17466.19	2.315	7.562	1.656	3.982
18	18280.04	2.277	7.506	1.644	4.055
19	19077.92	2.238	7.325	1.633	4.129
20	19860.17	2.199	7.447	1.622	4.202
21	20626.22	2.161	7.21	1.612	4.277
22	21376.46	2.121	7.219	1.602	4.352
23	22110.56	2.082	7.274	1.592	4.428
24	22828.35	2.043	7.013	1.584	4.504
25	23530.4	2.003	6.925	1.575	4.582
26	24216.94	1.965	6.9	1.567	4.66
27	24888.25	1.928	6.651	1.559	4.739
28	25545.21	1.893	6.413	1.552	4.818
29	26188.76	1.859	6.107	1.545	4.898
30	26820.65	1.83	5.537	1.538	4.977
31	27443.9	1.808	4.802	1.532	5.046
32	28673.89	1.765	6.183	1.519	5.196
33	29272.41	1.721	7.502	1.513	5.275
34	29851.42	1.681	5.231	1.508	5.353
35	30420.91	1.667	3.734	1.502	5.432
36	30986.68	1.64	6.712	1.497	5.511
37	31537.22	1.601	5.048	1.492	5.59

Table(7): Values of the eigenvalues  $E_v$ , the rotational constants  $B_v$  and the abscissa of the turning points  $R_{\min}$  and  $R_{\max}$  for the different vibrational levels of  $(1)^1\Pi$  state of the LaH molecule.

$v$	$E_v (cm^{-1})$	$B_v (cm^{-1})$	$D_v \times 10^5 (cm^{-1})$	$R_{\min} (\text{Å})$	$R_{\max} (\text{Å})$
0	669.943	3.367	8.65	2.081	2.398
1	1989.073	3.322	8.817	1.983	2.538
2	3278.032	3.274	8.969	1.921	2.645
3	4536.097	3.222	9.109	1.874	2.739
4	5762.631	3.169	9.176	1.835	2.827
5	6958.313	3.114	9.246	1.802	2.91
6	8123.311	3.058	9.255	1.774	2.991
7	9258.424	3.002	9.229	1.748	3.07
8	10364.71	2.946	9.146	1.726	3.148
9	11443.52	2.892	9.092	1.705	3.225
10	12495.67	2.837	8.994	1.686	3.3
11	13522.12	2.783	8.844	1.669	3.376
12	14524.46	2.731	8.622	1.653	3.451
13	15504.48	2.681	8.488	1.638	3.525
14	16463.11	2.639	8.302	1.625	3.598
15	17401.68	2.586	8.097	1.612	3.671
16	18321.3	2.54	7.952	1.599	3.743
17	19222.76	2.496	7.773	1.588	3.815
18	20106.92	2.453	7.63	1.577	3.886
19	20974.31	2.412	7.473	1.567	3.957
20	21825.5	2.371	7.377	1.557	4.028
21	22660.79	2.331	7.249	1.548	4.099
22	23480.51	2.291	7.084	1.539	4.17
23	24285.11	2.252	7.032	1.53	4.241
24	25074.68	2.214	6.94	1.522	4.313
25	25849.2	2.174	6.948	1.514	4.384
26	26608.25	2.135	6.805	1.507	4.457
27	27352.26	2.098	6.582	1.5	4.529
28	28082.07	2.061	6.616	1.493	4.603
29	28797.44	2.024	6.448	1.486	4.676
30	29498.84	1.989	6.195	1.48	4.75
31	30187.17	1.954	6.203	1.47	4.824
32	30862.52	1.922	5.821	1.468	4.899
33	31526.44	1.892	5.565	1.463	4.973
34	32180.3	1.865	5.063	1.457	5.043
35	32826.3	1.842	5.02	1.452	5.112
36	33464.31	1.815	5.576	1.447	5.187
37	34090.71	1.78	6.401	1.442	5.261
38	34701.84	1.744	5.303	1.437	5.335
39	35302.55	1.723	4.322	1.433	5.41
40	37615.18	1.615	5.813	1.415	5.712
41	38167.02	1.585	4.217	1.411	5.788
42	38710.93	1.563	5.253	1.408	5.866
43	39243.72	1.531	4.679	1.404	5.945

Table(8): Values of the eigenvalues  $E_v$ , the rotational constants  $B_v$  and the abscissa of the turning points  $R_{\min}$  and  $R_{\max}$  for the different vibrational levels of  $(2)^1\Pi$  state of the LaH molecule.

