

Adhesion, Clusters and Functionals

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1 Kurzzusammenfassung

Die vorliegende Arbeit gliedert sich in drei verschiedene Themenbereiche der Theoretischen Chemie.

Der erste Teil beschäftigt sich mit der Adhäsion von Polymeren auf Oberflächen und ist eine Anwendung von bereits entwickelten Methoden auf ein konkretes wissenschaftliches Problem. Untersucht wurde die Adsorbat-Oberflächen-Wechselwirkung des Polymers DGEBA unter Einfluss des Entwicklers DETA auf die oxidierte Oberfläche von Magnesium. Hierbei wurde im Rahmen der Dichtefunktionaltheorie eine Clustermethode verwendet, wie auch eine Herangehensweise unter Nutzung von periodischen Randbedingungen.

Die strukturellen und elektronischen Eigenschaften von stöchiometrischen CdS-Cluster werden im zweiten Teil der Arbeit dargestellt. Hierzu wurde ein paralleler und völlig unvoreingenommener Genetischer Algorithmus entwickelt und erfolgreich auf das Problem angewendet. Die Ergebnisse durch Anwendung einer parametrisierten Dichtefunktional-Tight-Binding Methode werden entsprechend dargestellt.

Der dritte und letzte Teil beschäftigt sich mit der mehr grundlegenden Fragestellung der Entwicklung eines Dichtefunktional für den Elektronenaustauschterm. Dessen erfolgreiche Anwendung auf die isoelektronische Sequenzen von He und des Hooke-Atoms, sowie dazwischenliegende Systeme werden ebenso dargestellt, wie die Applikation auf lineare Potentiale und homogene Powerpotentiale.

2 Abstract

This work is parted in three different parts within the field of theoretical chemistry.

The first part deals with the adhesion of polymers on surfaces and is an application of already developed methods on a specific scientific problem. The adsorbat-surface-interaction of the polymer DGEBA under the influence of the hardener DETA on the oxidized magnesium surface was investigated, applying to different ways: A cluster approach, as well as a periodic boundary conditions approach, both within the Density-Functional-Theory framework.

The structural and electronic properties of stochiometrisch CdS-clusters are presented in the second part of this work. A parallel und completely unbiased genetic algorithm had been developed and successfully applied to the problem. The results, using a parametrized density-functional based tight-binding method are presented.

The third and last part deals with the more basic problem of the development of a density-functional for the electron exchange correlation term. The successful application on the isoelectronic sequences of both, the helium and Hooke-atom, as well as intermediate systems are presented along with those for linear and homogenous power potentials.

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3 Table of Abbreviations

Abbrevitaion	Description
API	Application Programming Interface
ASPG	Group of Prof. Dr. W. Possart, Chair for Adhesion and Interphases in Polymers, Saarland University
CO	Carbon Oxide
DETA	Diethylenetriamine
DFT	Density Functional Theory
DFTB	Density Functional Tight Binding
DGEBA	Bisphenol A Diglycidyl Ether
DMA	Distributed Memory Architecture
E	Energy
GA	Genetic Algorithm
HOMO	Highest Occupied Molecular Orbital
IR	Infrared
LUMO	Lowest Unoccupied Molecular Orbital
Mg	Magnesium
MgO	Magnesiumoxyde
MO	Molecular Orbital
MPI	Message Passing Interface
N	No
O	Oxygen
OpenMP	Open Multi-Processing
RN	Random Number
RNG	Random Number Generator
SMA	Shared Memory Architecture
SP	Single Point Calculation
TV	Translational Vector
Y	Yes

Tab. 3.0.1: Table of used abbreviations

Contents

1	Kurzzusammenfassung	II
2	Abstract	III
3	Table of Abbreviations	VI
4	Introduction	1
5	Theoretical Background	4
5.1	The Density-functional Theory (DFT)	4
5.1.1	The Hohenberg-Kohn Theorems	5
5.1.2	The Kohn-Sham Equations	6
5.1.3	The Local-Density Approximation (LDA)	8
5.2	Density-functional Tight-Binding Method	9
5.3	B3LYP	13
5.4	Periodic Boundary Conditions	15
6	Adhesion of Polymers on Surfaces	16
6.1	Introduction	16
6.2	The Metallic Surface	18
6.2.1	Magnesium Oxide	18
6.2.2	Cluster Approach	20
6.2.2.1	Monolayer MgO Clusters	20
6.2.2.2	Multilayer MgO Clusters	22
6.2.2.3	Embedded Clusters: External Point Charge field	23
6.2.3	Periodic Boundary Conditions Approach	24

6.2.4	Revised Periodic Boundary Conditions Approach	26
6.3	The Epoxid Layer	29
6.3.1	DGEBA	30
6.3.2	DETA	34
6.4	Interaction with the Metal Surface	37
6.5	Conclusions	39
7	Cadmium Sulphide Clusters	41
7.1	Introduction	41
7.2	CdS Crystal Structure	42
7.3	The Genetic Algorithm	46
7.3.1	Motivation	46
7.3.2	What is a Genetic Algorithm?	47
7.3.3	Unbiasedness	48
7.3.4	Random Number Generation	55
7.3.5	Parallelization	56
7.3.5.1	OpenMP API	57
7.3.5.2	MPI API	58
7.3.6	Description of the developed Genetic Algorithm	59
7.3.7	Mating	63
7.3.7.1	ONEPAR	63
7.3.7.2	TWOPAR	64
7.3.8	Mutations	67
7.4	Structural Analysis	67
7.4.1	Radial Distribution Function	70
7.4.2	Similarity Functions	71
7.4.3	Stability Function	74
7.4.4	Shape Analysis	78
7.5	Electronic Properties	80
7.5.1	Mulliken gross populations	80
7.5.2	HOMO, LUMO and Band Gap	85

7.6	Conclusion	87
8	Towards the universal Functional	89
8.1	Introduction	89
8.2	Hooke's atom	90
8.3	Nonuniversality of commonly used correlation-energy density functionals .	90
8.4	Wigner's functional	91
8.5	Computational Notes	92
8.5.1	Hartree-Fock energies	92
8.5.2	Radially correlated energies	93
8.5.3	Exact energies	94
8.5.4	Total and radial correlation energies	94
8.5.5	Linear Potential	95
8.6	Reparametrization of Wigner's Functional	95
8.7	Correlation Energies for intermediate systems	98
8.8	A Procedure to determine Wigner Parameters	101
8.9	Tests on homogeneous power potentials	105
8.10	Conclusions	108
9	Summary and Conclusions	110
	Table of Figures	XIII
	List of Tables	XV
A	Technical Data	XVI
A.1	Technical Data of the epoxide DGEBA	XVI
A.2	Technical Data of the DETA	XVII
B	Structures of stoichiometric $(CdS)_n$ clusters for $n = 2 - 25$	XVIII
C	Hartree-Fock, exact energies and Wigner Correlation energies for the Coulomb-Hooke-Potential	XXIV
C.1	Energies for $Z = 2$ for the Coulomb-Hooke-Potential	XXIV

C.2	Energies for $Z = 3$ for the Coluomb-Hooke-Potential	XXVI
C.3	Energies for $Z = 4$ for the Coluomb-Hooke-Potential	XXVIII
C.4	Energies for $Z = 5$ for the Coluomb-Hooke-Potential	XXX
C.5	Energies for $Z = 6$ for the Coluomb-Hooke-Potential	XXXII
C.6	Energies for $Z = 7$ for the Coluomb-Hooke-Potential	XXXIV
C.7	Energies for $Z = 8$ for the Coluomb-Hooke-Potential	XXXVI
C.8	Energies for $Z = 9$ for the Coluomb-Hooke-Potential	XXXVIII
C.9	Energies for $Z = 10$ for the Coluomb-Hooke-Potential	XL
D	Expectation Values for the Coluomb-Hooke potential	XLII
D.1	Expectation Values for the Coluomb-Hooke potential for $Z = 2$	XLII
D.2	Expectation Values for the Coluomb-Hooke potential for $Z = 3$	XLIV
D.3	Expectation Values for the Coluomb-Hooke potential for $Z = 4$	XLVI
D.4	Expectation Values for the Coluomb-Hooke potential for $Z = 5$	XLVIII
D.5	Expectation Values for the Coluomb-Hooke potential for $Z = 6$	L
D.6	Expectation Values for the Coluomb-Hooke potential for $Z = 7$	LII
D.7	Expectation Values for the Coluomb-Hooke potential for $Z = 8$	LIV
D.8	Expectation Values for the Coluomb-Hooke potential for $Z = 9$	LVI
D.9	Expectation Values for the Coluomb-Hooke potential for $Z = 10$	LVIII
E	Papers, Talks and Posters	LX
E.1	Papers	LX
E.2	Talks	LXI
E.3	Posters and Conferences	LXI
F	Eidesstattliche Erklärung	LXII

4 Introduction

Theoretical chemistry is gaining more and more attention, not only in science, but also in industry. Although the roots are going back to the early years of the last century, it took several decades and the development of powerful computers to reach a fundamental basis for predicting chemical and physical properties.

This thesis consists of three parts, each dealing with a completely different scientific problem. The joined basis of all parts is the application of theoretical methods to obtain the desired information. An introductory chapter will give a short overview about the applied theory. Each part will have additional theoretical background, that it helps to understand the applied methods in more detail. Hence, every part includes a detailed introductory section, and we will refer to them for a more deepened perspective and will keep this one more shortly.

The three different parts of this thesis represents different ways of investigating scientific problems: Finding the appropriate scientific method to a specific problem; Modification and improvement of scientific methods to describe the investigated systems in a reasonable way; And lastly developing appropriate scientific tools and their tests on different simple scientific questions.

The first part investigates the adhesion of polymers on surfaces. It was induced by a collaboration with the Chair for Adhesion and Interphases in Polymers at the Saarland University.

The interaction of the polymers with the surface are of great interest, not only for the scientific community, but also for the industry. Within technical applications, the requirements to predict product properties are continuous increasing.

Nowadays the development of new materials is mainly done by empirical methods. Therefore, a fundamental understanding of the basic cohesion and disassociation mechanism is of utmost importance.

Furthermore, materials scientists are highly interested in the IR-spectra, i.e. the vibrational nodes of the glueing systems, to compare them with their experimental results. Unfortunately, there are mainly broad ranges of vibrational nodes in the literature available, which make the evaluation of a successful experiment quite difficult. Computing such properties requires highly accurate boundary conditions on both, the modeled system and the applied methods.

For this part, well known different proprietary programs have been used, as well as different techniques to investigate the systems. The possibilities and the limitations of both, the programs and the methods are presented.

The second part deals with structural and electronic properties of clusters. In the past years significant interest in clusters has been developed due to their fundamental importance in both basic and applied science. The properties of clusters are unique, i.e. they strongly depend on and vary with the size of the cluster, and by the promise the systems hold a wide spreaded application area, i.e. optical, magnetical and electronic devices and sensors.

Usually it is assumed that the structure of stoichiometric $(CdS)_n$ clusters is similar to fragments of the bulk phase. However, this might not be the case for small n .

An unbiased genetic algorithm has been further developed to obtain new clusters. The structure optimization has been done within a parametrized density-functional tight-binding framework. The potential for this calculations has been optimized and applied to gain the desired structural and electronic properties. Further more, the genetic algorithm and the structure optimization has been transferred to a parallel program version. The results are presented in detail for the investigated $(CdS)_n$ cluster for the size range $n = 2 - 25$.

The third and last part is a more fundamental investigation and development within the density functional theory. It is of great importance to have access to reasonable density functionals for describing the interatomic interactions. During the past years a lot of

different, more or less successful, functionals has been announced and applied. After applying some of them to very basic systems, i.e. the helium and hookes atom isoelectronic sequences, rather poor description of the interactions has been discovered.

Starting with a functional, originally proposed in 1938, we developed our own density functional and applied it successfully to different systems. The results are presented in detail.

5 Theoretical Background

In this introductory chapter the theoretical background of the applied methods will be given. Section 5.1 provides a short overview of density-functional theory, as being the basic principle for the work done in Chapters 6 and 7. Afterwards the density-functional tight-binding method (Section 5.2) is introduced, which has been applied in Chapter 7. The last section 6.2.3 of this theory overview deals with periodic boundary conditions as used in Chapter 6.

To a general overview about Density Functional Theory and its application we refer to the well known literature, e. g. [1, 2].

5.1 The Density-functional Theory (DFT)

Solving the Schrödinger equation [3–6]

$$\hat{H}\Psi = E\Psi \tag{5.1.1}$$

is the most central problem in quantum chemistry.

Since its development in 1960s, the density-functional theory is the traditional method of choice for physicists on the calculations of solids, whereas the chemists often use the Hartree-Fock method on rather small molecular systems. However, in the last twenty years the DFT methods became more and more important for the calculations of small, low-symmetric systems, not only due to the popularity of the *Gaussian* programme suite [7] and its use by organic chemists.

While we focus on the time-independent part ¹ of the Schrödinger equation [Eq: 5.1.1] and

¹The wavefunction Ψ_0 in the time-dependent Schrödinger equation $\hat{H}\Psi_0 = i\hbar\frac{\partial\Psi_0}{\partial t}$ can be written as a product of one time depending and one position and spin depending factor $\Psi_0(\mathbf{x}, t) = \Psi(\mathbf{x})A(t)$. This factorization leads to the time-independent Schrödinger equation as in Eqs. 5.1.1 and 5.1.2

apply the Born-Oppenheimer approximation² [8] the resulting equation for the electrons is

$$\hat{H}_e \Psi_e = E_e \Psi_e \quad (5.1.2)$$

where $\Psi_e = \Psi_e(\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_3, \dots, \mathbf{x}_N)$ is the electronic wavefunction depending on position $\mathbf{r}_i = (x_i, y_i, z_i)$ and spin σ_i of each electron i [$\mathbf{x}_i = (\mathbf{r}_i; \sigma_i) = (x_i, y_i, z_i; \sigma_i)$].

Thomas and Fermi [9, 10] proposed that one can determine the electron density in three-dimensional position-space instead of the electronic wavefunction and from that obtain all information of interest. The resulting equation that directly determines the electron density $\rho(\mathbf{r})$ is much easier to solve than the Schrödinger equation itself. This so-called Thomas-Fermi method has been one of the most important steps in the development of density-functional theory. Since the approach is constructed as an approximation instead of an exact alternative to solving the Schrödinger equation, the obtained results are very inaccurate. i. e. no electronic shell structures are given.

Density-functional theory itself is based on the two theorems by Hohenberg and Kohn [11] that have been published in 1964. In 1998 Walter Kohn has been honored with the Nobel-prize in chemistry for his development of the density-functional theory together with John A. Pople for his development of computational methods in quantum chemistry^{3,4} [12–14].

5.1.1 The Hohenberg-Kohn Theorems

The first Hohenberg-Kohn theorem states that it is possible to calculate any groundstate property of a given system by knowledge of the electron density $\rho(\mathbf{r})$ only. Therefore, the total electronic energy of the system E_e is a well-defined functional of the electron density:

$$E_E[\rho(\mathbf{r})] = F[\rho(\mathbf{r})] + \int \rho(\mathbf{r}) V_{ext}(\mathbf{r}) d\mathbf{r}. \quad (5.1.3)$$

²The Born-Oppenheimer approximation separates the electronic and nuclear motion within the Hamiltonian, so that they can be seen as fixed particles for the electrons, because the nuclei are much heavier than the electrons. I. e. the electrons are so light that they can react instantaneously to change their positions.

³Further information can be found at:

http://nobelprize.org/nobel_prizes/chemistry/laureates/1998/index.html

⁴John A. Pople is one of the founders of the *Gaussian* program suite [7]

$F[\rho(\mathbf{r})]$ is a universal functional which is independent of the external potential $V_{ext}(\mathbf{r})$ and of the geometry of the nuclei of the system. The external potential is determined first of all by the Coulomb potentials of the atomic nuclei but may, moreover, contain additional (i. e. electrostatic or gravitational) potentials. Through the potential, the electron density $\rho(\mathbf{r})$ determines the Hamilton operator and, thereby, all groundstate properties. The total number of electrons of the system is also defined by $\rho(\mathbf{r})$:

$$N = \int \rho(\mathbf{r}) d\mathbf{r}. \quad (5.1.4)$$

The second Hohenberg-Kohn theorem states that a variation of the groundstate electron density (starting from the exact electron density $\rho(\mathbf{r})$),

$$\tilde{\rho}(\mathbf{r}) = \rho(\mathbf{r}) + \delta\rho(\mathbf{r}), \quad (5.1.5)$$

results in a positive change of the total groundstate energy:

$$E_e[\tilde{\rho}(\mathbf{r})] \geq E_e[\rho(\mathbf{r})]. \quad (5.1.6)$$

By changing the electron density to $\tilde{\rho}(\mathbf{r})$ the number of electrons in the system has to be unchanged

$$\int \tilde{\rho}(\mathbf{r}) d\mathbf{r} = \int \rho(\mathbf{r}) d\mathbf{r}. \quad (5.1.7)$$

5.1.2 The Kohn-Sham Equations

The well known problem, that the Hohenberg-Kohn theorems do not explicitly give any functionals, is still unsolved. In 1965 Walter Kohn and Lu Jeu Sham published a method for the calculation of the electron density with the so-called Kohn-Sham equations [15]. They are a set of single-particle equations similar to the Hartree-Fock ones. The problem of how to calculate the total energy as a density functional has been transformed to the definition of this set of single-particle equations. For an N -particle system the total

electronic energy $E_e[\rho(\mathbf{r})]$ can be written as

$$E_e[\rho(\mathbf{r})] = T[\rho(\mathbf{r})] + \int \rho(\mathbf{r}) \left[V_{ext}(\mathbf{r}) + \frac{1}{2} V_C(\mathbf{r}) \right] d\mathbf{r} + E'_{xc}[\rho(\mathbf{r})], \quad (5.1.8)$$

with T as the kinetic energy of the system, $\int \rho(\mathbf{r}) V_{ext}(\mathbf{r}) d\mathbf{r}$ the energy resulting from the external potential and the Coulomb energy $\frac{1}{2} \int \rho(\mathbf{r}) V_C(\mathbf{r}) d\mathbf{r}$ resulting from the electron repulsion (the factor $\frac{1}{2}$ deletes the double-counted terms). E'_{xc} is the so called exchange-correlation energy and does contain all terms that are not included in the other three.

After exertion of the variational principle using the Lagrange multiplier μ (which is equivalent to the chemical potential for the electrons) we get

$$\frac{\delta T}{\delta \rho} + V_{ext}(\mathbf{r}) + V_C(\mathbf{r}) + \frac{\delta E'_{xc}}{\delta \rho} = \mu, \quad (5.1.9)$$

where μ has been introduced to satisfy the condition

$$N = \int \rho(\mathbf{r}) d\mathbf{r}. \quad (5.1.10)$$

Kohn and Sham introduced a system similar to the original one but with N non-interacting particles. These particles shall move in an external potential $V_{eff}(\mathbf{r})$ that is defined in such a way that the electron density and the energy are equal to the electron density and the energy of the original system of interacting particles. Equations 5.1.8 and 5.1.9 therefore become much easier for this fictive system:

$$E_e[\rho(\mathbf{r})] = T^{KS}[\rho(\mathbf{r})] + \int V_{eff}(\mathbf{r}) \rho(\mathbf{r}) d\mathbf{r}. \quad (5.1.11)$$

After applying the variational principle we obtain

$$\frac{\delta T^{KS}}{\delta \rho} + V_{eff}(\mathbf{r}) = \mu \quad (5.1.12)$$

with

$$V_{eff}(\mathbf{r}) = \frac{\delta T}{\delta \rho} - \frac{\delta T^{KS}}{\delta \rho} + V_{ext}(\mathbf{r}) + V_C(\mathbf{r}) + \frac{\delta E'_{xc}}{\delta \rho(\mathbf{r})}. \quad (5.1.13)$$

Note that the kinetic energy T^{KS} of the fictive system is not equal to the kinetic energy T of the real system.

The Hamiltonian is now simplified to a great extent and can be written as the sum of N single-particle operators $\hat{h}_{eff}$:

$$\hat{H} = \sum_{i=1}^N \left[-\frac{1}{2} \nabla_{\mathbf{r}_i}^2 + V_{eff}(\mathbf{r}_i) \right] \equiv \sum_{i=1}^N \hat{h}_{eff}(i) \quad (5.1.14)$$

We can write the many-body wavefunction as a single Slater determinant

$$\Psi \equiv |\psi_1, \psi_2, \dots, \psi_N|, \quad (5.1.15)$$

and the single-particle equations are

$$\hat{h}_{eff}(i)\psi_i = \epsilon_i\psi_i. \quad (5.1.16)$$

This determines the single-particle energies ϵ_i . Finally, the electron density is the sum over the N orbitals with the lowest single-particle energies ϵ_i :

$$\rho(\mathbf{r}) = \sum_{i=1}^N n_i |\psi_i(\mathbf{r})|^2 \quad (5.1.17)$$

where n_i is the occupation number of the i -th orbital.

The electron density of the system consisting of non-interacting particles has been constructed in such a way it is equal to the electron density of the real system. However, the single-particle wavefunctions of the non-interacting particles ψ_i and energies ϵ_i are not identical with those of the electrons but practice has shown that they provide a good approximation to them.

5.1.3 The Local-Density Approximation (LDA)

A problem originates from the exchange-correlation energy $E_{xc}[\rho(\mathbf{r})]$ and the accompanying potential

$$V_{xc}(r) = \frac{\delta T}{\delta \rho} - \frac{\delta T^{KS}}{\delta \rho} + \frac{\delta E'_{xc}}{\delta \rho} \equiv \frac{\delta E_{xc}}{\delta \rho}, \quad (5.1.18)$$

because they are unknown. However, the exchange-correlation energy can be written as

$$E_{xc}[\rho(\mathbf{r})] = \int \epsilon_{xc}(\mathbf{r})\rho(\mathbf{r})d\mathbf{r} \quad (5.1.19)$$

where ϵ_{xc} can be expressed approximately in terms of the electron density and its derivatives:

$$\epsilon_{xc}(\mathbf{r}) = \epsilon_{xc}[\rho(\mathbf{r}), |\nabla\rho(\mathbf{r})|, \nabla^2\rho(\mathbf{r}), \dots] . \quad (5.1.20)$$

The local-density approximation (LDA) approximates ϵ_{xc} as depending only on the electron density $\rho(\mathbf{r})$.

5.2 Density-functional Tight-Binding Method

The density-functional tight-binding (DFTB) program has been used in this work in the optimization of the structures of the investigated $(CdS)_n$ -clusters and to calculate their electronic properties as described in chapter 7. It has been developed by Seifert *et al.* [16–18].

This method is based on the density-functional theory of Hohenberg and Kohn [11] in the formulation of Kohn and Sham [15] as described in Section 5.1. According to the LCAO ansatz, the single-particle eigenfunctions $\psi_i(\mathbf{r})$ are expanded in a suitable set of localized atomic-like basis functions $\varphi_m(\mathbf{r})$:

$$\psi_i(\mathbf{r}) = \sum_m c_{im}\varphi_m(\mathbf{r}). \quad (5.2.21)$$

The index m being the atom at which the function φ_m is centered and the angular and radial dependence. These functions are derived by applying self-consistent density-functional calculations on the isolated atoms using a large set of Slater-type basis sets.

Within the eigenvalue problem

$$\hat{h}_{eff}\psi_i(\mathbf{r}) = \epsilon_i\psi_i(\mathbf{r}) \quad (5.2.22)$$

the Hamilton operator $\hat{h}_{eff}$ is defined as

$$\hat{h}_{eff} = \hat{t} + V_{eff}(\mathbf{r}), \quad (5.2.23)$$

with $\hat{t}$ being the kinetic-energy operator ($\hat{t} = -\frac{1}{2}\nabla^2$) and V_{eff} the effective Kohn-Sham potential. The latter is approximated as a simple superposition of the potentials of the neutral atoms,

$$V_{eff}(r) = \sum_j V_j^0(|\mathbf{r} - \mathbf{R}_j|), \quad (5.2.24)$$

with $\mathbf{R}_j$ being the position of the j -th atom.

In order to calculate the Hamiltonian matrix, one has to approximate the effective potential $V_{eff}(\mathbf{r})$ in an appropriate way. In a first step, the Kohn-Sham equations are solved self-consistently for the free and neutral atom

$$[\hat{t} + V^0(\mathbf{r})] \varphi_m(\mathbf{r}) = \epsilon_m \varphi_m(\mathbf{r}), \quad (5.2.25)$$

with $V^0(\mathbf{r})$ being the potential of the free and neutral atom modified by

$$V^0(\mathbf{r}) = V_{ext}(\mathbf{r}) + V_H(\mathbf{r}) + V_{xc}^{LDA}(\mathbf{r}) + \left(\frac{\mathbf{r}}{\mathbf{r}_0}\right)^N. \quad (5.2.26)$$

The Hartree potential V_H describes the electron-electron interactions, V_{xc}^{LDA} the exchange-correlation part of the LDA potential, and the additional term $\left(\frac{r}{r_0}\right)^N$ the long-distance parts of the wavefunction. In comparison to the isolated free atom this produces that the electron density is compressed, but kept unchanged in the bonding-relevant range. According to Seifert *et al.* [16] the exponent N has only marginal effects on the results and is kept equal to $N = 2$ for all atoms. The same authors proposed to set the cut-off radius r_0 to $r_0 = 2r_{cov}$, being r_{cov} the covalent radius of the atom [16].

The tight-binding approximation is used in the way, that the Hamilton matrix elements are

$$h_{mn} = \langle \varphi_m | \hat{t} + \sum_j V_j^0 | \varphi_n \rangle = \langle \varphi_m | \hat{t} + V_{jm}^0 + (1 - \delta_{j_n, j_m}) V_{j_n}^0 | \varphi_n \rangle, \quad (5.2.27)$$

where the m -th and n -th basis functions φ_m and φ_n are centered on the atoms at R_{j_m} and R_{j_n} , respectively. The inclusion of the Kronecker- δ assures that the potential is not counted twice for $j_m = j_n$. By applying it in the described way, in the Hamiltonian matrix only two-center terms will be considered, but all of those will be calculated exactly (i.e. $h_{mn} = \langle \varphi_m | \hat{h} | \varphi_n \rangle$, $S_{mn} = \langle \varphi_m | \varphi_n \rangle$).

These approximations lead to the same structure of secular equations,

$$\sum_m c_{im} (h_{mn} - \epsilon_i S_{mn}) = 0, \quad (5.2.28)$$

as in other (nonorthogonal) tight-binding schemes. It is important to point out that all matrix elements are calculated and none is obtained by fitting to experimental results.

By using the Kohn-Sham eigenvalues ϵ_i , the total energy $E_e[\rho(\mathbf{r})]$ can be written as

$$E_e[\rho(\mathbf{r})] = \sum_i^{occ} \epsilon_i - \frac{1}{2} \left[\int V_{eff}(\mathbf{r}) \rho(\mathbf{r}) d\mathbf{r} - \int V_{ext}(\mathbf{r}) \rho(\mathbf{r}) d\mathbf{r} \right] + E_{xc} - \frac{1}{2} \int V_{xc}(\mathbf{r}) \rho(\mathbf{r}) d\mathbf{r} + E_N, \quad (5.2.29)$$

where

V_{ext}	electronic potential from the nuclei
E_{xc}	exchange-correlation energy
V_{xc}	to E_{xc} corresponding potential
E_N	nuclear repulsion energy
$\rho(r)$	electron density.

Since the difference between superposed atomic electron densities and the true electron density of the investigated system remains small, and since by far the largest parts of the interatomic interactions are of fairly short range, the major part of the binding energy remains in the difference of the single-particle energies ϵ_i of the investigated systems, and the single-particle energies ϵ_{jm_j} of the isolated atoms (j being an atom index, m_j an orbital index), i. e.

$$-\epsilon_B \equiv \sum_i^{occ} \epsilon_i - \sum_j \sum_{m_j}^{occ} \epsilon_{jm_j}. \quad (5.2.30)$$

Approximating the short-ranged interactions by simple pair-potentials lead to the following expression for the binding energy

$$-E_B \approx \sum_i^{occ} \epsilon_i - \sum_j \sum_{m_j}^{occ} \epsilon_{jm_j} + \frac{1}{2} \sum_{j \neq j'} U_{jj'}(|R_j - R_{j'}|). \quad (5.2.31)$$

$U_{jj'}(|R_j - R_{j'}|)$ is obtained as the difference of ϵ_B and E_B^{SCF} for diatomic molecules, being E_B^{SCF} the total energy from parameter-free density-functional calculations. For the present work, the systems CdS , Cd_2 , and S_2 needed to be considered. All electrons were treated within a frozen-core approximation except for the valence electrons for the different atoms (i.e. Cd: 5s,4d; S:3s,3p).

Using the Hellmann-Feynman theorem [19, 20]

$$\mathbf{F}_j = -\frac{\partial E}{\partial \mathbf{R}_j} \quad (5.2.32)$$

will allow to calculate the forces $\mathbf{F}_j$ acting on the j -th atom of the investigated system. They can be splitted up into two parts: one electronic part ($\mathbf{F}_j^e$) and one acting on the nuclei only ($\mathbf{F}_j^N$):

$$\mathbf{F}_j = \mathbf{F}_j^e + \mathbf{F}_j^N. \quad (5.2.33)$$

Whereas the nuclear part consists of the sum of the derivatives of the repulsive contributions of the nuclei,

$$\mathbf{F}_j^N = \sum_{j \neq j'} \frac{\partial}{\partial \mathbf{R}_j} \left(\frac{Z_j Z_{j'}}{|\mathbf{R}_j - \mathbf{R}_{j'}|} \right), \quad (5.2.34)$$

the electronic part can be written as the sum of orbital contributions

$$\mathbf{F}_j^e = \sum_i n_i \mathbf{F}_{ji} = -\frac{\partial}{\partial \mathbf{R}_j} \left(\sum_i n_i \langle \varphi_i | \hat{h} | \varphi_i \rangle \right), \quad (5.2.35)$$

with n_i being the occupation number of the i -th orbital, either being $n_i = 0$ or $n_i = 1$, and as a consequence the summation is only done over the occupied orbitals ($N_i = 1, i = 1, \dots, occ$). The force $\mathbf{F}_{ji}$ can be written as

$$\mathbf{F}_{ji} = \sum_{m,n} c_{im} c_{jn} \left(-\frac{\partial H_{mn}}{\partial \mathbf{R}_j} + \epsilon_i \frac{\partial S_{mn}}{\partial \mathbf{R}_j} + \frac{\partial V_{mn}^{ee}}{\partial \mathbf{R}_j} \right), \quad (5.2.36)$$

being V_{mn}^{ee} the matrix elements of the electron-electron potential $V^{ee} = V_h + V_{xc}$. The components of the forces arising from this potentials is compensated by the nuclear part $\mathbf{F}_j^N$:

$$\mathbf{F}_j^N \approx \sum_{m,n} c_{im} c_{in} \frac{\partial V_{mn}^{ee}}{\partial \mathbf{R}_j}. \quad (5.2.37)$$

These two terms can be approximated by the parameter $U(R)$ which can be seen as an empirical repulsion:

$$U(R) = \begin{cases} a(R-R_1)^2 & \text{for } R < R_1 \\ 0 & \text{for } R \geq R_1. \end{cases} \quad (5.2.38)$$

Fitting the calculated equilibrium distances and vibrational frequencies in the diatomics to experimentally observed values will lead to the new introduced parameter a and R_1 [21]. The forces that are acting on an atom positioned at R_j can finally be calculated as

$$\mathbf{F}_j = -\nabla_j E_{tot} = \sum_i^{occ} \sum_{m,n} \left(-\frac{\partial H_{mn}}{\partial \mathbf{R}_j} + \epsilon_i \frac{\partial S_{mn}}{\partial \mathbf{R}_j} \right) + \frac{1}{2} \sum_{j \neq j'} \frac{\partial}{\partial \mathbf{R}_j} U_{jj'} (|\mathbf{R}_j - \mathbf{R}_{j'}|). \quad (5.2.39)$$

Thus, the energy calculations within the described DFTB program were performed without using empirical parameters, whereas empirical parameters enter the calculation of the forces.

5.3 B3LYP

Becke developed his hybrid approach. Within a short time, he published a series of papers, concerning the his 3 parameter-methods [22–26].

He showed that the LSDA tendency to overestimate the bonding, could be solved by an exchange-only density-gradient correction. Unfortunately he discovered that the exchange-only gradient led to non-good ionization potentials, which needed to be fixed by a dynamical correction coefficient.

Originally he assumed a 50:50 assignment between the exact exchange-energy and the LSDA, but that led to some success in certain fields and less glorious in different ones.

Once again he analyzed the exchange-correlation energy E_{xc} as given from the so called adiabatic connection

$$E_{xc} = \int_0^1 U_{xc}^\lambda d\lambda, \quad (5.3.40)$$

being λ the interelectronic coupling strength parameter and U_{xc}^λ the exchange-correlation potential energy at interacting strength λ . The lower limit $\lambda = 0$ represents the total decoupled reference system according to Kohn and Sham, whereas the upper limit $\lambda = 1$ the full coupling real system. The former used LSDA is based on an electrongas-approach for the U_{xc} , which led to inadequateness for λ being close to zero. Due to this, he proposed this exchange-correlation term

$$E_{XC} = E_{XC}^{LSDA} + a_0(E_X^{exact} - E_X^{LSDA}) + a_X \Delta E_X^{B88} + a_C \Delta E_C^{LYP} \quad (5.3.41)$$

being

a_0, a_X, a_C	semi-empirical coefficients, fitted by appropriate exp. data
E_X^{exact}	Hartree-Fock exact exchange-correlation energies
ΔE_X^{B88}	Beckes 1988 exchange gradient-approach (LSDA) [22]
ΔE_C^{LYP}	Lee, Yang and Perdew 1988 correlation gradient-correction [27]

The second term replaces the electrongas exchange-energy by exact ones in Equation 5.3.40, to solve the misbehavior for λ being close to zero. The coefficient a_0 takes the independence of the particles into account. The third and fourth terms help to find the appropriate mixing between the exchange- and correlation-correction.

The B3LYP-method is used in Chapter 6 with and without periodic boundary conditions.

5.4 Periodic Boundary Conditions

In computer simulations periodic boundary conditions (PBC) are often used to simulate large (infinite) systems (i. e. bulk phase) by modeling a small part (i. e. a unit cell or a simulation box) that is far from the boundaries.

There are several requirements, which need to be fulfilled in order to obtain good results:

- Symmetry: the system investigated needs to be (highly) symmetric to reduce the computational efforts (i.e. to use a small unit cell / simulation box)
- The small part needs to represent all physical and chemical properties of the whole system. Therefore it needs to be from the ‘inner’ parts, to prevent effects due to the phase interfaces

The PBC as implemented in the *Gaussian G03* program suite [7, 28, 29], used in Chapter 6, can not be explained in detail, due to the lack of references by the program authors, since the implementation of the PBC in the suite in 2003. On personal request, the authors refer to the program manual and the reference therein, which will be maintained ‘soon’ according to *Gaussian, Inc.* [30].

For a short overview of different applied PBC methods we refer to [31–38].

6 Adhesion of Polymers on Surfaces

This chapter deals with the adhesion of the polymeric glue Bisphenol A Diglycidyl Ether (DGEBA) on the metallic surface of oxidized magnesium. The problem was induced by experimental works at the group of Prof. Dr. W. Possart, Chair for Adhesion and Interphases in Polymers, Saarland University.

Please note that there exists theoretical work on a similar field already [39, 40].

For a overview about both, experimental and theoretical work, see [41–44].

6.1 Introduction

Within technical applications, the requirements to predict product properties are continuously increasing. Therefore the importance of the development of new materials is growing as well. Often, a combination of many different materials will lead to the desired solution and properties. One important issue are lightweight construction materials, as they are being used in aeronautics and space flights for many years. Moreover, by their goal to reduce the product weight and simultaneously the fuel consumption, they found their way into the automobile and train business. Aluminum has been used in this field for many years now. Magnesium will open a new range of applications. Instead of welding the materials, it is possible to glue them together, with the same favorable and aimed properties, e.g.: stability, corrosion, if proper glues can be identified. Gluing is one of the oldest joining techniques used by mankind. [45, 46]

The gluing efficiency is defined by the stability, the strain behavior and the resistance against physical and chemical influences. Stability is mainly given by cohesiveness and adhesion. Adhesion is the interaction driven coherence at the interface between glue, the adhesive, and the substrate, the adherents. Aging will degrade this stability and may cause a disassociation.

Nowadays the development of new materials is mainly done by empirical methods. [47]

Therefore, a fundamental understanding of the basic cohesion and disassociation mechanism is of utmost importance.

The basic theoretical investigations about the interaction between the polymers and the surface are a first step towards a more coordinated material development.

Preliminary work addresses the questions how to model the bulk phase of the infinite

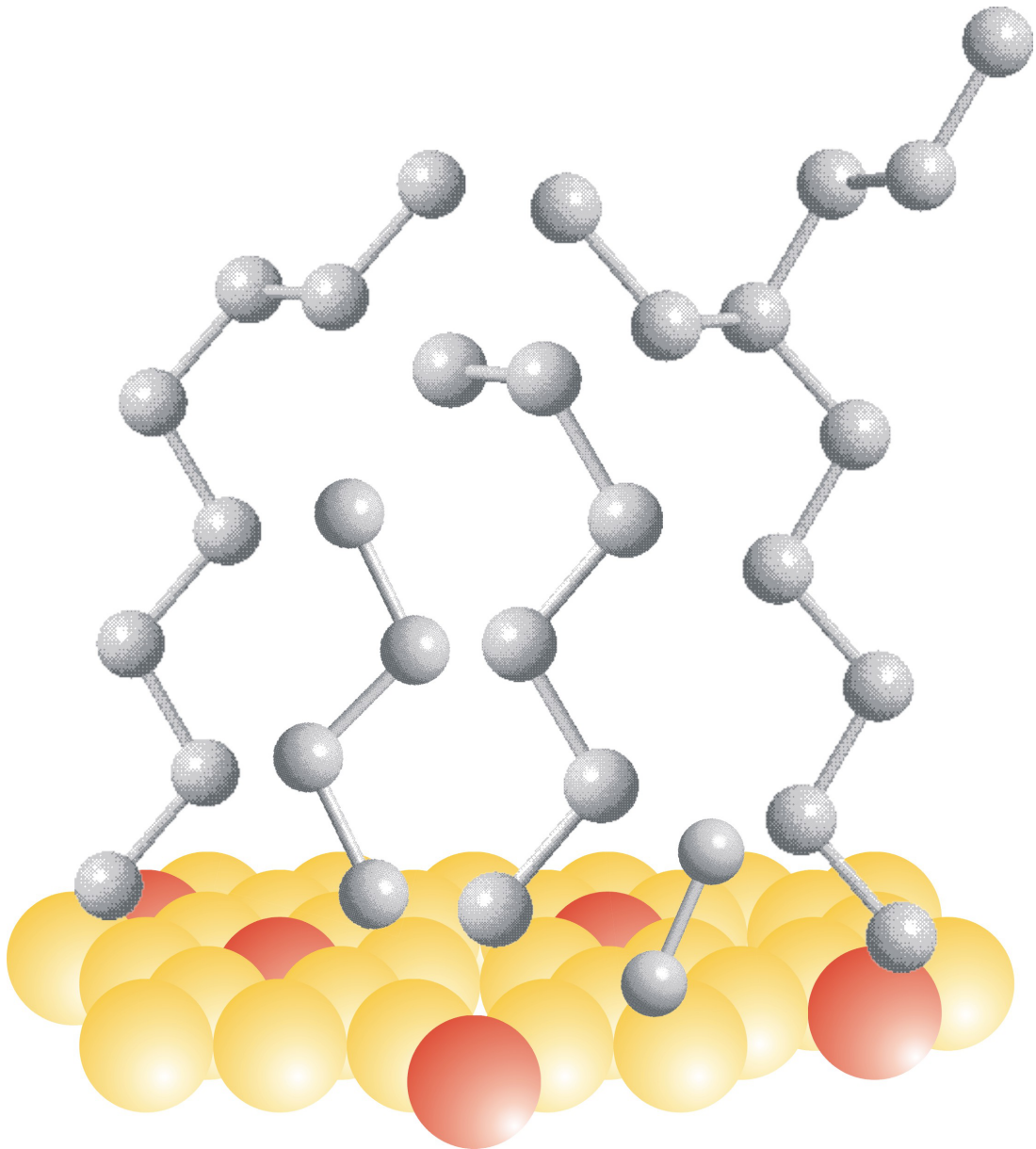


Fig. 6.1.1: Symbolic Adhesion of polymers on a surface

metallic surface, the treatment of the polymeric glue and the observation of the interaction of both.

6.2 The Metallic Surface

The main question to solve in the theoretical approach to model the adhesion of the polymers on the metal surface is how to model the metal surface itself. There are two different ways: The finite cluster approach and the use of periodic boundary conditions to model a ‘finite’ solid state phase. Preliminary work [40] revealed, at that time, problems using both approaches.

6.2.1 Magnesium Oxide

If one uses metallic magnesium in technical and industrial applications, the surface will be oxidized due to corrosion. Therefore the surface interaction will be established between the polymers and magnesium oxide layers, instead of pure magnesium. Corrosion is supported by bacterial contamination, usually introduced during technical production processes.

MgO is a white, solid and hygroscopic powder and crystallizes as octahedral resp. cubic-shaped geometry. The structure type is rocksalt-structure, space group $Fm\bar{3}m$, one Mg atom being coordinated by six O atoms and vice versa. Figure 6.2.2 illustrates the rocksalt-structure.

The most stable crystallographic surface of MgO is the (001) surface. The perfect (001) surface is characterized by a reduction of the coordination number of both, the anionic Oxygen and the cationic Magnesium from six to five. The presence of defects on the surface leads to important changes in surface properties, such as surface energy, charge distribution, and reactivity. [48]

The chemical activity of the MgO surface is in some reactions related to the presence of sites of low coordination attributed to point or topological defects. [49, 50] E. g. the water dissociation is energetically favorable not on the perfect (001) surface, but at steps and corners. [51] Further evidence of the importance of defective surfaces is the chemisorption of methane. [52, 53]

Fig. 6.2.2: Structure of the rocksalt-type: Mg atoms in green color, oxygen in grey color. The octahedral coordination can easily be seen by the implemented octahedrons.

Due to the fact that it is difficult to characterize metal oxides by experiments, several theoretical studies have been carried out to investigate the properties of perfect and defective surfaces, i. e. cluster calculations [54, 55], usage of supercell techniques [56, 57], at Hartree-Fock level [58], and ignoring the deformation of the cubic crystal structure [59]. Density-Functional Theory, which is very useful for studying the electronic structure of different systems, has been widely employed in the understanding of (oxide) surfaces and their interaction with molecules [60–75].

In all experiments in context of this thesis applying periodic boundary conditions, the initial geometry lattice constant is chosen to $4.2117\text{\AA}$ [76, 77].

6.2.2 Cluster Approach

Due to the previous infeasible study of the ‘infinite’ PBC approach (for details see Section 6.2.3), another way was chosen: the modeling of the surface by finite cluster systems.

By extrapolating properties from non-periodic cluster systems to periodic, infinite ones, one has to be very careful.

The crude way of cutting out the cluster from the solid leads to perturbing electronic states at the interfaces, which must be handled in a careful manner. Ionic solids are characterized by electrons, which are highly localized around the nuclei. This makes the cutting procedure in principle less severe. Nevertheless, the emerging long-range potential due to the infinite array of ions in solids is considered to be the main source of errors in cluster approaches.

Embedding such clusters in an array of point charges is one way to correct this unrealistic electronic properties. However, a number of problems arise:

- At the border, there is an interruption of the charge transfer. This is not compensated.
- Due to the absence of Pauli repulsion with electrons of surrounding atoms at the periphery of the cluster, large and distracting charge polarization may occur
- No geometry optimization can be performed. Whenever it is done, a collapse of the two parts may occur, which is due to the absence of Pauli repulsion.

For such reasons, extreme care is required when the adsorption process takes place at the borders of the cluster. [78]

The system is initialised with Mg and O atoms at an interatomic distance of $2.1\text{\AA}$ [77] in a rocksalt-structure.

6.2.2.1 Monolayer MgO Clusters

Table 6.2.1 presents some results of the monolayer MgO-cluster calculations for different numbers of atoms at the B3LYP,3-21G level.

Number of atoms	E [Hartree]	E/MgO [Hartree]	$r_{clustercore}$ [Å]
2 x 3	-821.43	-273,81	1.99
2 x 4	-1095.32	-273,83	2.08
3 x 3	-1294.36	-287,63	2.00
3 x 4	-1643.10	-273,85	1.84
4 x 4	-2190.95	-273,87	1.91
6 x 6	-4915.25	-273.07	1.91

Tab. 6.2.1: Monolayer MgO clusters at B3LYP,3-21G of the *Gaussian* program suite [28]

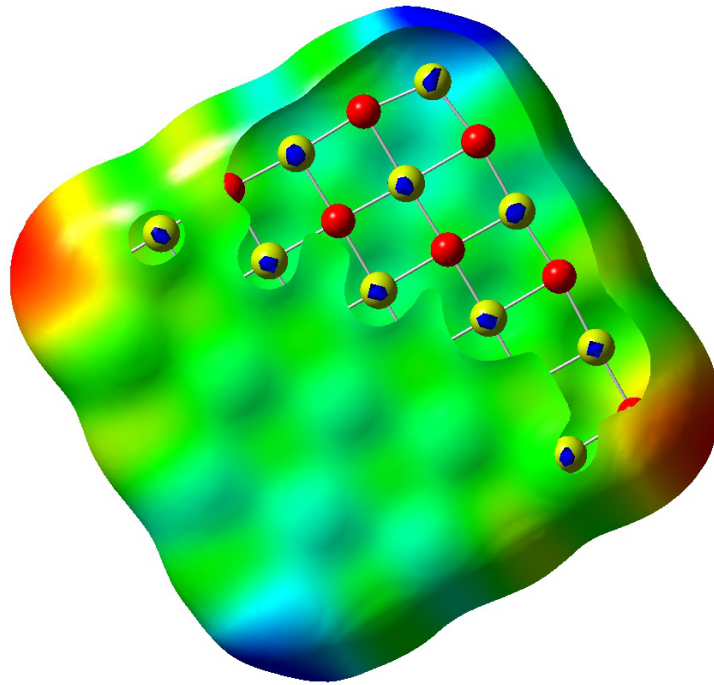


Fig. 6.2.3: Charge distribution of the 6x6 atoms monolayer MgO cluster at the B3LYP,3-21G level

Figure 6.2.3 shows the charge distribution of the 6x6 atoms monolayer MgO cluster. Oxygen atoms are in red color, whereas the magnesiums are presented in yellow. The charge distribution is given in a color scheme ranging from the negative end (in red color) to the positive one (in blue color). It can clearly be seen, that the density is more negative at corners, with oxygen atoms, while it is more positive at places with magnesium atoms.

6.2.2.2 Multilayer MgO Clusters

Table 6.2.2 presents some results of the calculation of different multilayer MgO clusters.

Number of layers	Number of atoms	E [Hartree]	E/MgO [Hartree]	$r_{clustercore}$ [Å]
2	2 x 3	-1643.30	-273,88	2.09
2	4 x 4	-4369.70	-273,11	1.95
3	3 x 4	-4930.93	-273.94	2.09
3	4 x 4	-6574.87	-273.95	2.02
2	6 x 6	-9832.68	-273.13	1.96

Tab. 6.2.2: Multilayer MgO clusters at B3LYP,3-21G of the *Gaussian* program suite [28]

Figure 6.2.4 illustrates a finite MgO cluster consisting of 8 layers, each containing 8x6 atoms.

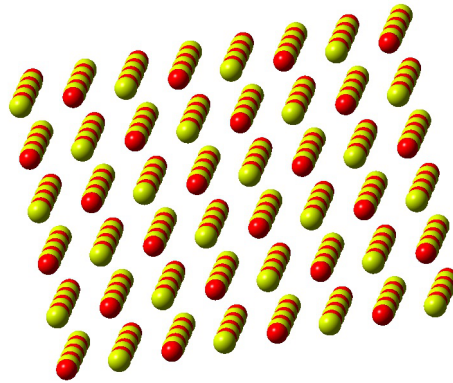


Fig. 6.2.4: Illustration of the eight layer 8x6 atoms MgO cluster

The results are in good agreement with other calculations [79, 80].

6.2.2.3 Embedded Clusters: External Point Charge field

An external point charge field requires a background charge distribution to be included in the calculation [81, 82].

It provides the extension of the Coulombic field of the cluster without the computational costs of real atoms. Therefore it should be an acceptable alternative to calculations with full atoms.

An application on *NiO* was performed by Xu *et al.* [83].

The first step to define the point charge field is the determination of the charge of each point charge. Therefore an *ab-initio* calculation of a single cluster is done and the Mulliken charge distribution of each atom is calculated. In order to avoid border effects, only the atoms in the core of the cluster are considered. Fig. 6.2.5 shows the results of this calculation for a 4x4 MgO cluster of 4 layers. The inner atoms provide Mulliken charges of roughly -1.5 for the oxygen atoms and $+1.5$ for the magnesium atoms, respectively. Those values will be taken to build the external point charges field.