$v$	$E_v (cm^{-1})$	$B_v (cm^{-1})$	$D_v \times 10^5 (cm^{-1})$	$R_{\min} (\text{Å})$	$R_{\max} (\text{Å})$
0	649.643	3.249	8.217	2.119	2.441
1	1933.073	3.209	8.213	2.02	2.577
2	3195.574	3.165	8.726	1.956	2.689
3	4418.835	3.105	8.983	1.908	2.787
4	5603.691	3.057	8.46	1.869	2.876
5	6764.4	3.002	9.264	1.836	2.961
6	7889.225	2.949	8.496	1.807	3.044
7	8989.454	2.894	9.19	1.781	3.124
8	10058.66	2.841	8.555	1.758	3.204
9	11102.91	2.785	8.95	1.737	3.282
10	12119.21	2.736	8.835	1.718	3.36
11	13109.57	2.681	8.262	1.701	3.437
12	14077.06	2.628	8.936	1.684	3.514
13	15018.86	2.58	8.348	1.669	3.591
14	15937.8	2.525	8.16	1.655	3.667
15	16834.15	2.474	8.797	1.642	3.745
16	17705.79	2.423	8.425	1.63	3.823
17	18553.13	2.366	8.267	1.618	3.903
18	19375.47	2.309	8.878	1.608	3.988
19	20171.64	2.257	8.033	1.597	4.073
20	20948.74	2.223	5.041	1.588	4.156
21	21725.17	2.22	2.734	1.579	4.203
22	22516.85	2.236	3.347	1.569	4.262
23	23321.47	2.235	5.489	1.56	4.324
24	24122.09	2.199	7.174	1.552	4.37
25	24904.81	2.154	6.547	1.543	4.434
26	25673.48	2.126	6.749	1.535	4.527
27	26427.21	2.079	8.2	1.528	4.586
28	27160.35	2.053	1.307	1.52	4.608
29	27908	2.089	1.847	1.513	4.685
30	28665.84	2.042	1.375	1.506	4.766
31	29368.89	1.908	1.222	1.499	4.843
32	30027.83	1.891	-8.432	1.493	4.917
33	30704.3	1.906	6.686	1.487	4.991
34	31361.87	1.803	1.312	1.481	5.079
35	31977.22	1.78	-5.71	1.476	5.161
36	32600.21	1.749	1.328	1.471	5.245
37	33188.03	1.701	-2.139	1.466	5.324
38	33786.67	1.704	1.131	1.461	5.407
39	34356.44	1.63	9.016	1.456	5.487

Table(9): Values of the eigenvalues  $E_v$ , the rotational constants  $B_v$  and the abscissa of the turning points  $R_{\min}$  and  $R_{\max}$  for the different vibrational levels of  $(1)^3\Delta$  state of the LaH molecule.