Fig. 6.2.6 shows the energies of the HOMO, LUMO and the difference of both, labeled GAP, for the unrelaxed and relaxed (labeled opt.) 4x4x4 MgO-cluster, plot against absolute values of external point charges. The calculation was done at B3LYP level of theory using a TZVP basis set [84], as implemented in the *TURBOMOLE* package [85–87]. Despite some irregularities in the range of external point charge 2.0, it is noted that with increasing absolute value of the external point charges, HOMO and LUMO keep increasing. For the point charges being higher than 0.7, the LUMO of the relaxed structures are of positive energy. The same is valid for HOMO above point charges of 2.5. This requires the results to be handled very carefully, because when HOMO and LUMO energies are positive, it can not be decided, whether the electrons are within the orbital range or not.

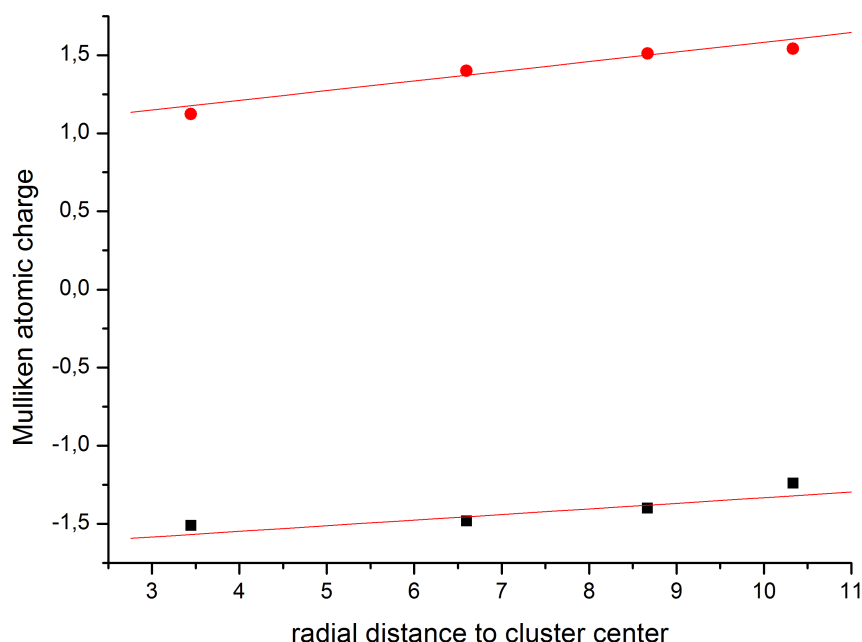


Fig. 6.2.5: Mulliken charges for a 4x4x4 MgO cluster plotted against the radial distance to the cluster center. Lower part represents the negatively charged oxygen atoms, whereas the upper part is the positive charge of the magnesium atoms.

6.2.3 Periodic Boundary Conditions Approach

The aim of the PBC is to include the whole solid behind a well-defined crystal surface, adding the molecules adsorbed on the surface, and treating such a semi-infinite system with an *ab-initio* all-electron method including electron correlation. It would provide the possibility to calculate the relevant quantities open to experiments, i.e. binding energies of the adsorbates at different coverages and on different crystal surfaces, IR and Raman spectra of the adsorbed molecules and data about the structure, which are not easily accessible by experiment.

Using the PBC approach as implemented in the *Gaussian* program suite in 2003 [28] led to some ‘inelegant’ results as follows: [40]

We consider a unit cell containing eight atoms (each four atoms oxygen and magnesium) as shown in Figure 6.2.7 for translation vectors (TV) of the length of $4.2\text{\AA}$ [76] along each of the three dimensional space vectors. The Mg-O distance was chosen to $2.1\text{\AA}$. [77] Table 6.2.3 gives the results by previous described calculation setup using *Gaussian* G03

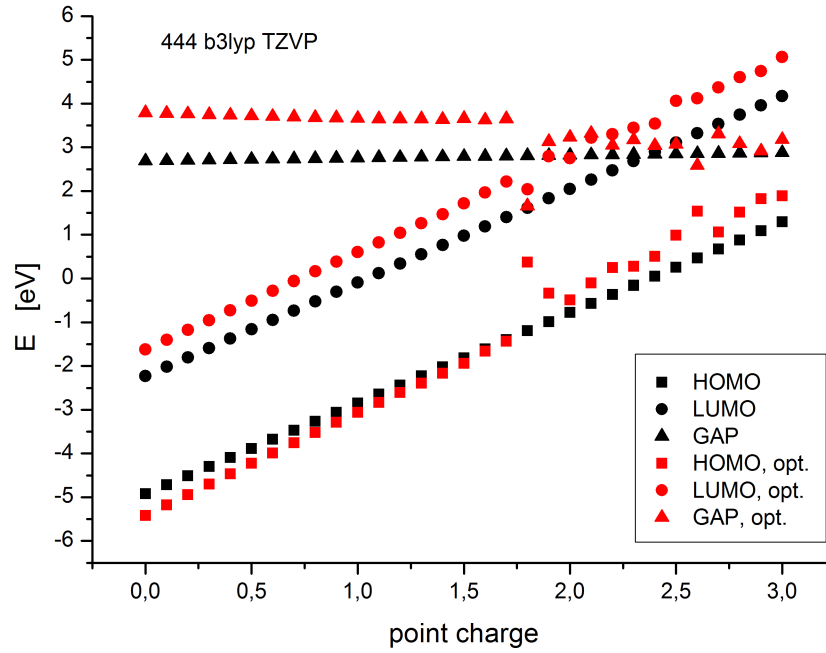


Fig. 6.2.6: HOMO, LUMO and HOMO-LUMO gap for a 4x4x4 MgO-Cluster in different external point charge field

B.03 [28] at the HF, 3-21g level. [88–96]. The table contains the different TVs, the total energy and the obtained Mulliken charges. For TVs shorter than 8.0 Å the obtained energies become unreliable. All obtained Mulliken charges are unreliable and proof the symmetry break in the supercell. Further discussion of the obtained results will not be done, due to their quality.

TV [Å]	E [Hartree]	Mulliken charges							
		1. O	2. O	3. O	4. O	1. Mg	2. Mg	3. Mg	4. Mg
10.0	-1160.92	0.193762	0.25486	0.287529	0.216771	-0.463799	0.358888	-1.682342	0.834328
9.0	-1255.96	0.322315	0.475996	0.268867	0.528501	-0.103169	0.047949	-0.860434	-0.680027
8.0	-1275.91	1.073890	1.216551	0.876449	0.804330	-1.848208	0.297080	-0.748457	-1.671635
7.0	-3577.53	2.049367	2.011230	2.355100	1.971959	-1.566255	-2.743406	-2.424737	-1.653257
6.0	-291215	3.862146	4.751939	3.138339	5.096061	-4.970684	-4.567581	-5.865767	-1.444453
5.0	-267965896	0.134789	0.378844	-2.415416	6.960813	-3.947455	1.205347	-3.527676	1.210754
4.9	-911115873	-0.003504	0.195558	-1.856485	7.427984	-2.847424	-0.927703	-2.391688	0.403262
4.8	-3232718757	-0.183251	-0.049697	-0.910120	7.642997	-2.817038	-1.826544	-1.634897	-0.221451
4.7	-13183756875	-0.625841	-0.516048	-1.933572	6.515850	-2.699451	5.635850	-3.737974	-2.638813
4.6	-66369794147	0.098297	-0.662161	-0.995107	6.663205	1.883794	-2.737769	1.954778	-6.205037
4.5		no results							
4.4	-948572541	-0.204461	1.197261	-7.492450	4.884375	-9.877449	3.256932	2.246245	5.989547
4.35	-2089680465	0.461510	1.830471	-7.219078	5.442104	-4.891956	1.970393	2.613812	-0.207256
4.3		no results							

Tab. 6.2.3: Energies and Mulliken Charges at different TV for MgO at HF,3-21G level by *Gaussian G03* B.03

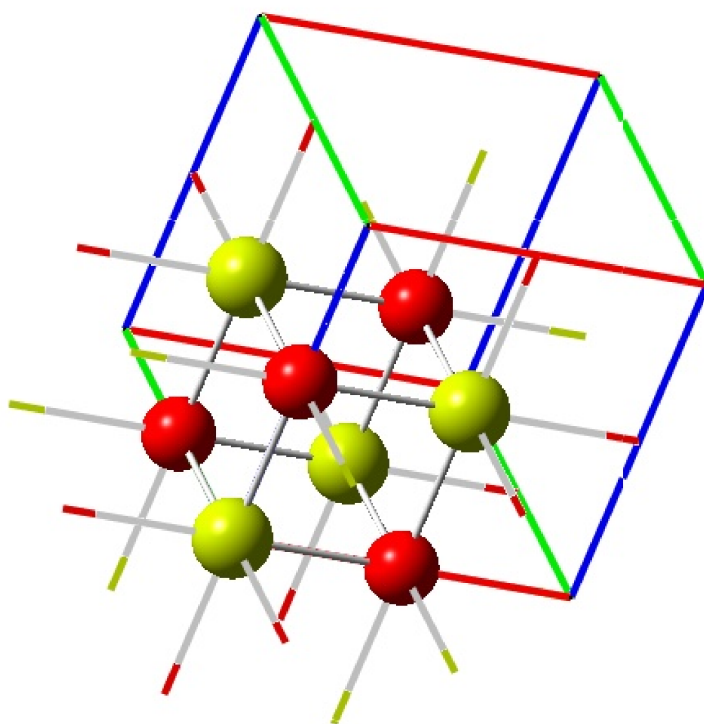


Fig. 6.2.7: Unit Cell of MgO

With TV shorter than $4.2\text{\AA}$ it was not possible to obtain any results. Other calculation approaches (e. g. HF, DFT, and MP2), as well as in combination with other basis sets (e. g. STO-3G, 3-21G, and 6-31G) have been used, but led to similar, unacceptable results.

6.2.4 Revised Periodic Boundary Conditions Approach

Due to the availability of the new revised *Gaussian G03* program suite, Revision E.03 [29] a new try was given to the PBC approach to model the MgO surface. Unfortunately, *Gaussian INC.* remains very uninformative concerning the applied approaches to the PBC system. Since the first availability of the PBC within the program suite in 2003, no bibliographic citations about the implementation can be found in the G03 User manual.

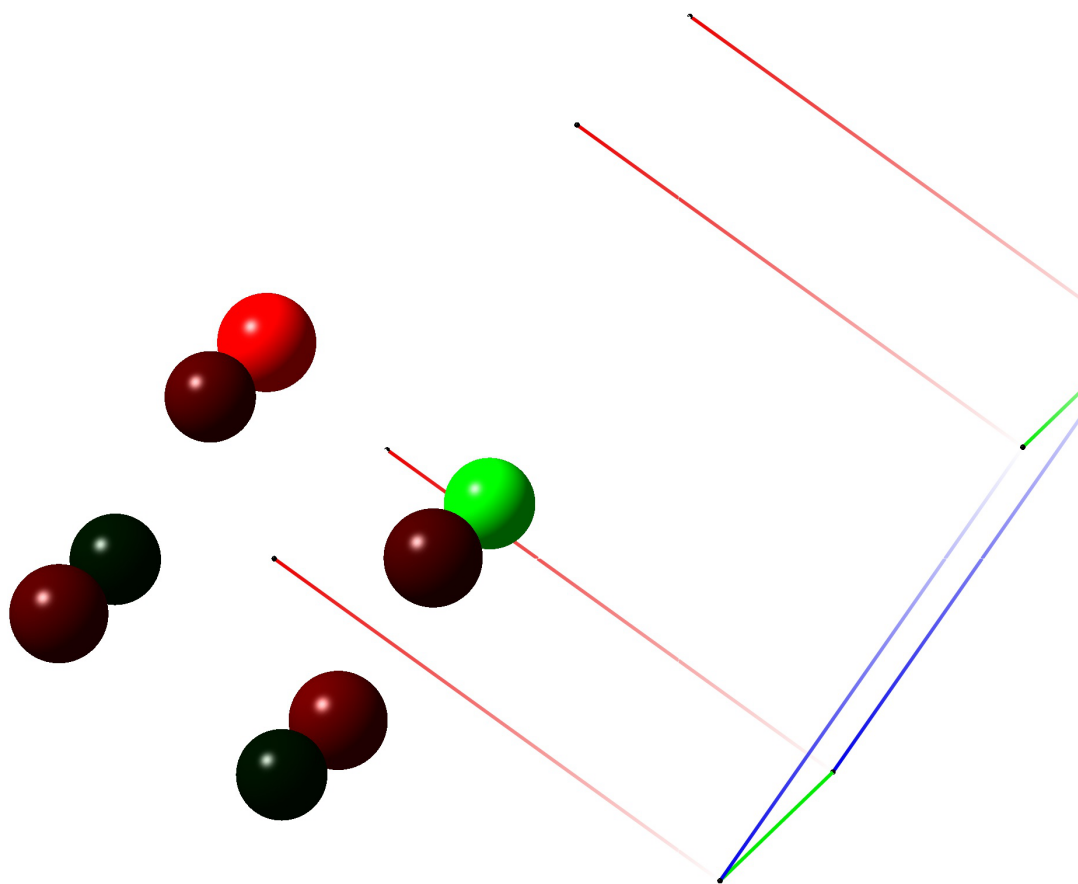


Fig. 6.2.8: Illustration of the Mulliken Charges obtained by a HF,3-21g calculation using the PBC as implemented in the *Gaussian* G03 B03 [28] program suite. The color range illustrates the charge range from -3.947 (red color) located on a Mg atom up to +6.961 (green color) located on a oxygen atom.

Figure 6.2.9 clearly indicates the enormous progress the of developers of the program suite on the inequally charge distribution: The symmetry break has vanished and the Mulliken charges are located in the supercell as they should do from the chemical point of view, with oxygen being negatively charged, while magnesium is positively charged.

A closer look at the results led to some disenchantment. Regarding the molecular orbitals as presented in Table 6.2.4 of the calculated supercell, the highest nine occupied MOs are at a positive energy level.

Allowing the structure to relax at the same level of theory led to even more positive MO

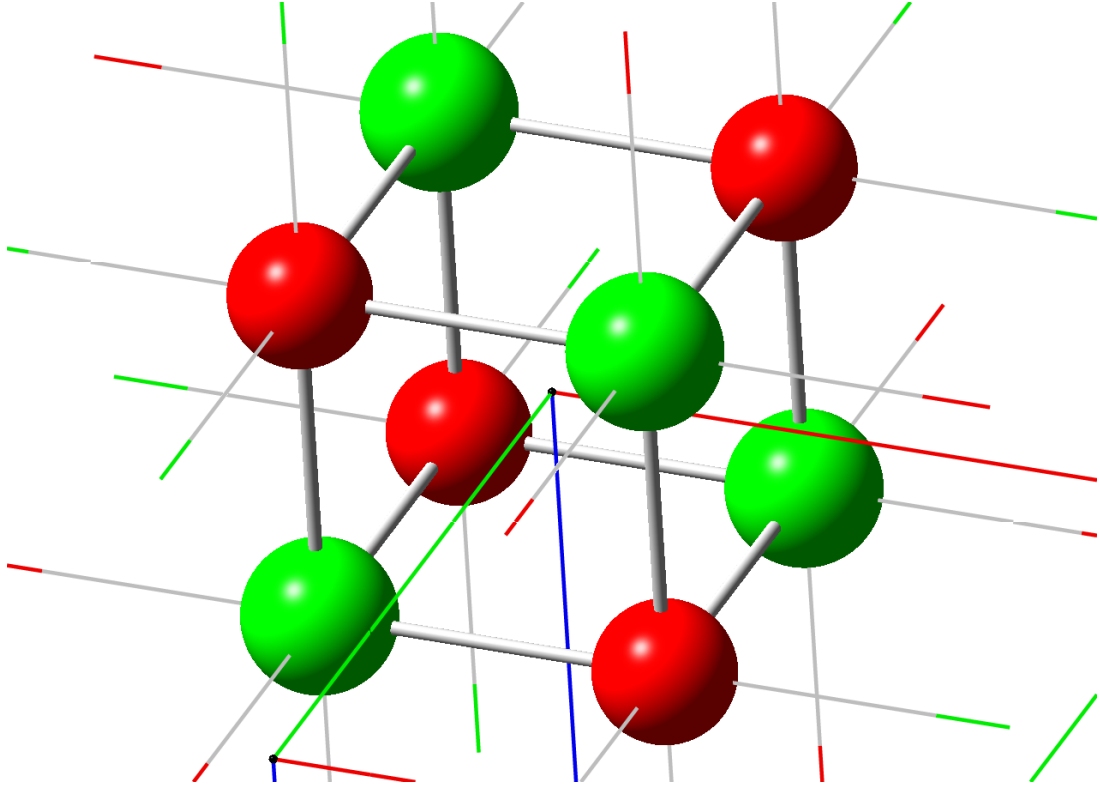


Fig. 6.2.9: Illustration of the Mulliken Charges obtained by a B3LYP,STO-3G [97, 98] calculation using the PBC as implemented in the *Gaussian G03* B03 [29] program suite. The color range illustrates the charge range from -0.617 (red color) located on a O atom up to +0.617 (green color) located on a Mg atom.

MO-No.	Occupation	Energy [a.u.]
40	$\uparrow\downarrow$	0.103
39	$\uparrow\downarrow$	0.103
38	$\uparrow\downarrow$	0.103
37	$\uparrow\downarrow$	0.038
36	$\uparrow\downarrow$	0.038
35	$\uparrow\downarrow$	0.038
34	$\uparrow\downarrow$	0.038
33	$\uparrow\downarrow$	0.038
32	$\uparrow\downarrow$	0.038
31	$\uparrow\downarrow$	-0.085

Tab. 6.2.4: Molecular Orbitals for MgO Single-Point calculation at B3LYP,STO-3G level by *Gaussian G03* E.03

energy levels. For details see Table 6.2.5

The relaxed structure led to a rearrangement of the cell constants, i.e. they are slightly

MO-No.	Occupation	Energy [a.u.]
40	$\uparrow\downarrow$	0.123
39	$\uparrow\downarrow$	0.123
38	$\uparrow\downarrow$	0.123
37	$\uparrow\downarrow$	0.047
36	$\uparrow\downarrow$	0.047
35	$\uparrow\downarrow$	0.047
34	$\uparrow\downarrow$	0.047
33	$\uparrow\downarrow$	0.047
32	$\uparrow\downarrow$	0.047
31	$\uparrow\downarrow$	-0.096

Tab. 6.2.5: Molecular Orbitals for the relaxed MgO supercell at B3LYP,STO-3G level by *Gaussian G03* E.03

smaller in comparison to the experimental values (for details see Table 6.2.6).

	SP	Relaxation	Experiment [76, 77]
Method	B3LYP	B3LYP	
Basis Set	STO-3G	STO-3G	
Energy [a.u.]	-1088.0814	-1088.1706	
Cell constant [$\text{\AA}$]	4.2117	3.953815	4.2117
r_{Mg-O} [$\text{\AA}$]	2.10585	1.97691	2.1

Tab. 6.2.6: Molecular Orbitals for the relaxed MgO supercell at B3LYP,STO-3G level by *Gaussian G03* E.03

Further calculations at a higher level of theory and/or with greater basis sets led to quantitative different results, while the quality of them kept unchanged, i.e. the obtained energies changed, whereas the energies of the occupied orbitals remained positive.

6.3 The Epoxid Layer

Epoxid systems are one of the most important glues used in the industry [99, 100]. Inter-alia they are used for gluing metals in the automobile and aeronautique industry, as well as corrosion protection by surface protection and coat of paint. [101]

Due to their strain hardening behavior the epoxids belong to the family of networking polymers. The experimental conditions differ from room temperature up to 150°C . The presence of amines, i.e. DETA, is essential to the network building.

The reasons for the great technical acceptance are, amongst others, a low toxic level, high stability, and the ability to bond to a lot of different surfaces.

Nevertheless the reasons for the good adhesive properties still remain mainly elusive, [102–105], especially concerning the aging and the percistency of the systems.

6.3.1 DGEBA

The epoxid DGEBA, the Bisphenol A Diglycidyl Ether, is the technical most used epoxid. The Group of Prof. Dr. W. Possart, Chair for Adhesion and Interphases in Polymers, Saarland University (ASPG) choosed for their experimental work, as well as for many applications [106], the almost monomer and difunctional form, as is available by Dow Plastics [107]. Figure 6.3.10 gives the structure of the monomeric DGEBA, whereas more detailed technical information can be found in Appendix A.1.

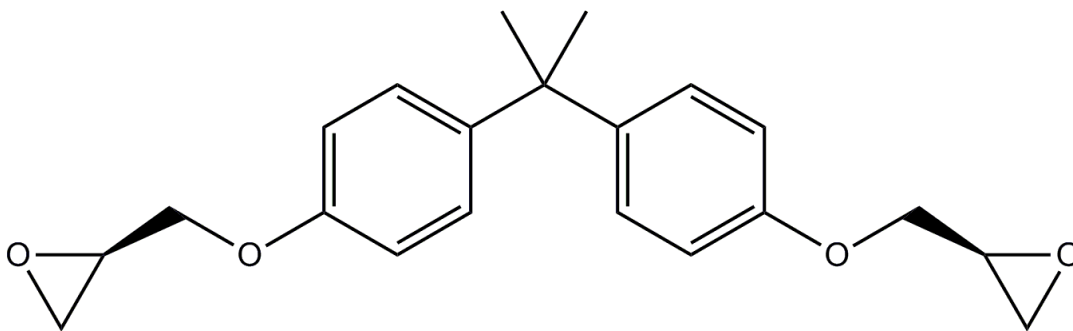


Fig. 6.3.10: Structure of the monomeric DGEBA

In the thermodynamical equilibrium at room temperature, DGEBA crystallizes in the monoclinic space group $P2_1/c$. One unit cell contains four DGEBA-units and the forces are due to van-der-Waals interaction, only. [108, 109]

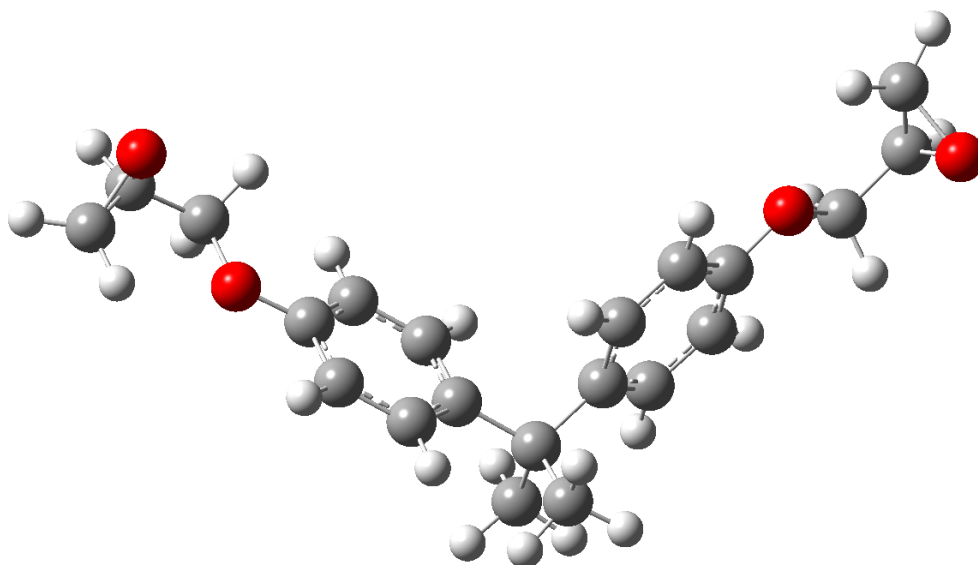


Fig. 6.3.11: Structure of the energy minimized DGEBA

Figure 6.3.11 shows the energy minimized structure of DGEBA, using the *Gaussian G03* program suite [7] at B3LYP/6-311g++d,p [25, 110–120] level.

The HOMO of the relaxed DGEBA is visualized in Fig. 6.3.12. It is mainly distributed along the molecular orbitals located at the phenyl rings and the bridging oxygen atoms and methyl group, whereas the oxirane rings stayed untouched.

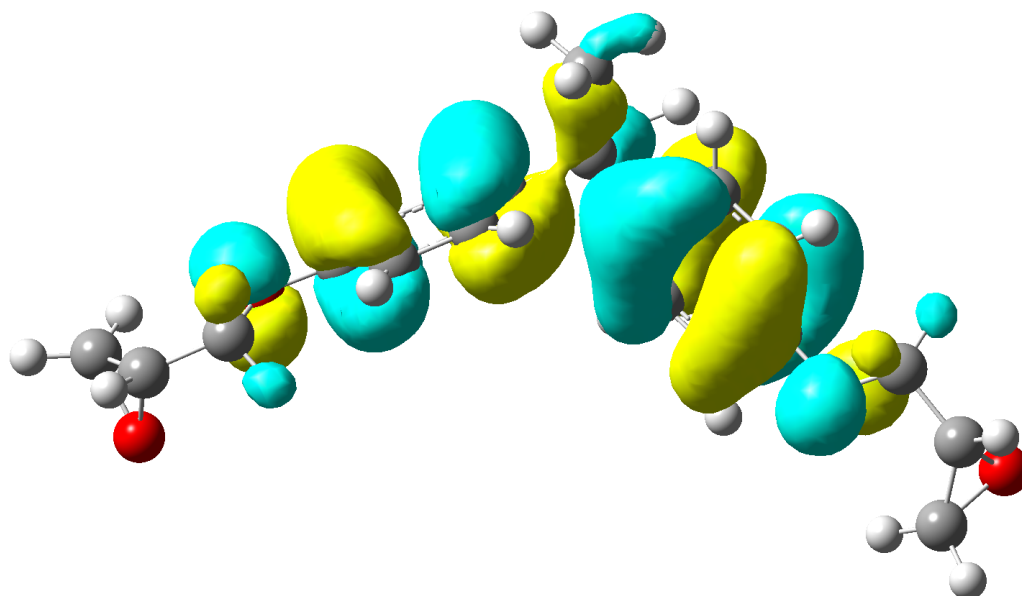


Fig. 6.3.12: HOMO of the energy minimized DGEBA

The visualized LUMO of the relaxed DGEBA is shown in Fig. 6.3.13. It is mainly located on the phenyl rings.

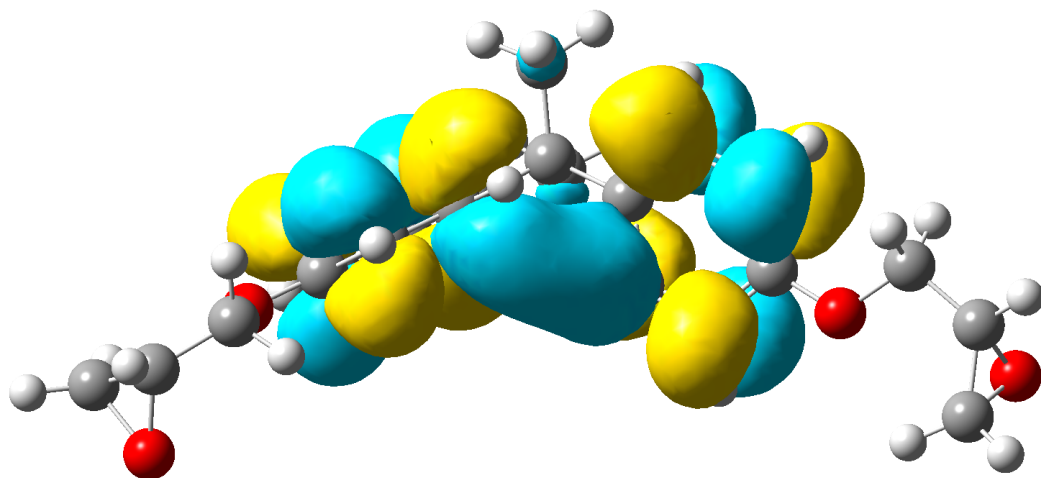


Fig. 6.3.13: LUMO of the energy minimized DGEBA

The visualized charge distribution of the relaxed DGBEA as shown in Fig. 6.3.14. The red color indicates the more negatively charged areas. The most negative charge can be found at the oxygen atoms of the two oxirane systems, indicating the most reactive parts of the organic system.

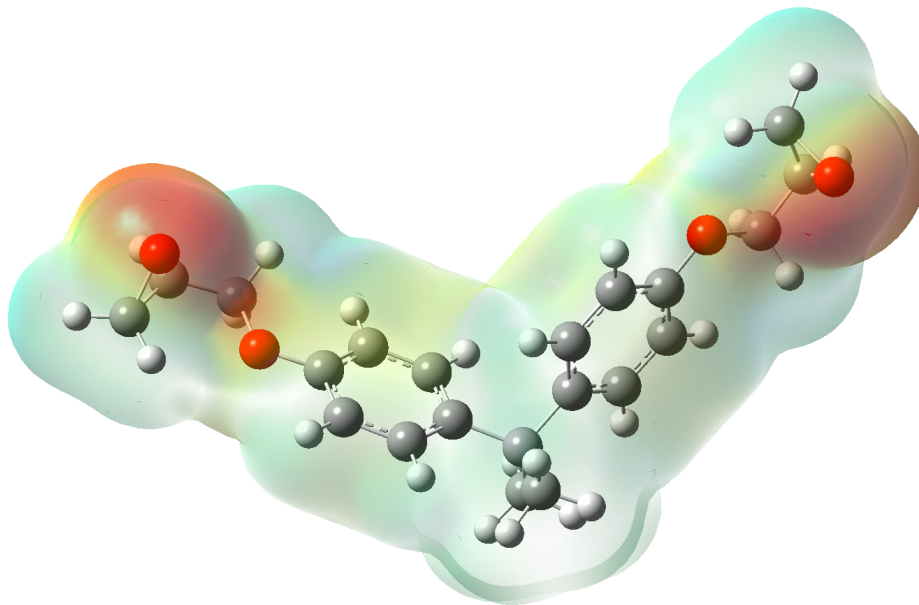


Fig. 6.3.14: Charge distribution of the energy minimized DGEBA. The more red color indicates the more negatively distributed charge.

6.3.2 DETA

Amines are commonly used curing agents for epoxide systems [121]. Diethylenetriamine (DETA) is an aliphatic polyamine curing agent and, in comparison to other aromatic amines, much more reactive to the oxiran rings of the epoxide systems by less toxicology. They belong to the first used ones, especially for roomtemperature reactions. [122] The ASPG chose for their experimental work the DETA available by Dow Plastics [123]. Figure 6.3.15 gives the structure of the DETA, whereas more detailed technical information can be found in Appendix A.2.

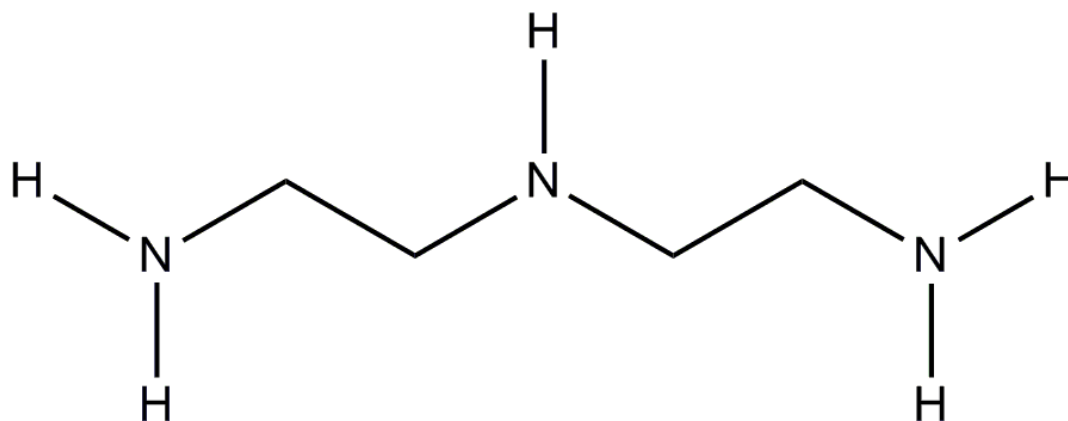


Fig. 6.3.15: Structure of the DETA

Figure 6.3.16 shows the energy minimized structure of DETA, using the *Gaussian G03* program suite [7] at B3LYP/6-311g++d,p [25, 110–120] level.

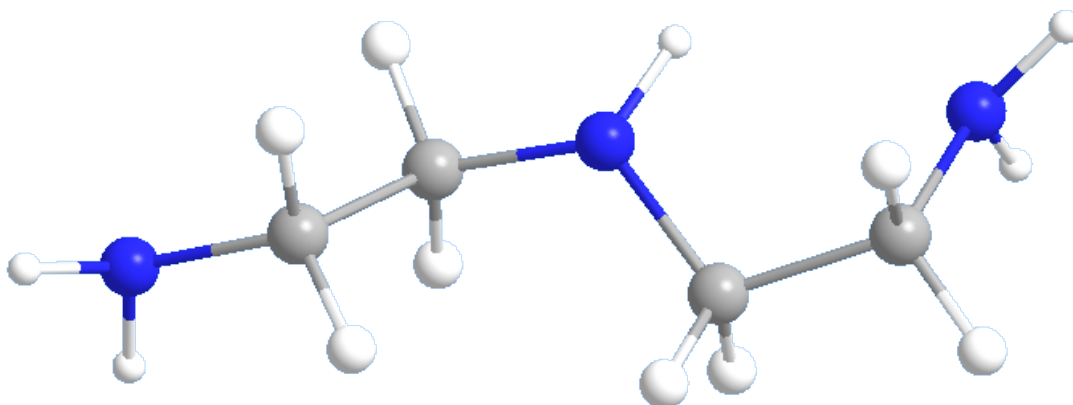


Fig. 6.3.16: Structure of the energy minimized DETA

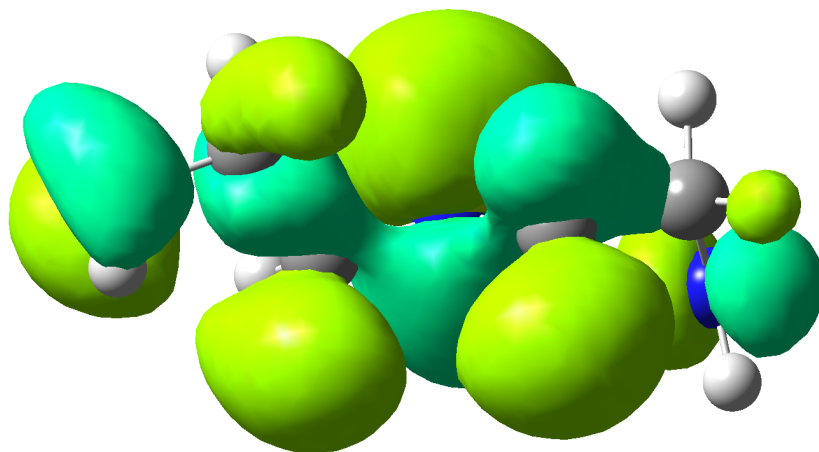


Fig. 6.3.17: HOMO of the energy minimized DETA

Fig. 6.3.17 presents the visualization of the HOMO of the relaxed DETA monomer. It is located mainly on the nitrogen atoms.

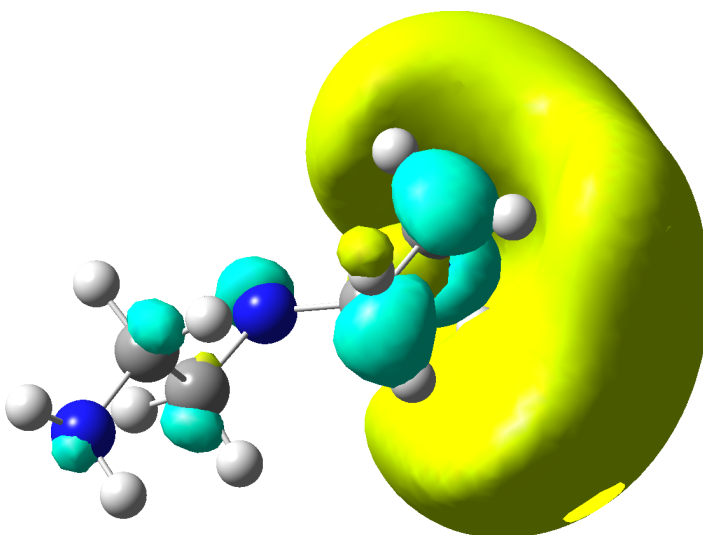


Fig. 6.3.18: LUMO of the energy minimized DETA monomer

The visualization of the LUMO of the relaxed DETA monomer is presented in Fig. 6.3.18. It is clearly located on one terminal nitrogen atom.

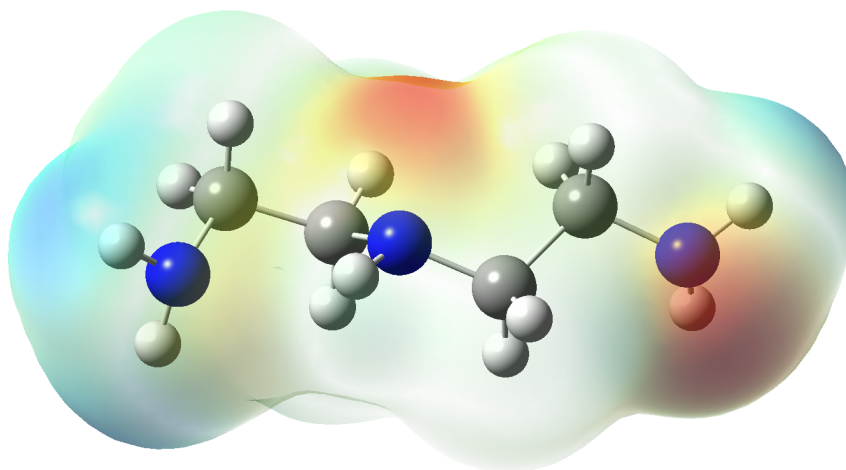


Fig. 6.3.19: Charge distribution of the energy minimized DETA

Fig. 6.3.19 visualizes the charge distribution of the relaxed DETA monomer. Increased red color indicates more negative parts of the systems. The highest electron concentration is on the nitrogen atoms, indicating the most reactive parts of the system.

6.4 Interaction with the Metal Surface

In general, an interface is the area between two different media with properties of neither the one nor the other material. Due to this fact, it is of great importance to model those properties within a theoretical framework to help understanding the mechanism of the interaction of the polymer with the surface.

There are two different ways of modeling the surface, i.e. those who are based on modeling the surface with a perfect solid state arrangement. The other way is more appropriate when local defects and perturbations should be considered, like cluster-models. Both approaches have their advantages and disadvantages. The aim of this work needs to include all electrons to model the desired properties in the right way. It is of great importance to allow the surface atoms (and the sub-surface-layer atoms) to relax when they interact with the adsorbing molecules and to investigate the corresponding changes of structural and electronic properties.

A commonly used starting point to model adhesion effects is the adsorption of CO on the surface, giving the advantage that the system investigated remains as small as possible. Despite this, the importance of the CO molecule within catalytic research have turned this species into a widely used probe in surface science, resulting in a wide range of studies of the interaction by both, experimentalists and theorists. A small overview about experimental work related to the CO adsorption on MgO surface can be obtained by [124–129]. Spoto provided a review about both, experimental and theoretical works [130]. Different theoretical approaches were done [131–154], i.e. embedded clusters [155–157], Hartree-Fock theory [158–163], or using periodic boundary conditions [164–166].

Regarding the size of the adsorbing molecules in question, a certain surface area is needed to ensure an appropriate surface-adsorbant interaction. Being almost $17\text{\AA}$ the largest dimension of DGEBA requires a surface of MgO, built of at least nine times nine MgO-units, containing 100 atoms in the surface layer. Additionally, the 49 atoms of the DGEBA needed to be considered. This led to a very sharp and a abrupt end of the surface and therefore of the interaction between the surface and the adsorbant, which describe the real situation inadequately. In order to avoid this and to get to a smoothing interaction zone, a surface layer of twice the size, consisting of 19 times 19 MgO-units, containing 200 atoms would be a good way. A single surface layer does for sure not describe the surface area of bulk Mg in a proper way. Additional layers to stabilize the surface layer and to enhance the properties towards the real bulk properties easily led up to an amount of 5-10 layers in total. Regarding this huge amount of atoms, i. e. 5 layers of MgO plus the adsorbant DGEBA gives 550- 1050 atoms, which should be treated within an

ab-initio level of theory, is a challenging effort and beyond the computational power which is available for this work.

Similar consideration is valid for the ideal surface approach, using other techniques, i.e. period boundary conditions, which led to similar problems.

Preliminary works on gluing of technical metal surfaces use epoxide resins (mainly DGEBA) with amine hardener showed a great chemical affinity of the latter to the polar interphase and is mainly located near to the surface. [167–175]

6.5 Conclusions

Modeling the adhesion of polymers on an oxidized metal surface within an *ab-initio* framework is a challenge. Several promising ways to obtain more information about the surface adsorbant had been undertaken.

The cluster approach, i.e. cutting out a part of the bulk phase to reduce the computational efforts, soon reached the available computational power. Trying to reduce it further by embedding the clusters in an external point charge field, yielded irregularities concerning the HOMO and LUMO energies.

Another main approach, using periodic boundary conditions, showed in preliminary works problems in the used program package. After obtaining a newer revision of the code, some problems, i.e. the distorted symmetry within the unit cell were solved, but new problems arised, e.g. the orbital energies. A change of the source code of the used program suite would have been beyond the scope of this work. Valero *et al.* [154] investigated the CO adsorption on MgO(001) surface. Their calculations were performed with a *locally modified version* of *Gaussian* program suite. Despite this, their surface to model the interaction with the very small CO-molecule consisted of 5x5 MgO units, to obtain proper results. Interpolation this to the systems of interest within this work, would led to MgO layers of $\approx 30 \times 30$ MgO units, with the corresponding computational efforts, treated at the *ab-initio* theory level.

Nevertheless, further improvement of the codes will be done, so that hopefully one day, the desired informations can be obtained. Another way would be the application of different codes to this problem.

7 Cadmium Sulphide Clusters

7.1 Introduction

During the last decades the interest in semiconductor nanoparticles increased significantly for both experimental and theoretical studies. One of the main reasons for studying clusters is their size-dependent behavior of their electronic, structural and optical properties (*‘Each atom counts’*). Considering the simplest approximation, this quantum-size effect [176–180] can be interpreted as an experimental realization of the particle in a box.

CdS has many different properties, which led to a variety of applications, e.g.:

- Pigment: Due to the magnitude of its band gap it appears colored. By adding varying amounts of other types (i.e. selenide) it is possible to change the usual yellow appearance to a color range from orange to red [181, 182]
- Core component of a photovoltaic cell in combination with a p-type semiconductor (a *CdS/Cu₂S* solar cell was one of the first efficient cells to be reported, already in 1954, [183, 184])
- Photoresistor due to its increasing conductivity when irradiated with light [185]
- Usage as a solid state laser [186, 187]
- Cathodoluminescence (being doped with an ‘activator’ (Cu^+) and a ‘coactivator’ (Al^{3+}), *CdS* luminescence under electron beam excitation) [188]
- Transistors: when being fabricated in thin films [189, 190]
- Electroluminescence [191]
- Piezoelectricity for both polymorphs, additional pyroelectricity for the hexagonal one [192, 193]

Usually it is assumed that the structure of stoichiometric $(CdS)_n$ clusters is similar to fragments of the bulk phase, i.e. wurtzite and zinc blende/sphalerite structures. For crystalline cadmium sulfide these two forms are energetically almost degenerate with the wurtzite structure being slightly more stable [194, 195].

Some of the studies on cadmium sulfide, resp. the chemically related systems cadmium selenide and cadmium telluride regarded the energetically lowest optical transitions [196–200]. Many studies had been made applying tight-binding methods on these systems, [201–215] and it has almost always been assumed that the structure of the cluster is comparable to that of a finite part of the infinite bulk system.

However, this might not be the case for small n . In the previous citation, the structural relaxation has not been taken into account except in a few cases, for instance Whaley *et al.* [201, 214, 215] and the DFT-works by Alhrichs *et al.* [210, 216]

Additional works on $(CdS)_n$ clusters and similar system were done by Joswig *et al.* [217–222].

In this study we used an unbiased theoretical method to determine the structure of small stoichiometric $(CdS)_n$ clusters. We present our results and discuss the resulting differences to the zinc blende and wurtzite structures. Especially, we present our results concerning stability, coordination of the atoms, band gaps, frontier orbitals, and the similarity of the structures.

7.2 CdS Crystal Structure

Cadmium sulfide can crystallize in the two forms: the more stable hexagonal wurtzite structure (figure 7.2.1 represents a 3D-model of the structure) and the cubic zinc blende structure. There is also known a high pressure form with the rocksalt structure. [223]

Fig. 7.2.1: 3D-model of the wurtzite CdS structure

The name of the sphalerite structure is derived from the zinc iron sulfide mineral $((Zn, Fe)S)$, whereas the wurtzite structure was named by its discoverer Charles Friedel after his teacher Charles Adolphe Wurtz. The wurtzite is a hexagonal crystal system (figure 7.2.2 presents the unit cell), which consists of tetrahedrally coordinated zinc (cadmium) and sulfur atoms (see figure 7.2.3 for an illustration), stacked in an ABABAB pattern, space group $P6_3mc$.

Fig. 7.2.2: Wurtzite unit cell

The figure, which is missing from the page, would typically illustrate the wurtzite crystal structure. This structure is a hexagonal lattice where two different atom types (Cd and S) form two interpenetrating hexagonal close-packed (hcp) sublattices. The atoms are arranged in a way that each atom is tetrahedrally coordinated by four atoms of the opposite type.

Fig. 7.2.3: Wurtzite structure

For the zinc blende structure, also known as sphalerite structure, the two atom types form two interpenetrating face-centered cubic lattices (figure 7.2.4 represents the sphalerite unit cell). It is similar to the diamond cubic system, but with alternating atom types at the different lattice sites. The space group is $F4\bar{3}m$



Fig. 7.2.4: Sphalerite unit cell

7.3 The Genetic Algorithm

7.3.1 Motivation

When studying clusters it is of great importance to have as much information as possible about the system to be investigated. For the calculation of structural and electronic properties of a cluster it is essential to obtain the global total-energy minimum structure. By varying the structure, i.e. by varying the atomic coordinates, the energy of the investigated systems changes. The main problem for a structure optimization is to find an initial structure that leads the system through the optimization to the structure corresponding

to the global total-energy minimum structure. There exists no method that will guarantee the identification of the global minimum structure with a computational effort that grows polynomial with the size of the investigated system. In fact it grows exponentially or even faster with respect to the size of the investigated system.

In this work we chose an unbiased approach, funding on randomly generated numbers, to get a reasonable initial structure to feed the applied genetic algorithm.

7.3.2 What is a Genetic Algorithm?

In the present context, genetic algorithms describe computational tools for searching the global minimum on a potential-energy hyper-surface. They have been inspired by the Darwinian evolution process [224] and are therefore also called evolutionary algorithms.

The computer simulations of evolution started already in 1954 with the work of Barricelli [225, 226]. Further pioneers on this field: Fraser (1957) [227], Fraser and Burnell (1970) [228], Crosby (1973) [229]. Reprints of many early papers can be found in [230].

In 1963 Barricelli reported about simulating the evolution of ability to play a simple game [231]. Applying artificial evolution to solve engineering problems led to a widely recognized optimization, mainly due to the work by Rechenberg [232] and Schwefel [233, 234].

The first genetic algorithms were designed to map the physical structure onto a binary number string. As a mating procedure string combination was used. [235]. Nowadays the algorithms work directly in coordinate space. A brief but not complete overview about currently used mating procedure approaches is given here:

- An algorithm with a mating procedure that forms one child cluster from two parents was proposed by Deaven and Ho [236, 237]: They randomly chose a cutting plane through the center of mass. The children are formed from the atoms of the first parents, which lie above the plane and those from the second parent which lie below the plane. If it does not contain the appropriate number of atoms, the parent clusters

are translated in opposite directions with respect to the plane. The optimization in this GA was done by conjugate-gradient minimization on a Lennard-Jones Potential. [238]

- The algorithm proposed by Hartke [239] measures a fitness function of each parent, which defines how many children will be passed into the next generation by each parent, including the possibility that one parent provides more than one child to the next generation.
- An algorithm similar to the Deaven and Ho one was proposed by Johnston *et al.* [240]. Instead of parallel cutting planes of the two parent clusters, they allow a rotation of the two parts after cutting. The interatomic interactions are described by Morse, Gupta [241, 242], or Murrell-Mottram potentials. [243]
- The best 20% of the clusters of one generation are passed unchanged into the next generation by the algorithm proposed by Niesse *et al.* [244]. The remainders of the populations are generated by using genetic operations like a crossover of different coordinates between two parent clusters, building new coordinates out of old ones by geometric means, and inversion of any two coordinates.

Many more approaches have been proposed but these few already illustrate the main differences and most important elements. The following sections will show the further developed GA for the studies of this work, explained in more detail.

7.3.3 Unbiasedness

In cluster calculations it is quite common to the scientific community that certain start geometries are specified, i.e. cutouts of the bulk phase. In this work a different goal was

followed: a complete unbiasedness of the initial structures. To ensure this the following two points are basic requirements: a random number generator (RNG) (as described below in Section 7.3.4 and a random growth of the cluster. To build a new cluster, two different ways have been chosen: one way was starting with a single CdS-unit and adding new units atom by atom, using a RNG to place them at the cluster (and fulfilling some boundary conditions, similar to the Aufbau-method) and let them relax. The other way was to take a relaxed structure obtained by first way and then adding a new unit. Figures 7.3.5 and 7.3.6 illustrate the two different ways of creating the initial geometries in a simplified way.