$v$	$E_v (cm^{-1})$	$B_v (cm^{-1})$	$D_v \times 10^5 (cm^{-1})$	$R_{\min} (\text{Å})$	$R_{\max} (\text{Å})$
0	655.042	3.262	8.237	2.115	2.436
1	1943.959	3.218	8.449	2.016	2.578
2	3201.588	3.172	8.547	1.955	2.686
3	4430.715	3.126	8.635	1.905	2.78
4	5631.745	3.077	8.829	1.865	2.868
5	6802.586	3.027	8.756	1.832	2.951
6	7945.941	2.976	8.907	1.802	3.032
7	9060.734	2.924	8.783	1.776	3.111
8	10148.96	2.872	8.85	1.753	3.188
9	11210.82	2.823	8.574	1.732	3.264
10	12249.41	2.774	8.505	1.712	3.339
11	13265.63	2.727	8.467	1.694	3.412
12	14259.95	2.68	8.164	1.678	3.485
13	15234.5	2.635	8.112	1.662	3.557
14	16189.99	2.592	7.917	1.648	3.629
15	17127.56	2.55	7.667	1.634	3.669
16	18048.54	2.51	7.648	1.621	3.769
17	18953.23	2.471	7.402	1.609	3.838
18	19842.68	2.433	7.244	1.598	3.907
19	20717.41	2.396	7.18	1.587	3.975
20	21577.77	2.36	7.093	1.577	4.043
21	22423.95	2.324	6.858	1.567	4.111
22	23256.53	2.288	6.84	1.557	4.179
23	24075.45	2.253	6.807	1.548	4.246
24	24880.77	2.219	6.693	1.54	4.314
25	25672.4	2.183	6.63	1.531	4.382
26	26450.09	2.148	6.604	1.523	4.451
27	27213.82	2.113	6.564	1.518	4.52
28	27963.69	2.078	6.474	1.509	4.59
29	28699.53	2.043	6.381	1.502	4.66
30	29421.34	2.008	6.324	1.495	4.732
31	30129.33	1.973	6.317	1.488	4.803
32	30823.48	1.939	6.088	1.482	4.876
33	31504.65	1.907	5.812	1.476	4.95
34	32174.16	1.878	5.302	1.471	5.024
35	32834.37	1.854	5.065	1.465	5.089
36	33486.31	1.829	5.634	1.46	5.161
37	34126.63	1.793	6.742	1.454	5.237

Table(10): Values of the eigenvalues  $E_v$ , the rotational constants  $B_v$  and the abscissa of the turning points  $R_{\min}$  and  $R_{\max}$  for the different vibrational levels of  $(2)^3\Sigma$  state of the LaH molecule.

$v$	$E_v (cm^{-1})$	$B_v (cm^{-1})$	$D_v \times 10^5 (cm^{-1})$	$R_{\min} (\text{\AA})$	$R_{\max} (\text{\AA})$
0	626.26	3.104	7.759	2.168	2.496
1	1858.973	3.062	7.964	2.067	2.641
2	3060.842	3.016	8.216	2.003	2.753
3	4229.556	2.968	8.242	1.954	2.851
4	5369.308	2.92	8.41	1.914	2.942
5	6479.368	2.87	8.379	1.88	3.029
6	7561.929	2.821	8.537	1.85	3.113
7	8616.115	2.77	8.43	1.823	3.194
8	9644.041	2.721	8.429	1.799	3.275
9	10646.84	2.672	8.354	1.777	3.354
10	11625.49	2.623	8.2	1.758	3.431
11	12581.86	2.578	8.177	1.739	3.509
12	13516.61	2.532	7.968	1.722	3.585
13	14431.07	2.488	7.897	1.706	3.66
14	15325.99	2.444	7.837	1.692	3.736
15	16201.8	2.401	7.651	1.678	3.81
16	17059.29	2.358	7.594	1.665	3.885
17	17898.63	2.316	7.625	1.653	3.96
18	18719.72	2.274	7.455	1.641	4.035
19	19522.89	2.232	7.379	1.63	4.111
20	20308.25	2.19	7.412	1.62	4.187
21	21075.83	2.149	7.286	1.61	4.263
22	21825.76	2.106	7.351	1.6	4.342
23	22556.97	2.061	7.509	1.591	4.421
24	23268.54	2.016	7.154	1.583	4.502
25	23962.34	1.976	6.966	1.575	4.854
26	24639.4	1.935	7.06	1.567	4.666
27	25299.35	1.895	6.364	1.56	4.748
28	25945.06	1.86	6.281	1.553	4.831
29	26577.55	1.827	5.789	1.546	4.913
30	27199.91	1.804	4.96	1.54	4.993
31	27816.37	1.786	4.152	1.534	5.053
32	28430.35	1.773	4.399	1.527	5.129
33	29039.73	1.746	6.349	1.521	5.809

Table(11): Values of the eigenvalues  $E_v$ , the rotational constants  $B_v$  and the abscissa of the turning points  $R_{\min}$  and  $R_{\max}$  for the different vibrational levels of  $(2)^3\Delta$  state of the LaH molecule.