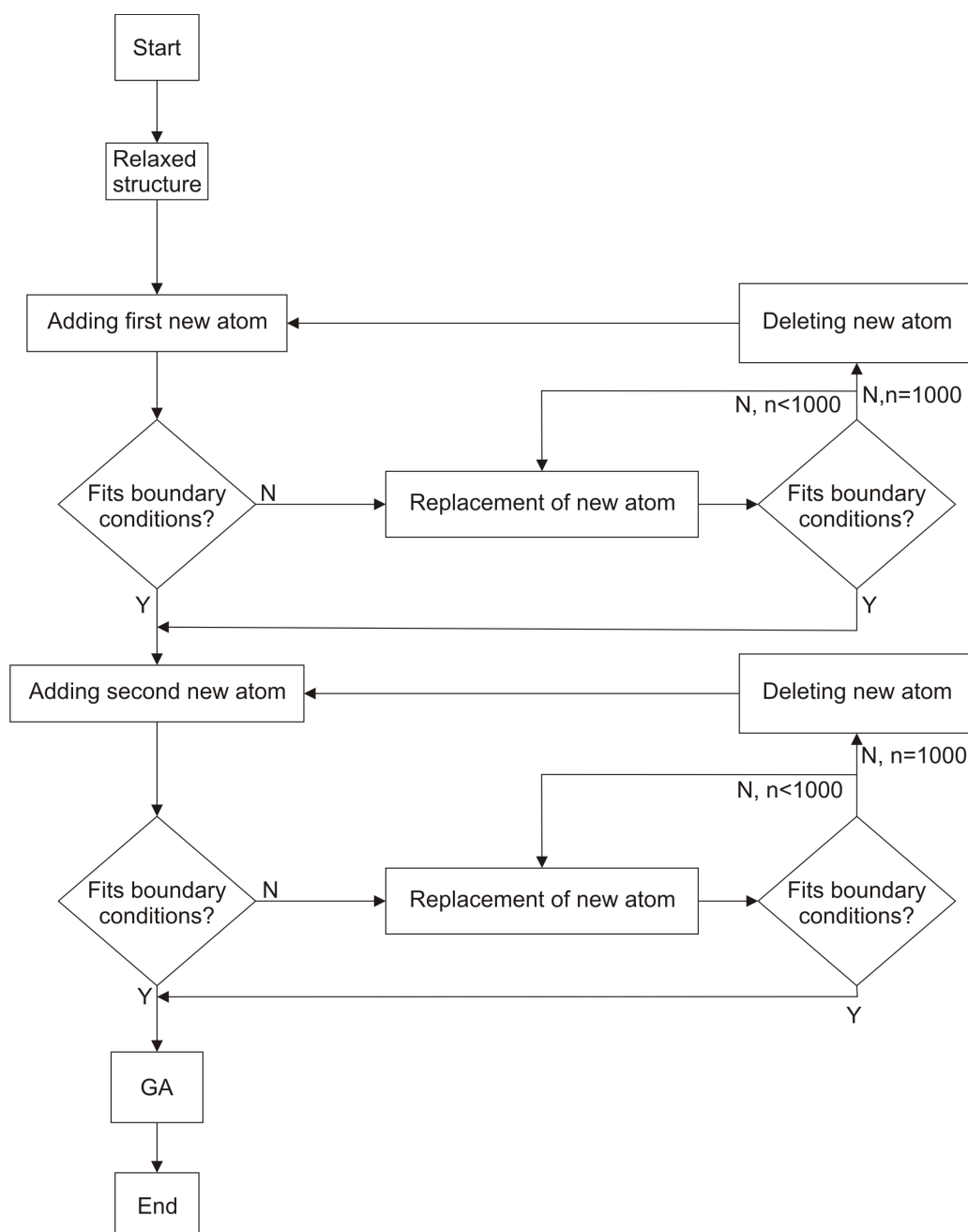


Fig. 7.3.6: Simplified flowchart for creating the unbiased initial cluster structures from a previously relaxed structure. Each single step is described in Section 7.3.3.

The following subsections are referring to the characterizations of the processes in the flowchart depicted in Figure 7.3.5.

‘Start’

Launching the program initializes the Random Number Generator [245] and checks whether

the first generated random number is different from the first generated number of the last run. As initial number for the RNG function, a build-in unix option is used to ensure a certain unbiasedness, as described in details in Section 7.3.4.

After the successful initialization of the RNG the necessary input data is read, containing information about the system, the structure from previous calculations (if available), which type of atom should be added and the definition of the boundary conditions. The read-in structure coordinates are converted from cartesian to spherical coordinates. The structural center point of the cluster is determined and all coordinates are defined relative to the center point. The maximum available distance within the cluster r_{max} is obtained by evaluating all positions with respect to the center point of the cluster.

‘Adding first new atom’

After determining the center of the cluster, a new atom is added. The two necessary angles to specify the position of the added atom within a spherical coordinate description are obtained by multiplying two randomly generated numbers with $2 \cdot \pi$ and π , respectively (Figure 7.3.7 illustrates the used spherical coordinate system.).

$$\Phi = RN \cdot 2 \cdot \pi \quad (7.3.1)$$

$$\Theta = RN \cdot \pi \quad (7.3.2)$$

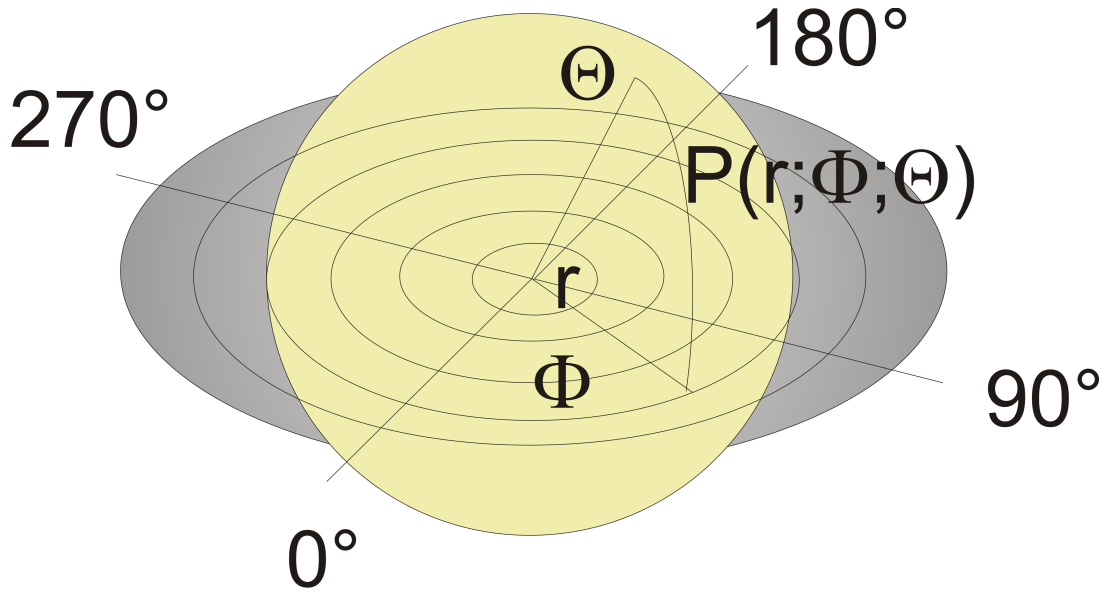


Fig. 7.3.7: Illustration of a spherical coordinate system.

The third required position parameter r is obtained by multiplying a randomly generated number with the sum of the maximal radial distance within the cluster r_{max} and 1.4 times the experimental bong length for $Cd - S$ within the bulk phase r_{CdS} :

$$r = RN \cdot (r_{max} + 1.4 \cdot r_{CdS}). \quad (7.3.3)$$

The value of 1.4 has been chosen according to the interaction distance for neighbors within condensed matter structures [246].

‘Fits boundary conditions?’

The first new atom has been determined by the type and the spherical coordinates using the unbiased random number generator.

To help the optimization routine to converge faster, specific boundary conditions have been established, which ensure that the new added atoms is placed within a reasonable range of interaction with the already existing atoms. Therefore the distances for the new added atom to all others atoms are calculated. Afterwards it is checked whether the condition

$$0.9 \cdot r_{A-B}^{exp} \leq r_{A-B} \leq 1.4 \cdot r_{A-B}^{exp} \quad (7.3.4)$$

is fulfilled, with r_{A-B}^{exp} being the bond length of the atoms A and B within the bulk phase, i.e. r_{Cd-Cd} , r_{Cd-S} , or r_{S-S} , r_{A-B} is the distance of the two atoms under investigation. The values of 0.9 and 1.4 in the equation 7.3.4 are chosen to ensure an appropriate interacting distance, so that a too low or too high repulsion of the the atoms is prevented, and according to the interaction distance for neighbors within condensed matter structures [246], respectively.

A positive check of the boundary conditions leads to the addition of the second new atom, whereas a false condition will try a replacement of the atom.

‘Replacement of new atom’

If the verification of the fulfillment of the boundary condition yields a negative result, the third spherical coordinate parameter r is recalculated, once again with the help of the RNG, followed by checking the boundary conditions. If this reestimation of the parameter r fails for 1000 times in a row, the angle Θ is rechosen randomly, followed by a new calculation of a reasonable distance. If the newly obtained angle Θ fails for 100 times in a row, the angle Φ is rechosen randomly and the replacement starts over again with the evaluation of the distance. In the very implausible case the determination of Φ fails for 100 times in a row (it never happened throughout the present work), the new added atom would be deleted and the section of adding the first new atom would be relaunched. During all retries of creating appropriate angles and distances the program ensures that no previously used randomly generated number is used once again.

‘Deleting new atom’

After the unsuccessful attempt of placing the new added atom within the boundary conditions, that atom is deleted and the procedure of adding a new atom is relaunched.

‘Adding second new atom’

The procedure of adding a second new atom is similar to adding a first new atom, but ensures that, for systems with two atom types, the other atom type is added. All descriptions made for adding a first new atom are valid as well.

‘Desired cluster size’

After the successful addition of two new atoms, it is checked, whether the demanded cluster size, as defined in the input data and reading during the start process, is reached. If not, the whole described process above is relaunched until the appropriate cluster size is reached.

‘GA’

The process GA calls the Genetic Algorithm function as described in detail in Section 7.3.6.

‘End’

This simply ends the program and writes the new obtained structures data (i. e. coordinates, energies, etc.) into files and creates the input files for the subsequent evaluation, e.g. visualization.

Additional processes in flowchart Figure 7.3.6:

‘Relaxed structure’

Relaxed structure will read in the coordinates of a previously obtained relaxed structure. The process of adding atoms will account for the presence of these atoms. All other descriptions are valid as described above.

Before the second approach of obtaining unbiased initial structures can be taken, the first relaxed cluster structure, i. e. the cluster $(CdS)_1$, must be obtained.

7.3.4 Random Number Generation

Although true randomness is fundamental feature of nature, their mathematical characterization is difficult [247]. The generation of random numbers must rely on an unpredictable

physical process [248–252]. In 2010 the first truly RNG was proposed by Pironio *et al.* [253], recurring to principles of quantum physics.

Although a certain randomness is required for an unbiased optimization algorithm, the scientific work needs to be reproducible. Therefore so called pseudorandom number generators are being widely used within the scientific community and are being implemented in standard programming suites. Such deterministic random bit generators do have the advantage of being sufficiently ‘random’, and the possibility to reproduce the same series of numbers by the same starting value, usually called *iseed* [254]. To produce a certain amount of different random numbers, the focus is to determine the *iseed*.

Throughout all processes, where a RNG was used, the *iseed* was set to the nanoseconds part of the current time, as implemented in standard UNIX systems. This combines a sufficient randomness and the ability to reproduce the numbers. The generation of the random numbers had been tested and yielded an even distribution.

7.3.5 Parallelization

The aim of parallelizing a computer program is to gain computational speed by carrying out many calculations within the same program simultaneously [255]. It is assumed that a large problem can be splitted up into several independent smaller ones, which can be solved concurrently. In general, parallel computer programs are more difficult to write than sequential ones [256], due to the concurrency which introduces several new classes of potential software bugs, mainly the so called race conditions [257–259].

Despite the additional possible failure sources and the increased efforts, the gain of speed is limited by the sequential fraction of the program. This maximum expected improvement, named Amdahl’s Law [260], is illustrated in Figure 7.3.8.

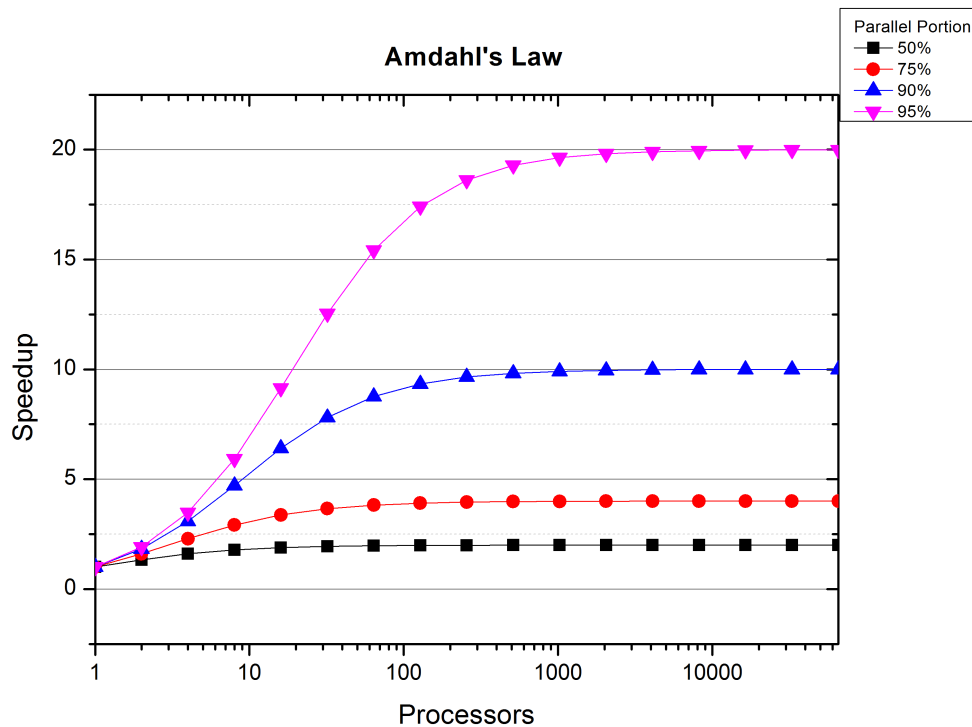


Fig. 7.3.8: Amdahl's Law, illustrating the maximum speedup on parallelizing a computer program for different amount of sequential program code

Despite the pessimistic outlook of Amdahl, a super linear speedup can be obtained in parallel programming [261, 262].

Depending on the computer system architectures, there are two different ways of applying the parallelization to the sequential program. For shared memory architectures (SMA), where the different processors access the same memory, it is more convenient to use the so called (Open)MP [263] API, whereas on distributed memory architectures with physically separated processors and memories, the MPI [264] API is the appropriate choice.

7.3.5.1 OpenMP API

Implementing the OpenMP is the easier way to obtain a parallelized program. The additional program code is written in a way, that the code still can be compiled by a standard

(non-parallel) compiler, as it surplus codes phrases as comments. This provides the advantage, that the code can still be transfered from one architecture to another without any changes. The efforts are much smaller than using the MPI API, due to the lack of synchronization commands to manage the different program progress at the different, physically separated processes, as all processes access the same memory. Additionally this decreases the amount of possible bug sources.

The limitation to SMA machines, which were well used inside the scientific area, seems to be a problem in former days, hence those machines were pushed aside by cheaper PCs. With the emerging multicore systems and the upcoming Version 3.0 of the OpenMP API, there will be a renaissance of its importance in high-performance computing [265].

7.3.5.2 MPI API

Physically separated computer systems need, in addition to be synchronized to the parallelizing commands, communication information, to manage and synchronize themselves. A very common implementation is the Message Passing Interface which provides, additional to the parallel program section, the required information receiving and sending commands. The higher number of available options can easily increase the possible amount of pitfalls, which can easily lead to a slowdown of the program. Another bottleneck are the messages needed to be sent to the other involved machines themselves: They consume additional computational power and cause additional a certain amount of network traffic, which will make the parallelization less efficient. Nevertheless it is the choice for distributing a large calculation on a big amount of machines, including the possibility to use different types of architectures, e.g. intel-based and sparc-based processors at the same time.

The MPI API is the parallelization method applied to the Genetic Algorithm within this work, as it promised the most advantages, considering time efforts to change the program and possible speedup.

Nowadays a computer cluster usually consists of a mixture of shared and distributed memory systems, which complicates the efforts of speedup. The ultimate way would be

a program that contains both parallelization means, the OpenMP and MPI API, to gain the theoretical available increase. Despite the academic challenge for such an implementation, which is surely reasonable for huge problems, it would blast time and efforts of the present work. Regarding the systems used for this work, which offered a dual-core SMA, the possible speedup would have been marginal in comparison to a purely DMA-based implementation.

7.3.6 Description of the developed Genetic Algorithm

The basic genetic algorithm is a development by Joswig [220]. It has been modified to satisfy the needs within this work. The simplified flowchart of the developed and applied genetic algorithm is presented in Figure 7.3.9.

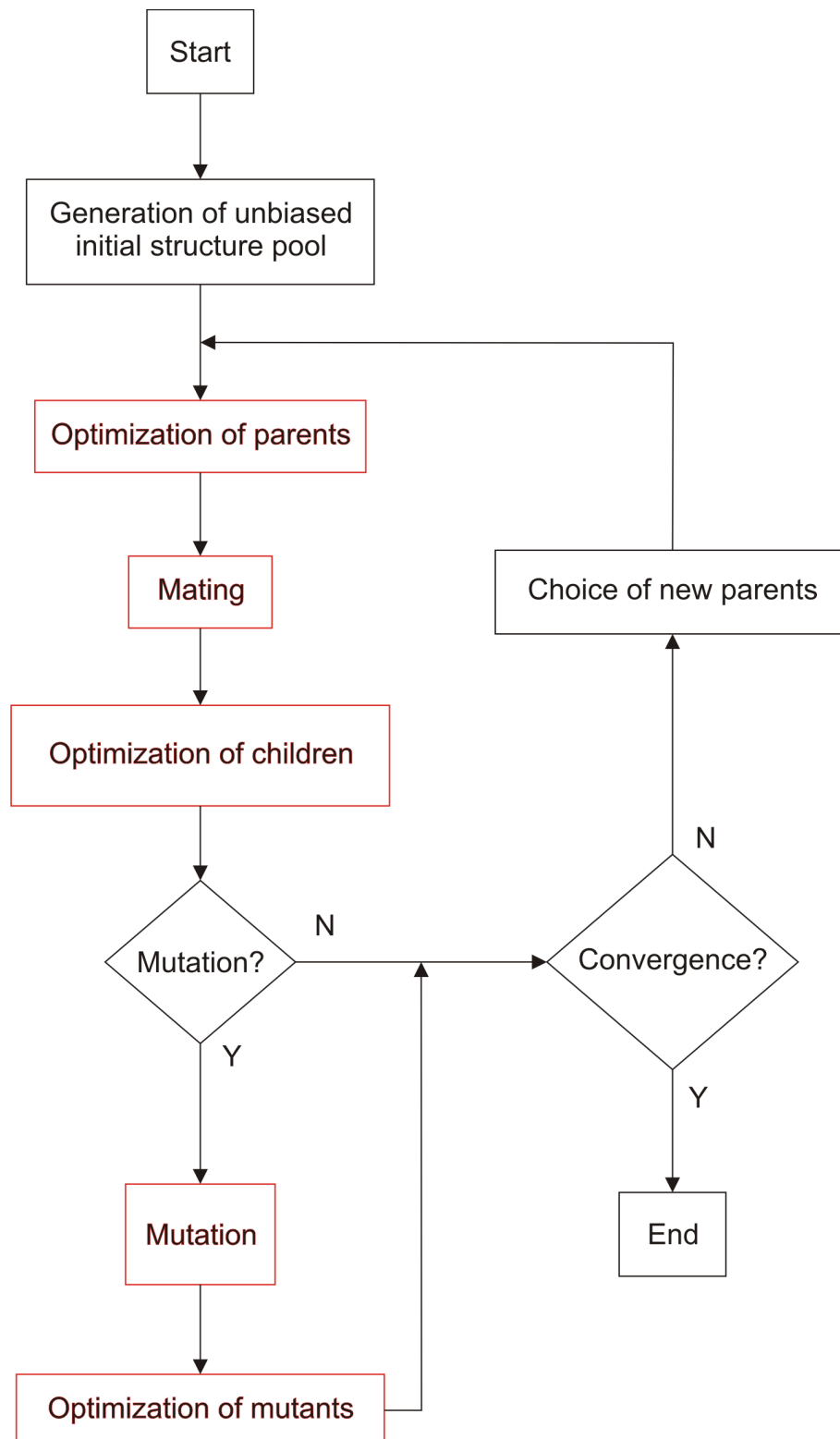


Fig. 7.3.9: Simplified flowchart of the developed and applied genetic algorithm. Each single step is described in Section 7.3.6.

The following sections are referring to the characterizations of the processes in that flowchart and will describe the procedure in detail. The processes lined in red color are the parallelized steps of the GA.

‘Start’

Launching the program initializes the Random Number Generator [245] and checks whether the first generated random number is different from the first generated number of the last run. As initial number for the RNG function, a build-in unix option is used to ensure a certain unbiasedness, as described in details in Section 7.3.4.

After the successful initialization of the RNG the necessary input data is read, containing information about the system, the structure from previous calculations (if available), which type of atom should be added, and the definition of the boundary conditions. Reading structure coordinates are converted from cartesian to spherical coordinates. Structural center point of the cluster is determined and all coordinates are redefined relative to the center point. The maximum available distance within the cluster r_{max} is obtained by evaluating all positions with respect to the center point of the cluster.

‘Generation of unbiased initial structure pool’

After starting the program, a set of unbiased initial structures is generated as described in Section 7.3.3. It provides the basis for the GA to work on.

‘Optimization of parents’

The initial structures, obtained by the unbiased producing procedure, are being relaxed to the local energy minimum within the described DFTB-method. Those structures are the parents and will be mated during the next step.

‘Mating’

The mating procedure is the most important part of the complete GA. There are two different mating routines, which will be discussed in detail in later in Section 7.3.7. Depending which mating routine is chosen, the child generation is build from one parent (in case of the routine *ONEPAR*) or from two parents (routine *TWOPAR*).

‘Optimization of children’

The children produced during the mating routine will be optimized to the local energy minimum by applying the DFTB-method.

‘Mutation’

The program itself randomly chooses whether the relaxed children will be mutated or not (a mutation can be forced by specifying in the input file). It then will randomly change the position of a random amount of atoms a random distance. All the random specified parameters can be explicitly given in the input file.

‘Optimization of mutants’

The obtained mutants will be relaxed to the local energy minimum using the DFTB-scheme.

‘Convergence’

All obtained and relaxed structure will be compared with respect to the energy minimum, which is the convergence criterium. The process converged when the energy minimum did not change within the convergence criterion for 100 times in a row. If this is violated, the GA will choose a new set of parents and start all over.

‘Choice of new parents’

If the convergence criteria is not reached, a new set of randomly chosed parents is used from the pool of initial unbiased structures and will be passed into the optimization and mutation process.

‘End’

Finishing the GA will write the obtained data for the several structures into files and prepare for the subsequent analysis and visualization.

7.3.7 Mating

The mating routine, which is the most important part within the GA procedure besides the optimization, will create new structures, the children. Depending on how many parents are used for the creation of the children, we distinguish between the routine ONEPAR, using 1 parent and TWOPAR, using 2 clusters for the parents.

During the mating process, the cluster is randomly cut at a certain plane and will be rearranged.

7.3.7.1 ONEPAR

The routine ONEPAR uses only one parent cluster to create one child cluster. This generation is illustrated in Figure 7.3.10.