$v$	$E_v (cm^{-1})$	$B_v (cm^{-1})$	$D_v \times 10^5 (cm^{-1})$	$R_{\min} (\text{Å})$	$R_{\max} (\text{Å})$
0	616.604	3.003	7.268	2.205	2.536
1	1827.232	2.957	7.469	2.105	2.685
2	3005.126	2.91	7.632	2.042	2.798
3	4151.209	2.862	7.775	1.992	2.898
4	5266.14	2.813	7.872	1.951	2.991
5	6351.05	2.764	7.934	1.917	3.079
6	7407.282	2.716	7.926	1.885	3.165
7	8436.778	2.668	7.905	1.86	3.248
8	9441.204	2.622	7.815	1.836	3.329
9	10422.65	2.578	7.76	1.814	3.408
10	11382.3	2.534	7.708	1.794	3.483
11	12321.23	2.493	7.527	1.775	3.562
12	13241.4	2.453	7.498	1.758	3.637
13	14143.38	2.415	7.32	1.741	3.711
14	15028.63	2.377	7.27	1.726	3.785
15	15897.65	2.341	7.12	1.712	3.857
16	16751.4	2.306	7.064	1.698	3.929
17	17590.23	2.271	6.965	1.685	4.001
18	18414.66	2.238	6.879	1.672	4.072
19	19224.97	2.204	6.806	1.661	4.142
20	20021.42	2.171	6.765	1.65	4.213
21	20804.07	2.138	6.656	1.639	4.283
22	21573.21	2.106	6.603	1.629	4.354
23	22328.95	2.074	6.525	1.619	4.425
24	23071.45	2.042	6.433	1.61	4.496
25	23800.83	2.01	6.406	1.601	4.567
26	24517.15	1.978	6.282	1.592	4.639
27	25220.73	1.947	6.169	1.584	4.711
28	25911.76	1.914	6.13	1.576	4.785
29	26590.39	1.886	6.014	1.568	4.856
30	27256.98	1.856	5.845	1.561	4.929
31	27912	1.827	5.693	1.554	5.003
32	28556.17	1.8	5.589	1.547	5.072
33	29189.86	1.773	5.61	1.541	5.148
34	29812.23	1.742	5.988	1.534	5.224
35	30421.03	1.708	5.961	1.528	5.3
36	31016.42	1.678	5.29	1.522	5.378
37	31601.31	1.652	5.41	1.517	5.45
38	32174.78	1.62	5.836	1.511	5.535
39	32734.98	1.59	5.119	1.506	5.615
40	33284.47	1.562	5.572	1.501	5.697
41	33821.46	1.529	5.386	1.496	5.78
42	34346.29	1.502	5.203	1.492	5.865
43	34859.32	1.468	5.628	1.487	5.951

44	35359.13	1.439	5.213	1.483	6.04
45	35846.45	1.404	5.81	1.479	6.131

Table(12): Values of the eigenvalues  $E_v$ , the rotational constants  $B_v$  and the abscissa of the turning points  $R_{\min}$  and  $R_{\max}$  for the different vibrational levels of  $(1)^3\Pi$  state of the LaH molecule.