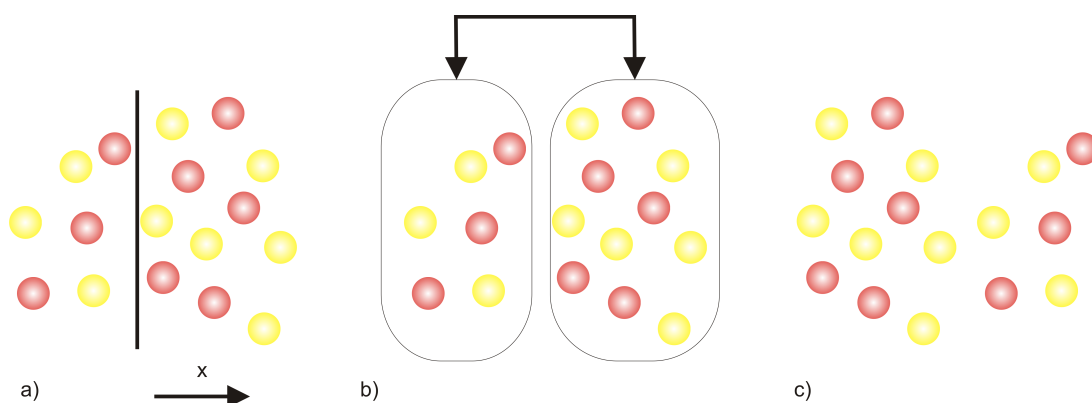


Fig. 7.3.10: Schematic illustration of the routine ONEPAR generating a child generation out of one parent, for the two-dimensional case for a two-component cluster: a) after a cutting plane and the sizes of the two parts are chosen randomly; b) the cluster is cut into two parts; c) the two parts are rigidly interchanged. Structures a) and c) are a parent and a child, respectively.

Since all atoms of the parent cluster will be part of the child cluster, there is no need to take care if the stoichiometry, the atoms of the parent structure will just be rearranged in a new geometry. Therefore it is only necessary to choose the number of atoms L that determines the number of atoms in both parts of the cluster (L and $N - L$). The vector v that describes the direction of the cutting plane is chosen randomly. It is moved onto the positive part of the x axis and the parent cluster is cut into the two parts of the size

L and $N - L$ atoms using the sorted x coordinates. The obtained two parts are rigidly interchanged and brought to an interacting distance.

In contrary to the routine TWOPAR, the routine ONEPAR has the advantage of providing a starting geometry of the optimization of a child cluster in every case. It might happen that the parts of the cluster, although being moved into an interacting distance, may only interact with two atoms, which is an unfavourable situation. But overall, the routine ONEPAR works better, faster, and more reliably for two-component system, and it can be used for homo-atomic clusters as well.

7.3.7.2 TWOPAR

The routine TWOPAR uses two parent clusters to generate two child clusters, by cutting, interchanging, and pasting as schematically illustrated in Figure 7.3.11.

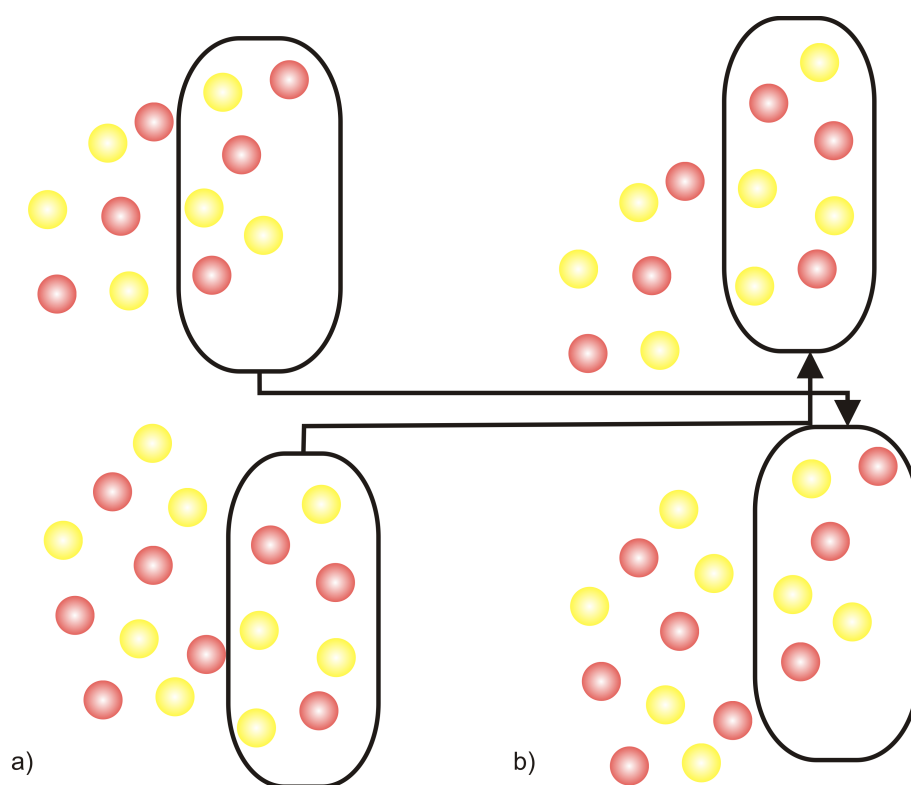


Fig. 7.3.11: Schematic illustration of the routine TWOPAR generating a child generation out of two parents, for the two-dimensional case for a two-component cluster: a) two parent clusters are cut and pasted; b) the two child clusters.

The most important issue in this routine is to maintain the stoichiometry. The routine works as follows. First, from the whole population of M clusters (each consisting of N atoms) $\frac{M}{2}$ pairs of each two clusters are chosen randomly, while no cluster is allowed to be member of more than one pair of clusters, as illustrated in Figure 7.3.11 a). The different colors of the atoms represent different atom types. In the second step, a randomly chosen number L defines the number of atoms in each of the two parts the clusters are cut into. One part is containing L atoms, while the other part is containing $N - L$ atoms. Thirdly, the cutting plane is defined by randomly choosing two angles in the spherical coordination system. By this two angles a cutting plane is fully described. Then we have angles in the range of $0 - 179$ and in the range of $180 - 360$ which will define the two clusters. The clusters are sorted with respect to increasing angle.

After the cutting of the two clusters the parts are interchanged as illustrated in Figure 7.3.11 b), keeping the two new parts at a distance that allows interaction, but on the other hand, being not too close to avoid too high forces. The new obtained child generation will then be relaxed by the optimization routine.

As long as the routine deals with one-component clusters, it is working very well. Regarding hetero-atom clusters requires special attention to maintain the stoichiometry, without limiting the possibility of generating new child generations. The problem is illustrated in Figure 7.3.12.

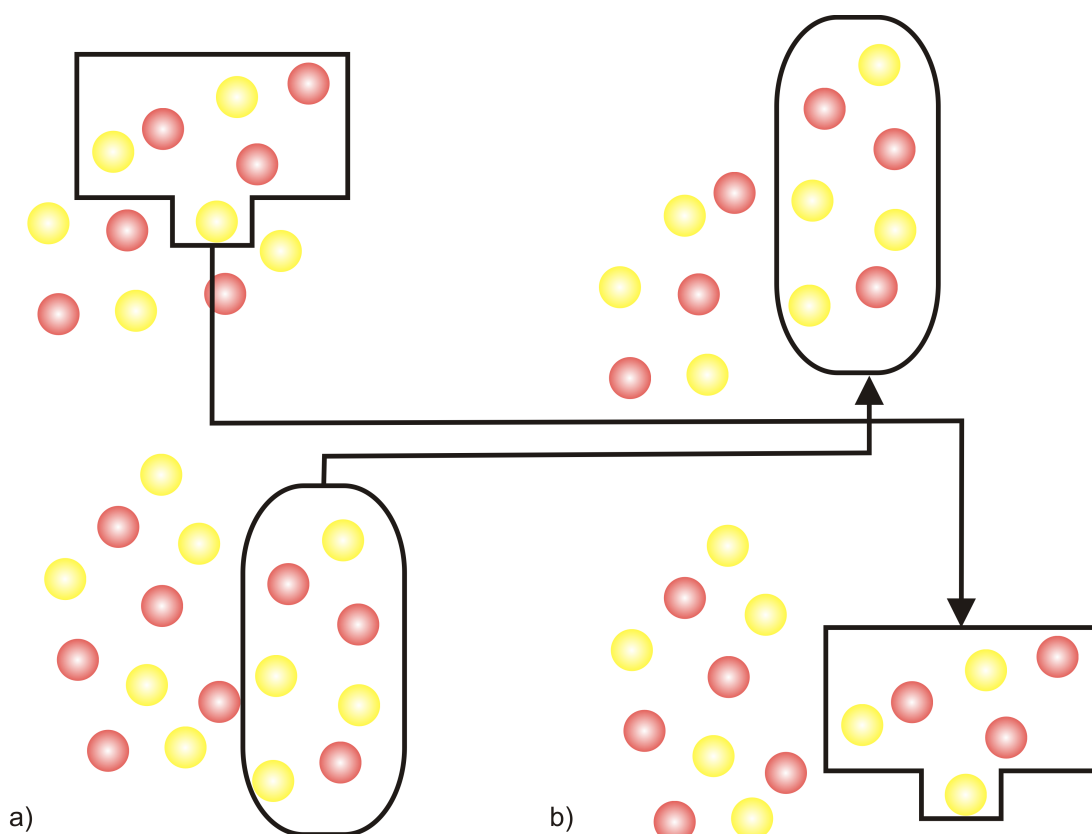


Fig. 7.3.12: Schematic illustration of the routine TWOPAR generating a child generation out of two parents, for the two-dimensional case for a two-component cluster: a) two parent clusters are cut and pasted; b) the two child clusters with a hole.

Whereas the stoichiometry of the cluster is remained, the cutting and pasting led to a hole within the cluster and therefore to poor interactions, as illustrated in the lower part of Figure 7.3.12 b). The different atom types are represented by different colors. The interaction is only possible by two single atoms of each part. After the optimization the relaxed structure will therefore most likely be not of a lower energy than that of the parent generation.

This problem is solved in the following way. After the pasting procedure, all interatomic distances are calculated. The new child generation is passed to the optimization routine only, if all atoms are in a reasonable and interacting distance. Otherwise the rotation and pasting of the new part will be redone until the interaction is ensured.

7.3.8 Mutations

After a successful generation of new child clusters and the relaxation of the new obtained structures, the program has the possibility to introduce a mutation. The decision whether the mutation will take place, as well as the mutation process itself is chosen randomly. During the mutation an atom (ore more) is moved to a new, randomly chosen position. The atom, as well as the amount of movable atoms, is chosen randomly. The mutation provides the advantage of destroying the cluster geometry and thereby introducing new structural elements. It is possible to fix the number of atoms to be moved, as well as to generally switch on the mutation.

7.4 Structural Analysis

In this section different structural analysis of the obtained clusters are presented. The geometry of the lowest-energy clusters as well as those of the next two isomers can be found in Appendix B.

The optimization has been done with respect to the energy minimum and obtained total energies are presented in Table 7.4.1.

n -units	$E_{tot}^{cluster}$	$\Delta E_{tot}^{wurtzite}$	$\Delta E_{tot}^{sphalerite}$	ΔE_{tot} by [266]	ΔE_{tot} by [267]
2	0.0			0.22222	0.22188
3	0.0			0.0	1.69067
4	0.0	1.31743	6.91315	7.5540	0.0
5	0.0			5.58824	0.0
6	0.0			11.72184	0.00490
7	0.0			10.29112	0.66450
8	0.0			12.92571	0.0
9	0.0				0.0
10	0.0	2.27637	2.31744		0.0
11	0.0				0.0
12	0.0				0.0
13	0.0				0.0
14	0.0				0.0
15	0.0				0.0
16	0.0	10.63928	10.44344		0.0

Tab. 7.4.1: Obtained relative total energies for $(CdS)_n$ clusters, $n = 2 - 25$. All energies are given in eV.

The tables contains in the first column, the number of $(CdS)_n$ -units, in the second column the obtained total energies E_{tot} for the investigated clusters, applying the developed genetic algorithm, set to $E_{tot} = 0.0$ for each cluster. To ensure the quality of the algorithm, additional to the clusters, the DFTB-method had been applied to a cutout from the lower energy bulk structure, i.e. CdS -wurtzite structure, for cutout size $n = 4, 10, 16$. All energies are given in relation to the total energy for each investigated cluster. That the total energy of the investigated clusters lower than that of the bulk cutout supports the finding of a new low-energy structure. The fourth column contains the total energy for sphalerite structures, similar to the wurtzite ones in the third column. The fifth column contains the total energy of the structure proposed by Troparevsky *et al.* [266] but here calculated with the DFTB-method used in our optimization process. They investigated $(CdS)_n$ clusters with $n = 2 - 8$ and presented the structures. Their structures differ much from our obtained ones, except for $(CdS)_3$, where we found the same planar structure. Our structures are of lower total energies than those by Troparevsky. Finally the sixth column presents our calculated energies for structures obtained by Wang et al [267] for ZnO -systems, transfered to the cadmium sulfide clusters and relaxed locally. There is

good structural agreement for the structures with $n = 4, 5, 8 - 16$.

Junkermeier *et al.* [268] presented structures for $(CdS)_n$ with $n = 264, 280, 281, 293, 329, 357$, which have not been investigated within this work, so no comparison is made.

Unfortunately, to the best of our knowledge there are few papers containing structure information for $(CdS)_n$ clusters. Therefore no further structure comparisons are presented.

For $(CdS)_4$ one special structure is obtained. It is totally planar, which is unexpected for an eight atoms cluster, but this result is in good agreement with the similar structure for $(ZnO)_4$, found by Wang *et al.* [267]. Figure 7.4.13 represents the structure of the $(CdS)_4$ cluster.

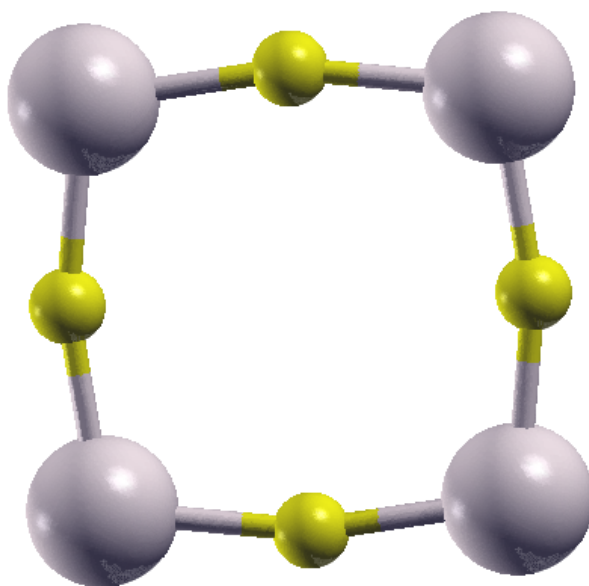


Fig. 7.4.13: The totally planar structure of $(CdS)_4$ cluster is shown. The cadmium atoms are in grey color and the sulfur in yellow, respectively.

7.4.1 Radial Distribution Function

Figure 7.4.14 represents the size dependence of the radial distribution of the atoms for Cd and S .

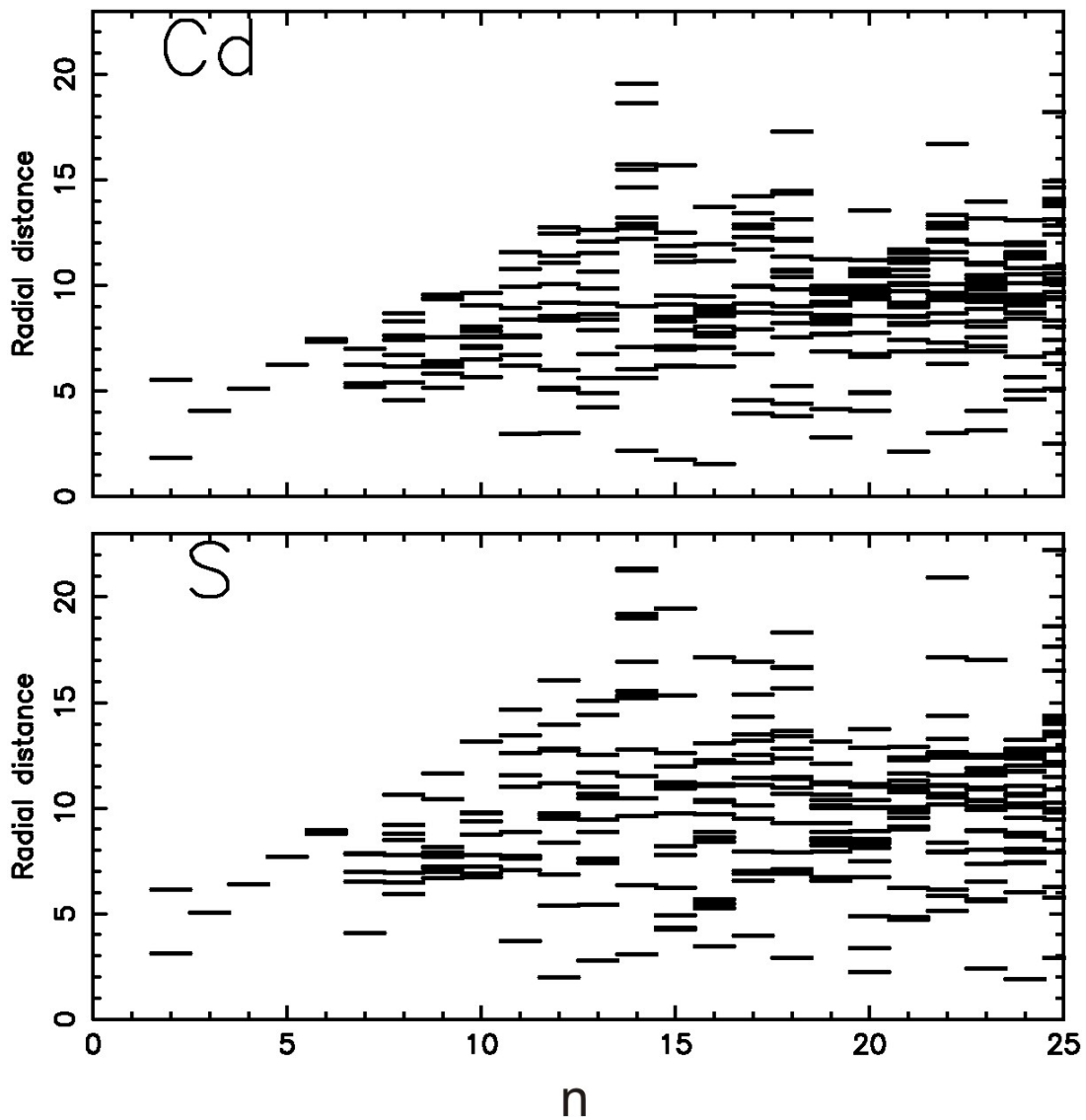


Fig. 7.4.14: Radial distribution r_i for $(CdS)_n$ clusters as functions of the number of $(CdS)_n$ -units. Each horizontal line represents one or more atoms of that specific distance to the center of mass, located at $y = 0$. The left panel represents the radial distribution for the Cadmium atoms, the right panel for the Sulfure atoms, respectively.

The radial distribution function is defined as follows. For each atom of a $(CdS)_n$ cluster the distance to the geometrical center of the cluster, which is positioned at $\mathbf{R}_0$, $R_i =$

$|\mathbf{R}_i - \mathbf{R}_0|$ is calculated, with

$$\mathbf{R}_0 = \frac{1}{2n} \sum_{i=1}^{2n} \mathbf{R}_i \quad (7.4.5)$$

with $\mathbf{R}_i$ being the position of the i -th atom, for each component. All the n obtained distances are displayed in one diagram for each component and shown as a function of the cluster size (number of atoms n). The upper panel shows the radial distribution function for the cadmium atoms in the cluster, the lower panel those for the sulfide atoms, respectively.

One aspect which can be seen in the resulting Figure 7.4.14 is the increasing radius of the clusters with increasing number of CdS -units n . The radius is represented by the horizontal lines with largest distance to the origin located at $y = 0$. Although in general, the radius is increasing with increasing n of the clusters, there occur some irregularities, i.e. the cluster is slightly decreasing with increasing n . In most cases these irregularities are due to a rearrangement of the system.

A more detailed view at the structures of the investigated clusters can be found in Section 7.4.4.

In the investigated range of n , no building of shells of atoms can definitely be discovered. Further investigations for cluster size $n > 25$ need to be done to find this.

7.4.2 Similarity Functions

The similarity functions help to understand whether a cluster with n units can be considered as a product of the cluster with $n - 1$ units plus an additional unit. Therefore two similarity functions are defined and shown in Figures 7.4.15 and 7.4.16.

The similarity function based on the interatomic distances s_1 is shown in Figure 7.4.15.

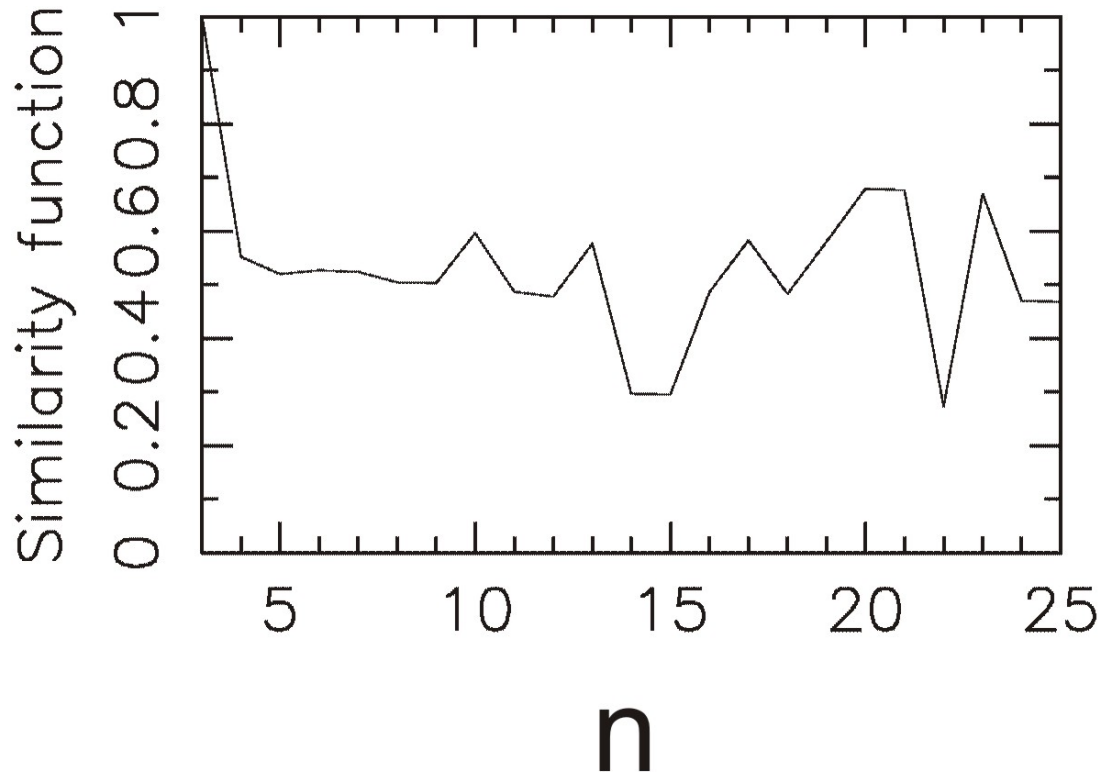


Fig. 7.4.15: Similarity Function s_1 using interatomic distances as defined in Equation 7.4.9. The function is 1 for a cluster that is obtained by adding a single unit to the $(n - 1)$ -unit cluster, and approach 0 for very different structure.

For a $(CdS)_n$ cluster the radial distance for each of the $2n$ atoms is

$$\mathbf{R}_i = |\mathbf{R}_i - \mathbf{R}_0| \quad (7.4.6)$$

being $\mathbf{R}_0$ the geometric center of the cluster,

$$\mathbf{R}_0 = \frac{1}{2n} \sum_{i=1}^{2n} \mathbf{R}_i, \quad (7.4.7)$$

defined from the positions $\mathbf{R}_i$ of the $2n$ atoms.

Any two structures with the same number of atoms are compared by sorting these distances for each structure, separately, and subsequently calculated the similarity function

s_1 using the interatomic distances

$$q_1 = \Delta_d = \sqrt{\frac{2}{2n(2n-1)} \sum_{i=1}^{\frac{2n(2n-1)}{2}} (d_i^1 - d_i^2)^2}, \quad (7.4.8)$$

$$s_1 = \frac{1}{1 + q_1/u_l} \quad (7.4.9)$$

the upper indices 1 and 2 referring to the two different structures.

The similarity function is 1 for a cluster obtained by adding a single unit to the $(n-1)$ -unit cluster, and approaches 0 for very different structures. As can be seen, the similarity function remains with small values, indicating very different structures.

The second similarity function s_2 , presented in Figure 7.4.16 depends on the radial distances of the atoms of the $(n-1)$ -unit and n -unit cluster.