$\nu$	$E_v (cm^{-1})$	$B_v (cm^{-1})$	$D_v \times 10^5 (cm^{-1})$	$R_{\min} (\text{\AA})$	$R_{\max} (\text{\AA})$
0	666.56	3.384	8.859	2.075	2.393
1	1979.685	3.339	9.024	1.977	2.533
2	3263.38	3.291	9.152	1.915	2.64
3	4517.59	3.241	9.221	1.868	2.734
4	5742.997	3.189	9.326	1.829	2.821
5	6938.867	3.136	9.353	1.796	2.904
6	8105.74	3.082	9.355	1.767	2.984
7	9244.235	3.027	9.322	1.741	3.062
8	10355.2	2.973	9.247	1.719	3.139
9	11439.74	2.918	9.159	1.698	3.214
10	12498.72	2.865	9.126	1.679	3.289
11	13532.47	2.811	8.938	1.662	3.364
12	14542.54	2.76	8.761	1.646	3.438
13	15530.45	2.71	8.629	1.631	3.511
14	16496.97	2.661	8.442	1.617	3.583
15	17443.2	2.614	8.294	1.604	3.656
16	18370.02	2.567	8.15	1.591	3.728
17	19278.01	2.522	7.96	1.58	3.799
18	20167.94	2.477	7.924	1.569	3.871
19	21039.87	2.433	7.745	1.559	3.942
20	21894.31	2.39	7.683	1.549	4.014
21	22731.21	2.346	7.597	1.54	4.086
22	23550.71	2.303	7.519	1.531	4.159
23	24352.92	2.26	7.415	1.522	4.231
24	25137.94	2.217	7.389	1.514	4.305
25	25905.29	2.172	7.592	1.507	4.381
26	26653.71	2.127	7.449	1.499	4.457
27	27383.58	2.083	7.111	1.492	4.535
28	28096.27	2.04	7.217	1.486	4.614
29	28791.31	1.996	7.006	1.48	4.694
30	29469.58	1.956	6.612	1.473	4.774
31	30132.8	1.918	6.544	1.468	4.854
32	30781.79	1.884	5.682	1.462	4.934
33	31420.27	1.856	5.168	1.457	5.016
34	32051.32	1.836	4.419	1.451	5.072
35	32677.94	1.817	5.25	1.446	5.154
36	33295.7	1.783	6.671	1.441	5.233
37	33896.74	1.737	6.685	1.437	5.31
38	34482.13	1.711	3.502	1.432	5.386
39	35064.69	1.699	4.842	1.428	5.462

40	36758.04	1.624	5.444	1.415	5.689
41	37305.71	1.589	4.565	1.411	5.764
42	37845.52	1.578	3.571	1.407	5.837
43	38380.64	1.55	5.468	1.403	5.838
44	38905.53	1.533	2.99	1.4	5.988
45	39426.36	1.508	5.983	1.396	6.064

Table(13): Values of the eigenvalues  $E_v$ , the rotational constants  $B_v$  and the abscissa of the turning points  $R_{\min}$  and  $R_{\max}$  for the different vibrational levels of  $(2)^3\Pi$  state of the LaH molecule.

$v$	$E_v (cm^{-1})$	$B_v (cm^{-1})$	$D_v \times 10^5 (cm^{-1})$	$R_{\min} (\text{\AA})$	$R_{\max} (\text{\AA})$
0	650.428	3.252	8.3	2.117	2.44
1	1927.252	3.203	8.47	2.019	2.584
2	3172.106	3.153	8.587	1.957	2.693
3	4386.242	3.102	8.672	1.909	2.79
4	5570.163	3.048	8.789	1.871	2.88
5	6723.218	2.995	8.797	1.837	2.965
6	7846.845	2.94	8.828	1.809	3.048
7	8941.585	2.887	8.665	1.783	3.129
8	10010.14	2.834	8.677	1.76	3.208
9	11053.15	2.783	8.506	1.739	3.285
10	12072.46	2.733	8.264	1.72	3.361
11	13070.25	2.686	8.326	1.703	3.436
12	14046.48	2.639	7.976	1.686	3.51
13	15003.62	2.595	7.845	1.671	3.583
14	15942.51	2.552	7.682	1.657	3.655
15	16864.28	2.511	7.517	1.644	3.727
16	17769.91	2.471	7.332	1.631	3.797
17	18660.27	2.433	7.201	1.619	3.867
18	19535.94	2.396	6.974	1.608	3.936
19	20397.7	2.359	6.95	1.597	4.004
20	21245.74	2.324	6.863	1.587	4.073
21	22080.33	2.289	6.619	1.577	4.14
22	22901.98	2.255	6.559	1.567	4.208
23	23710.7	2.221	6.524	1.559	4.276
24	24506.56	2.187	6.49	1.55	4.343
25	25289.54	2.154	6.392	1.542	4.411
26	26059.6	2.121	6.184	1.534	4.479
27	26816.98	2.087	6.213	1.526	4.548
28	27561.51	2.054	6.269	1.519	4.617
29	28292.99	2.022	6.104	1.512	4.686
30	29011.6	1.988	6.022	1.505	4.756
31	29717.31	1.956	6.011	1.499	4.827
32	30410.04	1.923	5.895	1.493	4.898

Table(14): Values of the eigenvalues  $E_v$ , the rotational constants  $B_v$  and the abscissa of the turning points  $R_{\min}$  and  $R_{\max}$  for the different vibrational levels of  $(1)^3\Phi$  state of the LaH molecule.

$v$	$E_v (cm^{-1})$	$B_v (cm^{-1})$	$D_v \times 10^5 (cm^{-1})$	$R_{\min} (\text{Å})$	$R_{\max} (\text{Å})$
0	633.012	3.185	8.212	2.139	2.465
1	1878.37	3.141	8.393	2.039	2.61
2	3093.565	3.094	8.559	1.975	2.8
3	4278.174	3.044	8.661	1.927	2.818
4	5433.048	2.994	8.738	1.887	2.909
5	6558.774	2.942	8.79	1.853	2.995
6	7655.966	2.891	8.766	1.824	3.078
7	8726.066	2.84	8.69	1.798	3.159
8	9770.735	2.789	8.644	1.774	3.238
9	10790.93	2.74	8.506	1.753	3.316
10	11788.28	2.692	8.377	1.733	3.393
11	12764.12	2.645	8.267	1.715	3.468
12	13719.43	2.6	8.044	1.699	3.543
13	14655.87	2.557	7.962	1.683	3.617
14	15574.06	2.514	7.72	1.668	3.689
15	16475.39	2.474	7.632	1.655	3.761
16	17360.36	2.434	7.447	1.642	3.833
17	18229.87	2.396	7.317	1.63	3.904
18	19084.41	2.358	7.189	1.618	3.974
19	19924.46	2.321	7.059	1.607	4.044
20	20750.46	2.286	6.972	1.597	4.114
21	21562.66	2.25	6.807	1.587	4.183
22	22361.5	2.216	6.721	1.577	4.252
23	23147.2	2.182	6.678	1.568	4.322
24	23919.74	2.148	6.542	1.559	4.391
25	24679.31	2.114	6.458	1.551	4.461
26	25426.12	2.081	6.373	1.543	4.531
27	26160.42	2.049	6.271	1.535	4.6
28	26882.26	2.016	6.207	1.528	4.671
29	27591.75	1.985	6.121	1.521	4.741
30	28289.09	1.953	6.042	1.514	4.812
31	28974.29	1.922	5.926	1.508	4.884
32	29647.69	1.891	5.866	1.501	4.956
33	31600.84	1.803	5.84	1.483	5.172
34	32228.5	1.769	6.246	1.478	5.247
35	32841.51	1.734	5.862	1.473	5.324
36	33441.44	1.704	5.258	1.468	5.4

Table(15): Values of the eigenvalues  $E_v$ , the rotational constants  $B_v$  and the abscissa of the turning points  $R_{\min}$  and  $R_{\max}$  for the different vibrational levels of  $(1)^3\Sigma$  state of the LaH molecule.