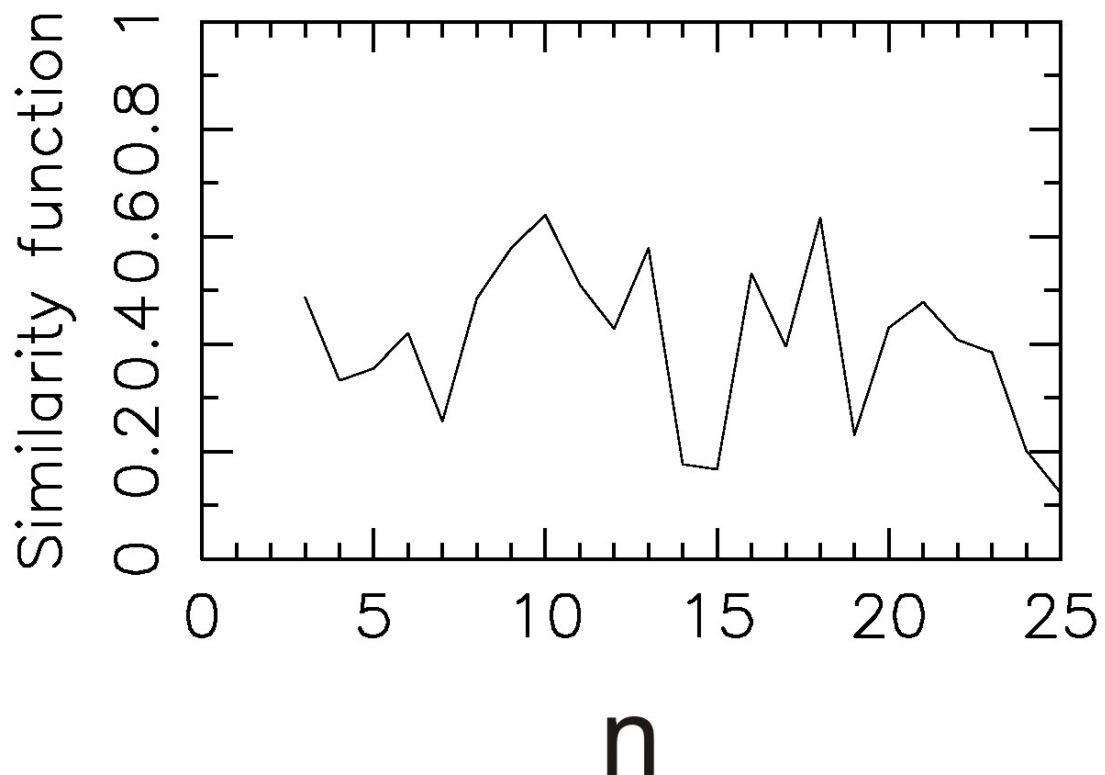


Fig. 7.4.16: Similarity Function using radial distances as defined in Equation 7.4.11. The function is 1 for a cluster that is obtained by adding a single unit to the $(n-1)$ -unit cluster, and approach 0 for very different structure.

It is defined as

$$q_2 = \Delta_r = \sqrt{\frac{1}{2n} \sum_{i=1}^{2n} (r_i^1 - r_i^2)^2}, \quad (7.4.10)$$

$$s_2 = \frac{1}{1 + q_2/u_l} \quad (7.4.11)$$

the upper indices 1 and 2 referring to the two different structures.

The similarity function is 1 for a cluster obtained by adding a single unit to the $(n - 1)$ -unit cluster, and approaches 0 for very different structures. As can be seen, the similarity function remains with small values, indicating very different structures.

7.4.3 Stability Function

In Figures 7.4.17, 7.4.18 and 7.4.19 the size dependence of the relative stability of the investigated $(CdS)_n$ clusters is shown.

Figure 7.4.17 shows the total energy per CdS unit converging smoothly, whereas Figure 7.4.18 is a zoomed in cut out for the higher values of n .

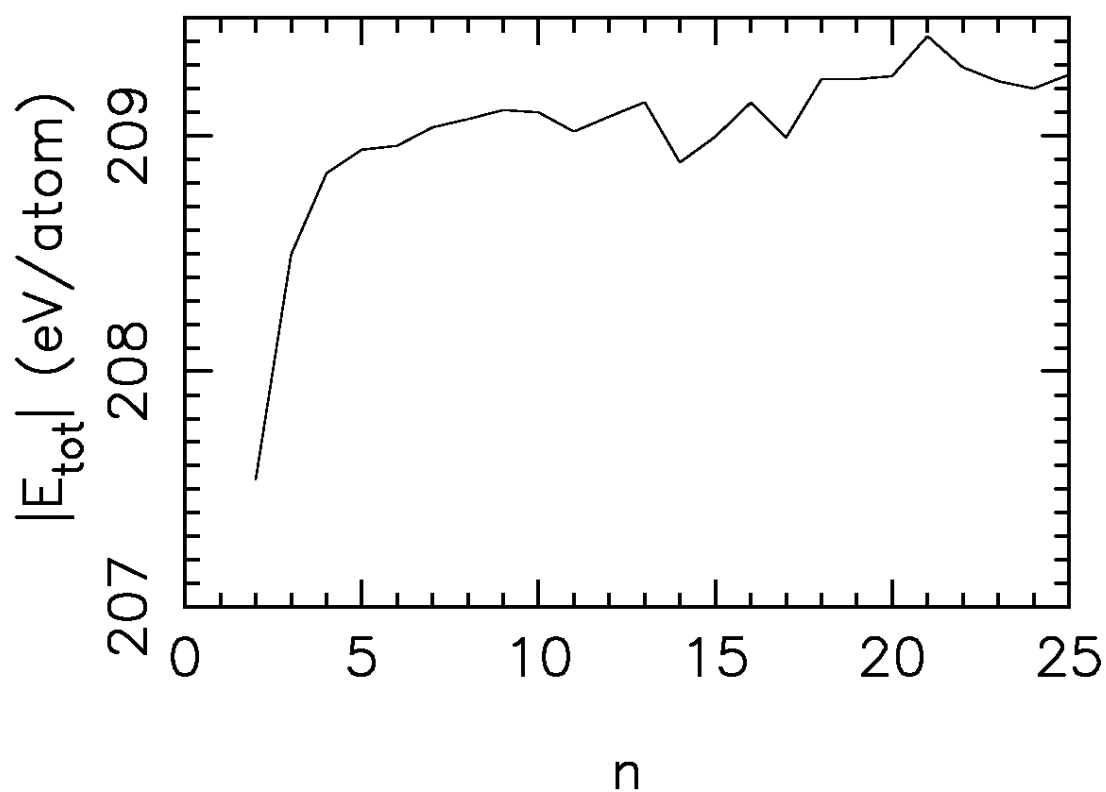


Fig. 7.4.17: Relative total energy per CdS unit (absolute value) for $(CdS)_n$ with $n = 2 - 25$.

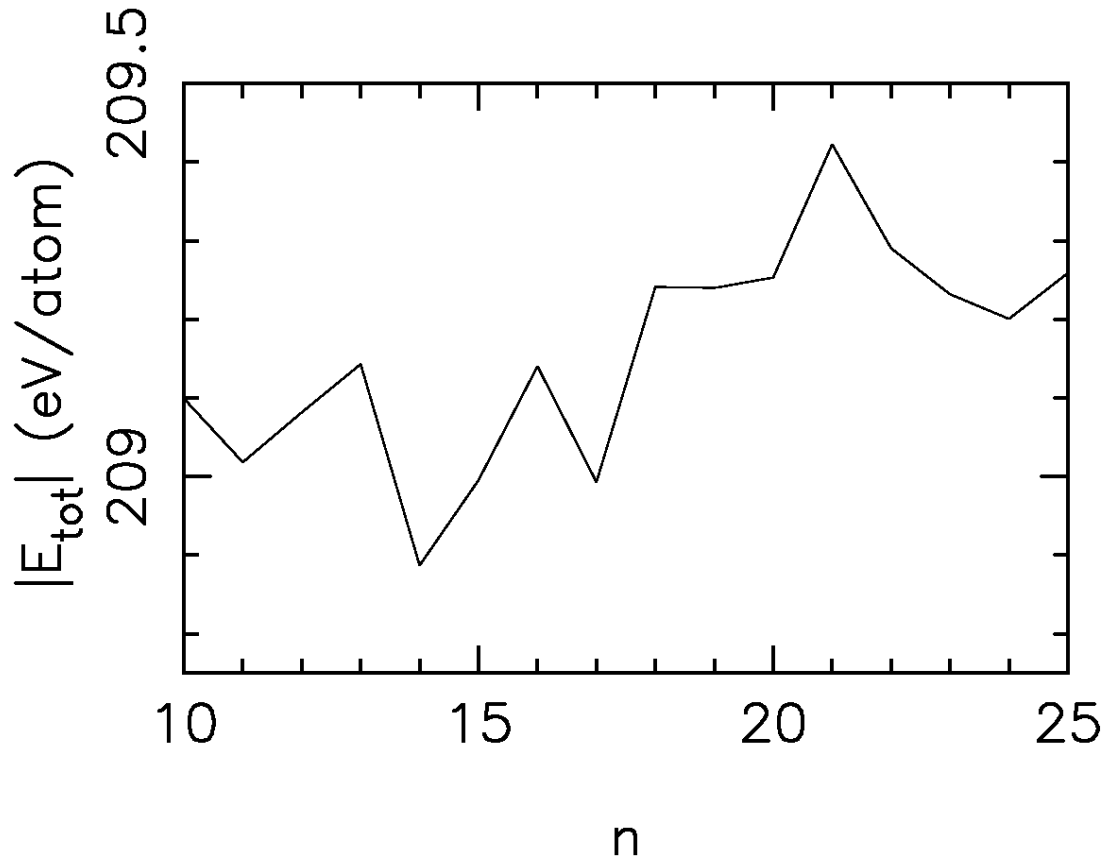


Fig. 7.4.18: Cutout of Figure 7.4.17 showing the total energy per CdS unit (absolute value) for $(CdS)_n$ with $n = 10 - 25$ in a more detailed view.

However, there are a few irregularities in the curvature. The total energy of $(CdS)_{11}$, $(CdS)_{14}$, $(CdS)_{17}$, and $(CdS)_{24}$ are particularly low, i.e. those clusters are particularly unstable. This is supported by the stability function E_{stab} , defined as

$$E_{stab} = E_{n+1} + E_{n-1} - 2E_n, \quad (7.4.12)$$

being E_n the total energy of a $(CdS)_n$ cluster and shown in Figure 7.4.19.

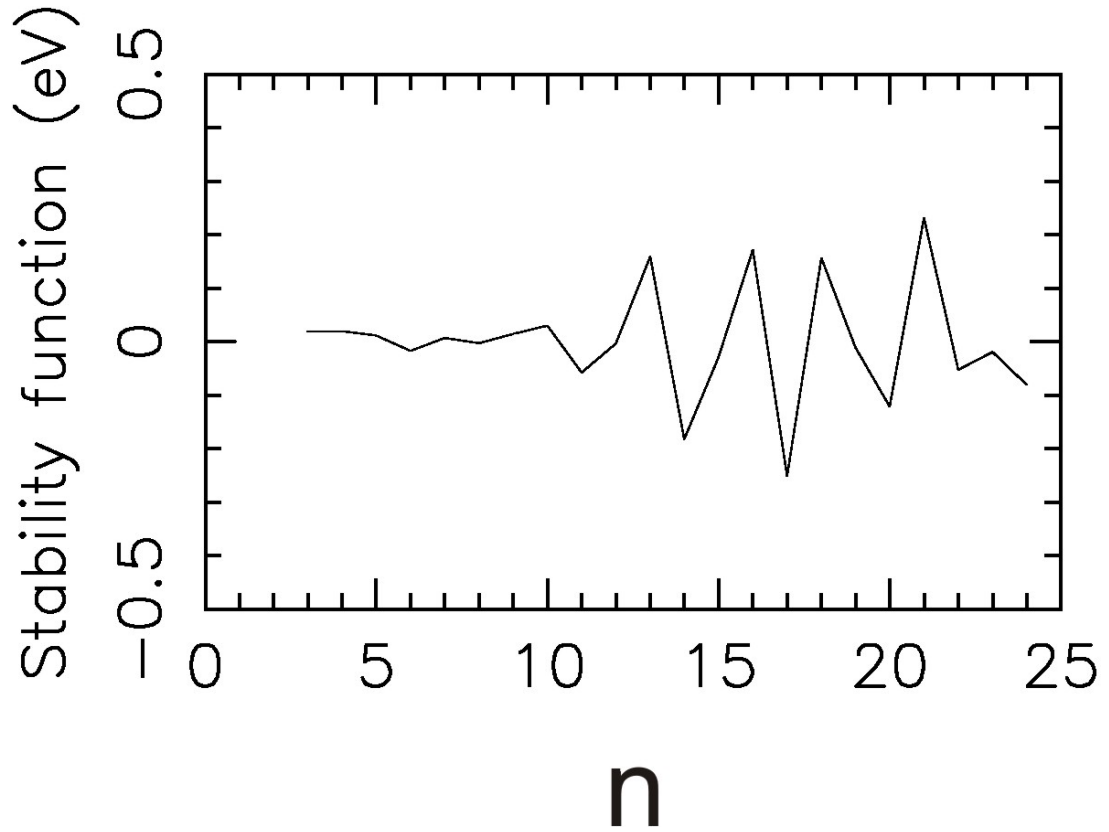


Fig. 7.4.19: Stability Function for the $(CdS)_n$ cluster, with $n = 2 - 25$. A cluster is particularly stable, if the stability function has a positive value ($E_{stab} > 0$).

The clusters $(CdS)_{11}$, $(CdS)_{14}$, $(CdS)_{17}$, $(CdS)_{20}$, $(CdS)_{22}$, $(CdS)_{24}$ have the most negative values which indicates that they are particularly unstable. For the clusters $(CdS)_{11}$, $(CdS)_{14}$, $(CdS)_{17}$, $(CdS)_{20}$ this instability can be explained, because the stability function of a cluster with n units strongly depends on the clusters with $n - 1$ and $n + 1$ units, which are particularly stable.

Another possibility to explain the instability of the clusters is that the applied genetic algorithm did not find the global minimum. However, this case is unlikely because after obtaining the minimum for each cluster of the size n , additional 20,000 generations have been considered that did not yield a lower energy minimum. In addition, the achieved results were compared with bulk cutouts of the wurtzite structure, which is to be considered the lower energy bulk structure, and is found to be higher than that of the single clusters.

A correlation between the symmetry and stability can not be seen on the first view.

7.4.4 Shape Analysis

In the previous sections, the stability of the cluster has been discussed. Besides it, the overall shape of the investigated clusters and its size dependence is of significant interest. The overall shape of the clusters can be studied by considering the 3×3 matrix containing the elements

$$I_{st} = \frac{1}{u_l^2} \sum_{n=1}^N (R_{n,s} - R_{0,s}) (R_{n,t} - R_{0,t}) \quad (7.4.13)$$

with $u_l = 1\text{\AA}$ being a length unit, s and t being x , y , and z ,

$$\vec{R}_0 = \frac{1}{N} \sum_{n=1}^N \vec{R}_n \quad (7.4.14)$$

being the center of the cluster, and $R - n$ being the position of the n th atom. The three eigenvalues of this matrix, $I_{\alpha\alpha}$, can be used in separating the clusters into being overall spherical (all eigenvalues are identical), more cigar-like shaped (one eigenvalue is large, the other two are small), or more lens-shaped (two large and one small eigenvalue). Moreover, the average of the three eigenvalues, $\langle I_{\alpha\alpha} \rangle$, is a measure of the overall extension of the cluster. For a homogeneous, spherical jellium cluster with n atoms, the eigenvalues are proportional to $N^{\frac{5}{3}}$. Therefore, in Figure 7.4.20 we scale the eigenvalue by $N^{-\frac{5}{3}}$.

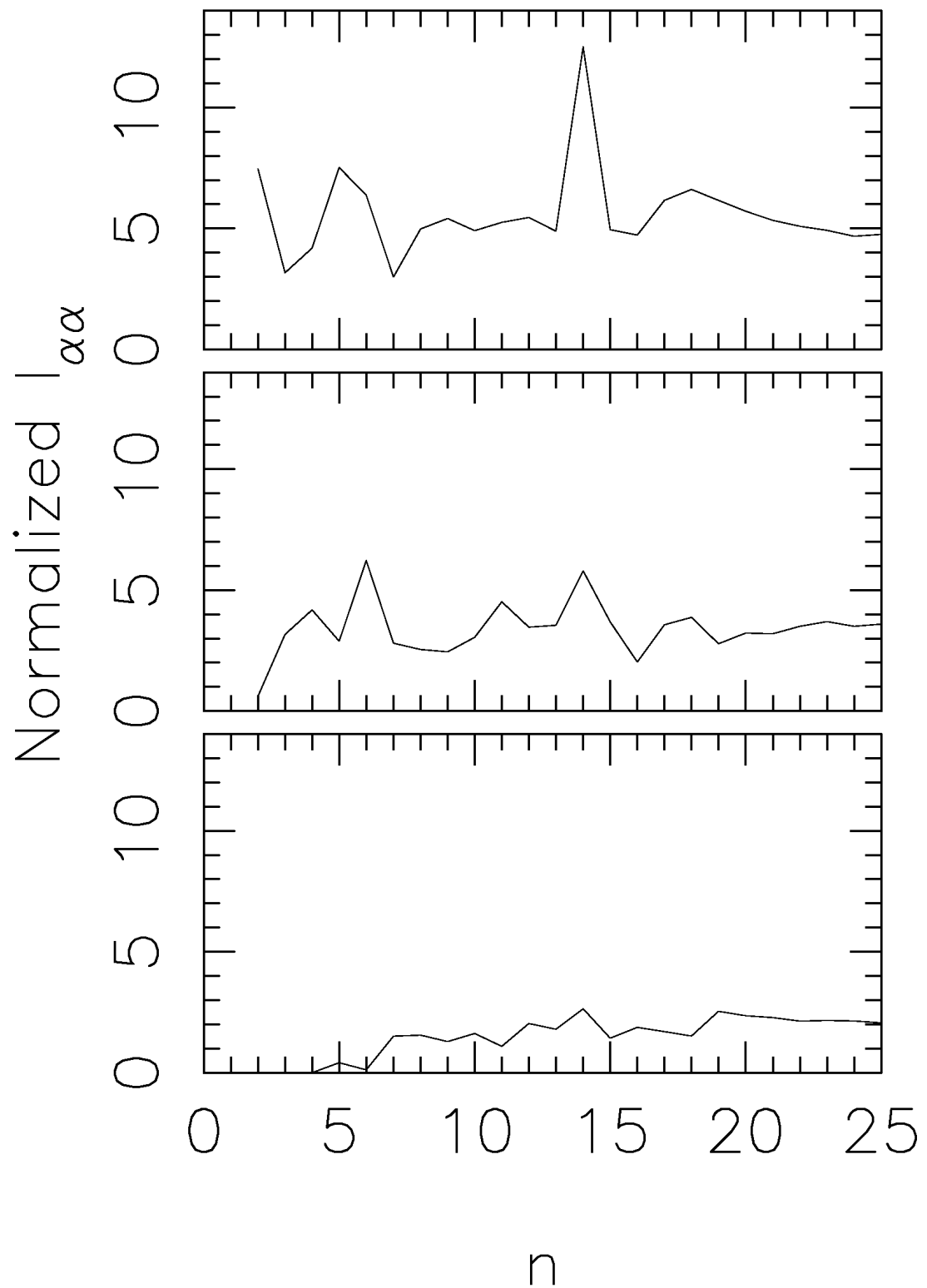


Fig. 7.4.20: Size dependent shape analysis for the $(CdS)_n$ clusters, with $n = 2 - 25$. Presented are the three different normalized eigenvalues $I_{\alpha\alpha}$ of the matrix containing the moments of inertia.

The obtained eigenvalues are different for all three eigenvalues. This indicates there is no spherical shaped cluster. For $n = 2, 3, 4$ one eigenvalues is equal to zero, which is in agreement with the planar structure of the clusters.

7.5 Eletronic Properties

In this section the eletronic properties of the investigated clusters are presented, i.e. the Mulliken gross populations, HOMO and LUMO energies, as well as the difference of HOMO and LUMO.

7.5.1 Mulliken gross populations

The Mulliken gross populations [269] illustrate the atomic contributions of electron charge to the total electron density ρ . These values show a tendency of charge distributions and transfers in the clusters. They give no absolute charges contributed by the atoms as the electron density is distributed over the entire space and can not be separated into single atomic components. The Mulliken populations are deduced from the density matrix P , with the elements

$$P_{jk} = \sum_i n_i c_{ij}^* c_{ik} \quad (7.5.15)$$

being

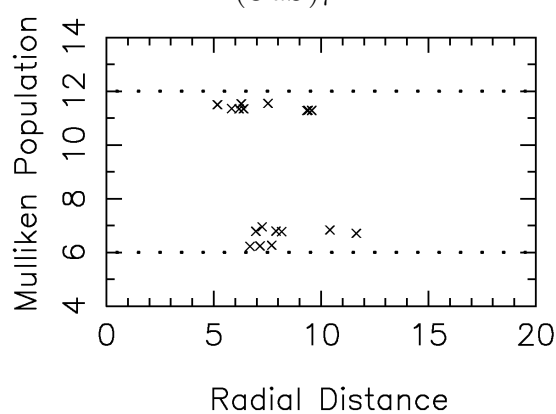
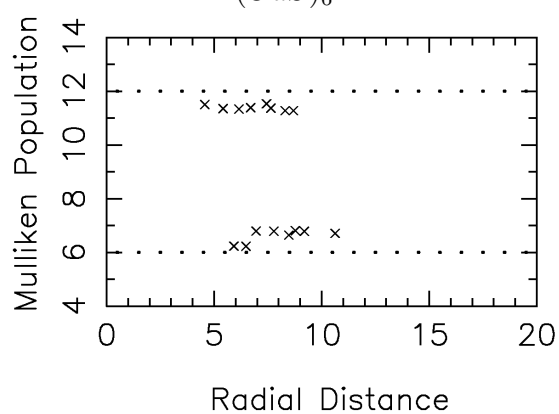
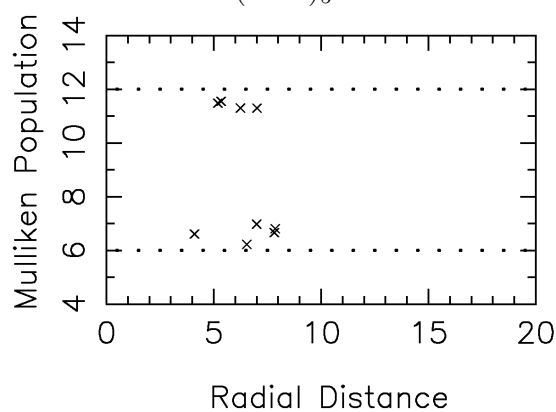
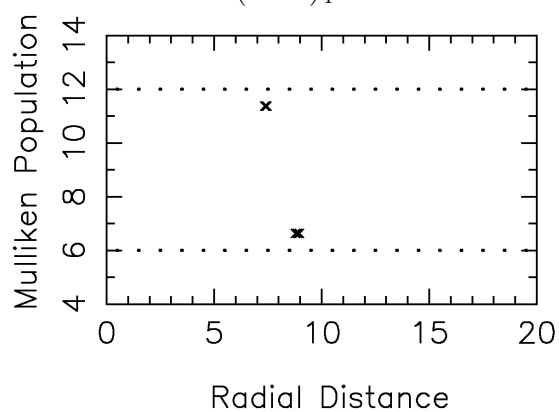
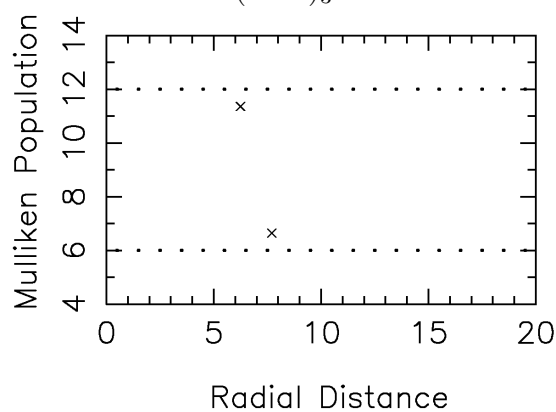
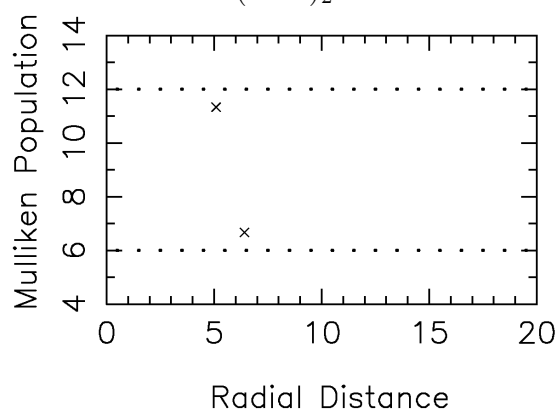
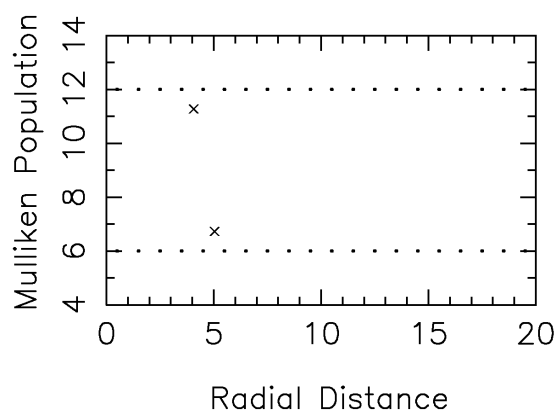
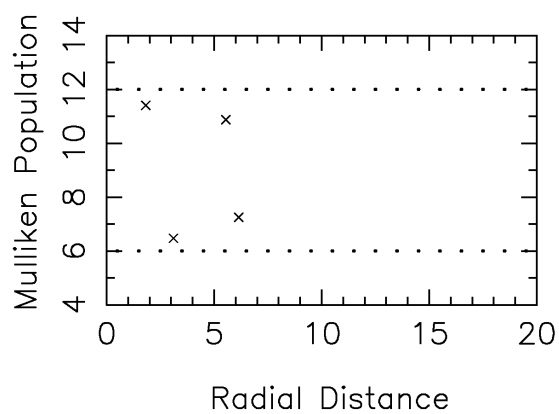
n_i	number of electrons of the i -th orbital
c_{ij}	coefficients of the molecular orbital $\psi_i = \sum_j c_{ij} \varphi_j$