$v$	$E_v (cm^{-1})$	$B_v (cm^{-1})$	$D_v \times 10^5 (cm^{-1})$	$R_{\min} (\text{\AA})$	$R_{\max} (\text{\AA})$
0	659.422	3.359	8.866	2.082	2.402
1	1956.83	3.31	9.002	1.984	2.544
2	3223.732	3.258	9.111	1.923	2.653
3	4460.017	3.204	9.194	1.876	2.749
4	5665.758	3.149	9.249	1.837	2.837
5	6841.211	3.093	9.267	1.805	2.922
6	7986.97	3.036	9.253	1.777	3.004
7	9103.854	2.98	9.173	1.751	3.084
8	10193.31	2.924	9.053	1.729	3.162
9	11256.93	2.87	8.963	1.708	3.239
10	12295.64	2.817	8.8	1.69	3.315
11	13310.98	2.766	8.609	1.673	3.39
12	14304.54	2.716	8.48	1.657	3.464
13	15277.27	2.668	8.223	1.642	3.538
14	16230.86	2.622	8.095	1.628	3.61
15	17166.12	2.578	7.849	1.615	3.682
16	18084.38	2.535	7.716	1.603	3.752
17	18986.3	2.494	7.497	1.591	3.823
18	19872.82	2.454	7.358	1.58	3.892
19	20744.48	2.416	7.208	1.57	3.961
20	21601.78	2.378	7.041	1.56	4.03
21	22445.2	2.341	6.952	1.551	4.098
22	23274.92	2.305	6.799	1.542	4.166
23	24091.27	2.269	6.707	1.533	4.235
24	24894.35	2.233	6.638	1.525	4.303
25	25684.21	2.198	6.504	1.517	4.371
26	26461	2.163	6.458	1.509	4.439
27	27224.68	2.129	6.393	1.502	4.508
28	27975.25	2.097	6.275	1.495	4.577
29	28712.82	2.06	6.244	1.488	4.647
30	29437.31	2.026	6.195	1.482	4.717
31	30148.75	1.992	6.082	1.476	4.788
32	30847.22	1.958	6.029	1.47	4.859
33	31532.74	1.925	5.997	1.464	4.931
34	32205.35	1.892	5.912	1.458	5.004
35	32865.1	1.858	5.853	1.453	5.077
36	33511.94	1.825	5.879	1.448	5.152
37	34145.57	1.791	5.887	1.443	5.228
38	34765.79	1.757	5.758	1.438	5.305
39	35372.87	1.725	5.61	1.433	5.382

Table(16): Values of the eigenvalues  $E_v$ , the rotational constants  $B_v$  and the abscissa of the turning points  $R_{\min}$  and  $R_{\max}$  for the different vibrational levels of  $(2)^1\Delta$  state of the LaH molecule.

$v$	$E_v (cm^{-1})$	$B_v (cm^{-1})$	$D_v \times 10^5 (cm^{-1})$	$R_{\min} (\text{Å})$	$R_{\max} (\text{Å})$
0	644.764	3.307	8.812	2.098	2.422
1	1916.667	3.262	8.868	1.999	2.564
2	3163.217	3.214	8.991	1.936	2.673
3	4380.856	3.16	9.111	1.889	2.769
4	5568.037	3.106	9.06	1.85	2.858
5	6726.815	3.051	9.232	1.817	2.943
6	7854.971	2.993	9.151	1.789	3.026
7	8954.039	2.936	9.217	1.764	3.107
8	10024.07	2.879	9.025	1.741	3.187
9	11067.21	2.823	9.106	1.721	3.266
10	12083.32	2.768	8.802	1.702	3.343
11	13075.19	2.715	8.841	1.685	3.421
12	14042.43	2.66	8.771	1.669	3.498
13	14985.95	2.61	8.46	1.654	3.575
14	15907.68	2.558	8.508	1.64	3.651
15	16807.51	2.51	8.299	1.627	3.727
16	17686.83	2.461	8.141	1.615	3.803
17	18546.18	2.414	8.025	1.604	3.879
18	19386.28	2.368	7.943	1.593	3.955
19	20207.59	2.323	7.719	1.583	4.031
20	21011	2.279	7.478	1.573	4.108
21	21797.71	2.238	7.182	1.564	4.185
22	22569.48	2.2	7.045	1.555	4.256
23	23326.8	2.161	7.319	1.547	4.333
24	24066.73	2.112	7.829	1.539	4.411
25	24786.01	2.065	7.161	1.531	4.49
26	25488.99	2.031	6.396	1.524	4.569
27	26178.86	1.99	7.288	1.517	4.648
28	26851.15	1.948	6.295	1.51	4.728
29	27510.31	1.917	6.403	1.504	4.808
30	28156.13	1.877	6.212	1.498	4.888
31	28789.58	1.851	5.195	1.492	4.967
32	29415.06	1.824	5.316	1.486	5.04
33	30033.24	1.807	4.319	1.481	5.108
34	30646.06	1.776	6.565	1.475	5.19

Table (17): Values of the eigenvalues  $E_v$ , the rotational constants  $B_v$  and the abscissa of the turning points  $R_{\min}$  and  $R_{\max}$  for the different vibrational levels of  $(3)^1\Delta$  state of the LaH molecule.

$v$	$E_v (cm^{-1})$	$B_v (cm^{-1})$	$D_v \times 10^5 (cm^{-1})$	$R_{\min} (\text{Å})$	$R_{\max} (\text{Å})$
0	686.419	3.308	7.835	2.102	2.416
1	2034.21	3.257	8.032	2.007	2.556
2	3346.081	3.205	8.198	1.946	2.664
3	4622.709	3.151	8.338	1.9	2.759
4	5864.623	3.096	8.439	1.862	2.847
5	7072.674	3.04	8.517	1.83	2.931
6	8247.614	2.984	8.566	1.802	3.013
7	9390.273	2.927	8.593	1.777	3.093
8	10501.49	2.87	8.617	1.754	3.171
9	11581.67	2.812	8.704	1.734	3.251
10	12630.47	2.753	8.541	1.715	3.329
11	13650.8	2.701	8.005	1.698	3.409
12	14648.91	2.654	7.906	1.682	3.481
13	15625.74	2.605	7.897	1.668	3.556
14	16581.48	2.561	7.417	1.655	3.629
15	17519.79	2.518	7.603	1.642	3.701
16	18439.69	2.477	7.152	1.63	3.772
17	19344.06	2.439	7.394	1.617	3.843
18	20232.03	2.4	7.02	1.606	3.912
19	21105.74	2.365	7.326	1.595	3.981
20	21964.26	2.331	6.963	1.584	4.05
21	22809.33	2.297	7.247	1.575	4.118
22	23640.14	2.265	6.965	1.565	4.186
23	24457.76	2.232	6.937	1.556	4.254
24	25262.13	2.2	6.93	1.547	4.321
25	26052.96	2.167	6.54	1.539	4.389
26	26830.78	2.134	6.564	1.531	4.457
27	27595.2	2.101	6.189	1.524	4.529
28	28346.74	2.067	5.98	1.518	4.594
29	29085.27	2.033	6.039	1.509	4.664
30	29810.38	1.999	5.753	1.503	4.734
31	30522.37	1.964	5.773	1.496	4.805
32	31220.86	1.929	5.979	1.49	4.876
33	31905.26	1.894	6.127	1.484	4.949
34	35675.13	1.68	6.689	1.453	5.427

Table (18): Values of the eigenvalues  $E_v$ , the rotational constants  $B_v$  and the abscissa of the turning points  $R_{\min}$  and  $R_{\max}$  for the different vibrational levels of  $(3)^3\Delta$  state of the LaH molecule.

$v$	$E_v (cm^{-1})$	$B_v (cm^{-1})$	$D_v \times 10^5 (cm^{-1})$	$R_{\min} (\text{\AA})$	$R_{\max} (\text{\AA})$
0	647.035	3.256	8.428	2.115	2.438
1	1915.207	3.202	8.722	2.018	2.586
2	3144.135	3.145	8.781	1.956	2.697
3	4339.858	3.09	8.925	1.909	2.796
4	5501.183	3.026	9.282	1.871	2.89
5	6623.283	2.963	9.204	1.838	2.98
6	7709.173	2.894	9.57	1.811	3.069
7	8755.739	2.826	9.437	1.786	3.158
8	9765.372	2.753	9.686	1.764	3.247
9	10736.36	2.68	9.915	1.745	3.337
10	11667.81	2.604	9.684	1.727	3.429
11	12561.57	2.527	1.007	1.711	3.523
12	13416.22	2.449	1.018	1.697	3.62
13	14231.48	2.367	1.012	1.684	3.72
14	15007.33	2.283	1.072	1.672	3.823
15	15741.12	2.194	1.131	1.661	3.934
16	16430.07	2.098	1.148	1.651	4.053
17	17074.98	2.009	9.776	1.642	4.185
18	17689.03	1.953	6.466	1.634	4.294
19	18293.41	1.931	4.661	1.626	4.395
20	18899.96	1.921	3.817	1.618	4.476