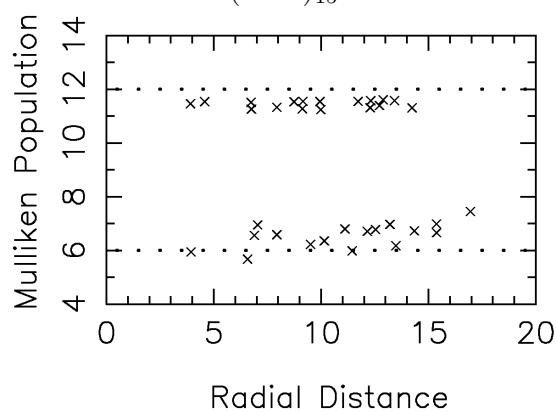
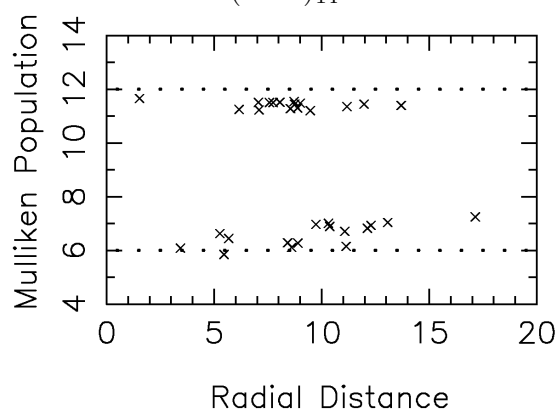
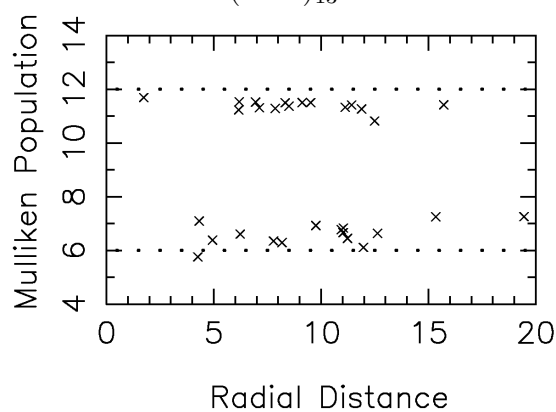
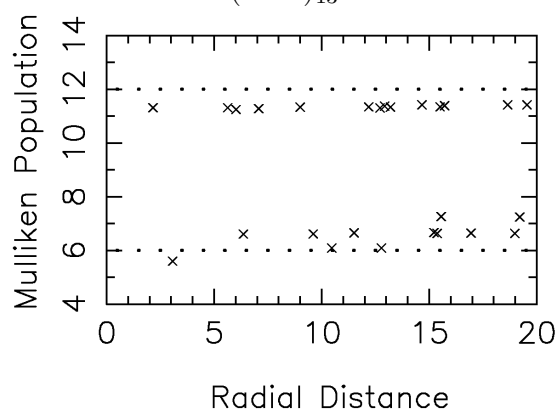
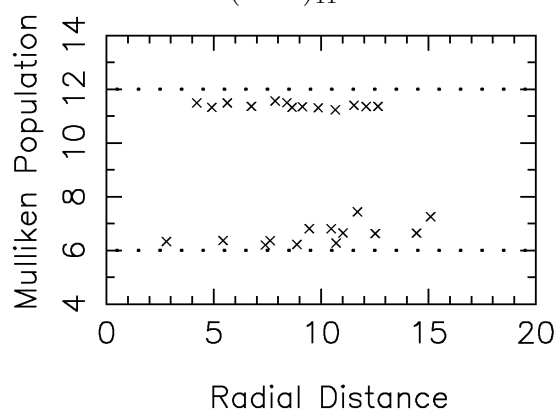
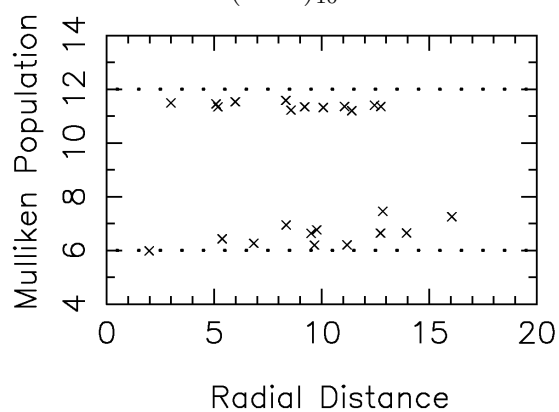
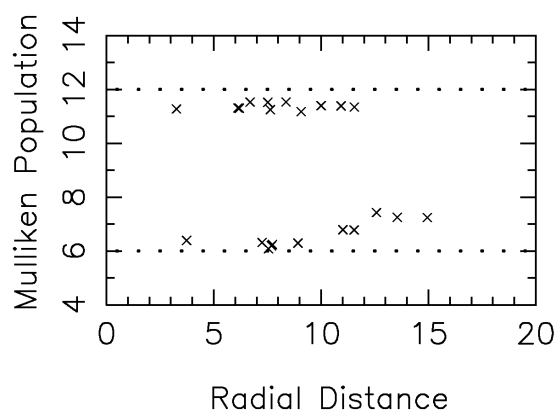
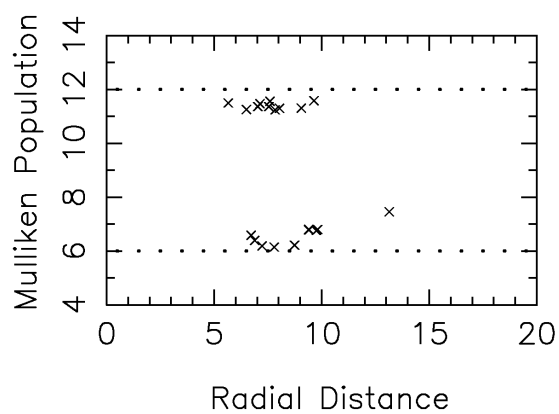
The Mulliken gross population Q_i of the i -th orbital is defined as:

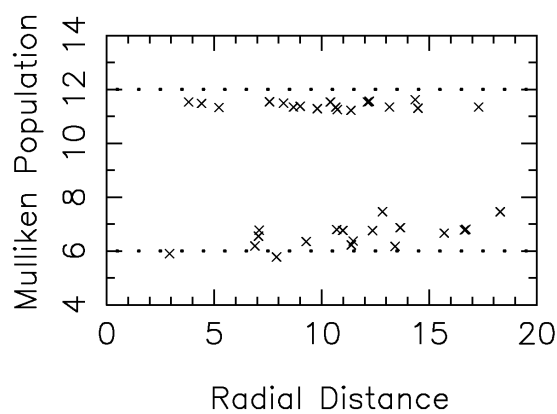
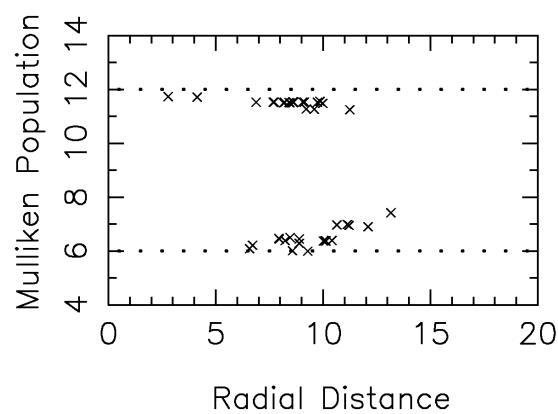
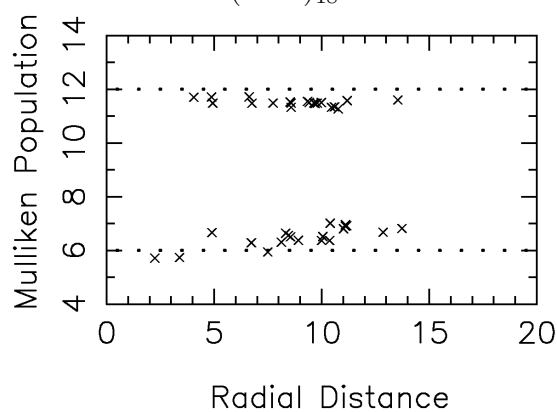
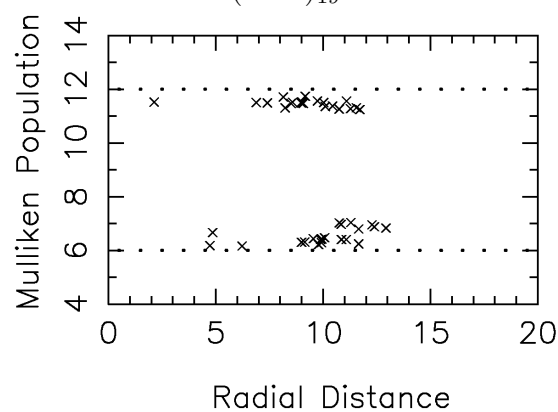
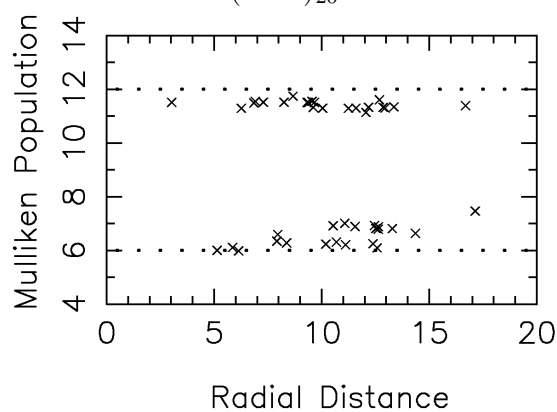
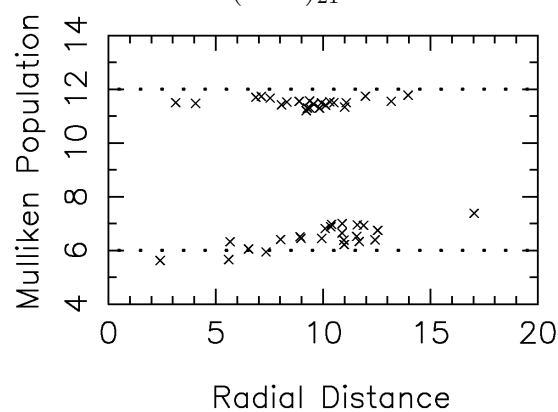
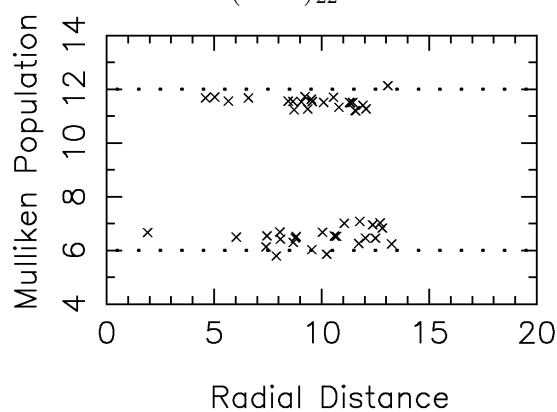
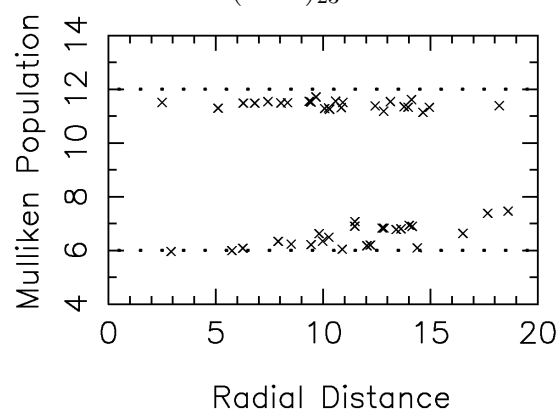
$$Q_i = P_u S_u + \frac{1}{2} \sum_{i \neq m} P_{im} S_{im} \quad (7.5.16)$$

being S_{im} the overlap integral $S_{im} = \langle \varphi_i | \varphi_m \rangle$. Summing over all Q_i for orbitals φ_i belonging to that atom will give the total number of electrons on an atom.

The following figures are presenting the radial distribution of the Mulliken gross populations for each cluster size. The horizontal dotted lines mark the number of valence electrons of the neutral atoms, i.e. 12 for cadmium and 6 for sulfur atoms. In the figures it can clearly be seen, that in the inner parts of the cluster, the gross populations are very close to those of the neutral atoms. The values in this part are almost constant for all atoms with Mulliken gross populations of approximately 11.5 for the cadmium atoms and 6.5 for the sulfur atoms. Therefore the Mulliken charges are +0.5 and -0.5 for cadmium and sulfure, respectively. On the other hand, in the outermost regions a charge transfer can be observed from the cadmium atoms to the sulfur atoms. This might support a proposal of a surface layer, with different electronic properties to those in the bulk parts, which is not supported by the structural analysis. The obtained results are in good agreement with [217].



 $(CdS)_{16}$ $(CdS)_{17}$

 $(CdS)_{18}$  $(CdS)_{19}$  $(CdS)_{20}$  $(CdS)_{21}$  $(CdS)_{22}$  $(CdS)_{23}$  $(CdS)_{24}$  $(CdS)_{25}$

7.5.2 HOMO, LUMO and Band Gap

The highest occupied and the lowest unoccupied molecular orbital (HOMO and LUMO) are the two most important orbitals of the clusters. They define the HOMO/LUMO gap which is the difference of their orbital energies

$$\epsilon_{gap} = |\epsilon_{HOMO} - \epsilon_{LUMO}|. \quad (7.5.17)$$

Formally the term ‘band gap’ is only valid for infinite systems with continous energy bands instead of discrete energy levels, like in clusters. To simplify matters we will refer to the HOMO/LUMO gap as ‘band gap’.

Figure 7.5.21 represents the HOMO energy and the band gap depending on the cluster size.

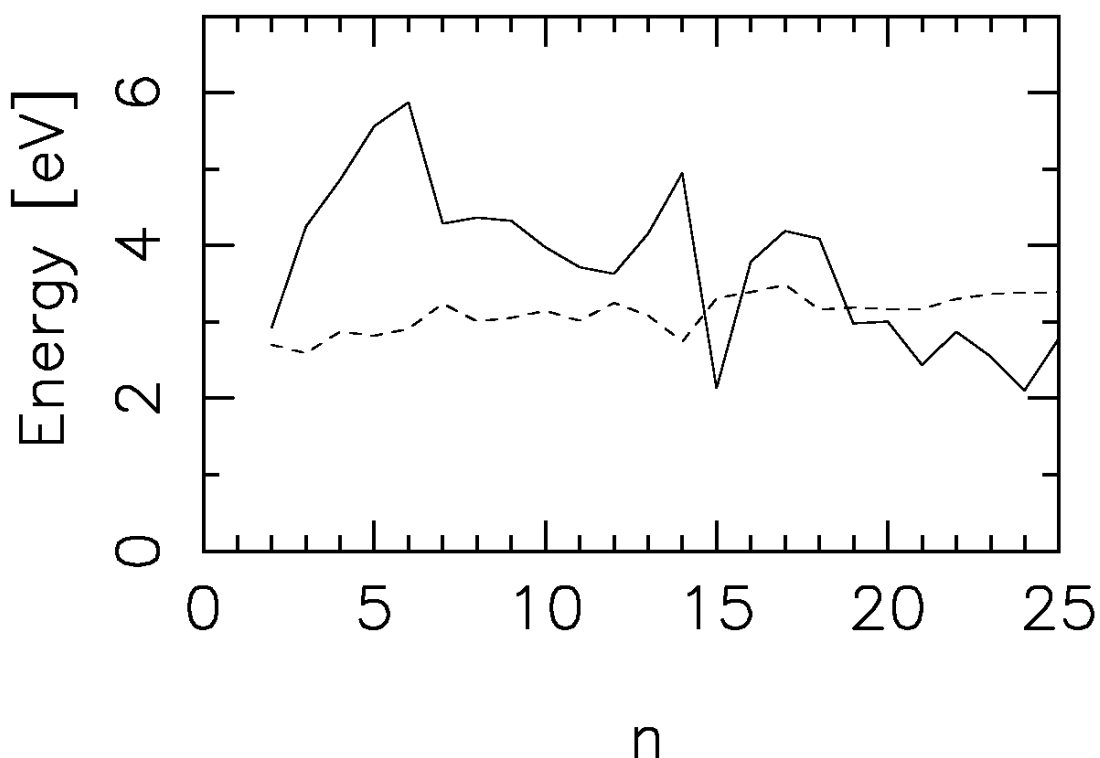


Fig. 7.5.21: HOMO energy (dashed curve) and HOMO/LUMO gap depending on the cluster size. The HOMO curve has been shifted by a constant value to be visualised in the same diagram

The Figure shows a smooth dependence of the HOMO energy on the cluster size.

Figure 7.5.22 represents the LUMO energy and the band gap depending on the cluster size.

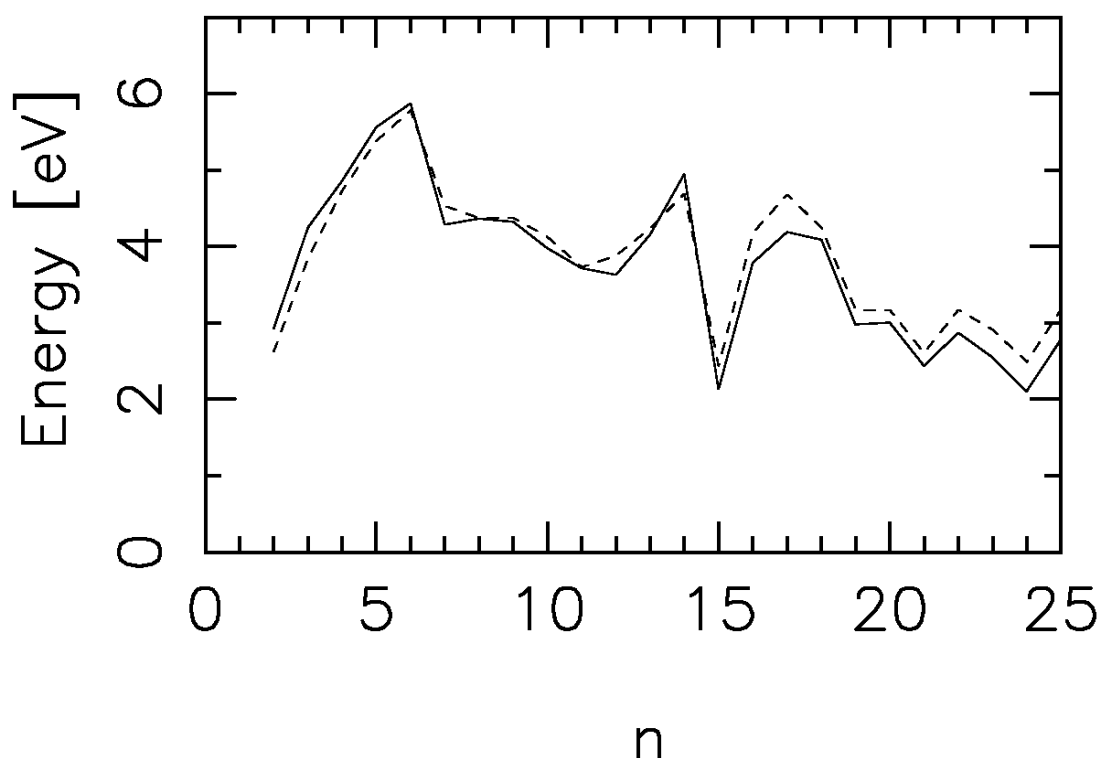


Fig. 7.5.22: LUMO energy (dashed curve) and HOMO/LUMO gap depending on the cluster size. The LUMO curve has been shifted by a constant value to be visualised in the same diagram

The LUMO curve indicates that the irregularities in the band gap are derived from the LUMO behavior as a functional of the cluster size. The unusual low gap for $(CdS)_n$ is caused by the relatively low LUMO energy.

Figure 7.5.23 represents the total energy and the band gap dependence on the cluster size.

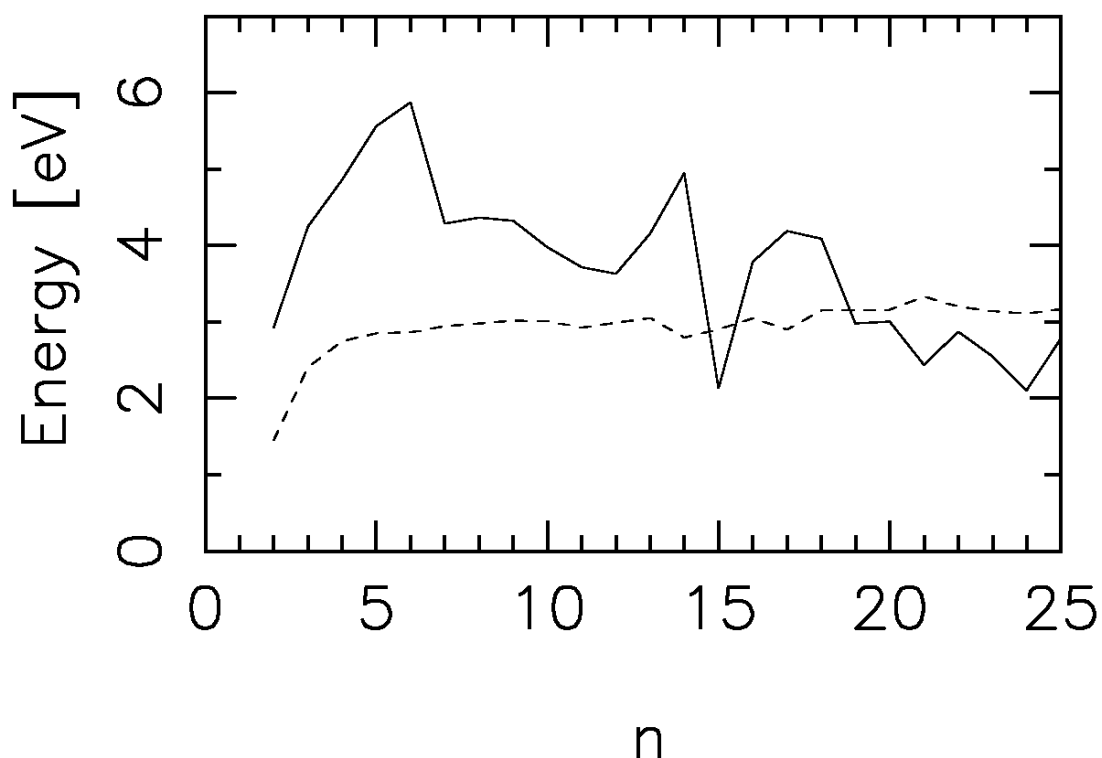


Fig. 7.5.23: Relative total energy per unit (dashed curve) and HOMO/LUMO gap depending on the cluster size. The total energy curve has been shifted by a constant value to be visualised in the same diagram

As can clearly be seen from the figure, there is no dependence of the band gap and the total energy of the clusters.

7.6 Conclusion

In this chapter we presented our results of the investigated stoichiometric $(CdS)_n$ -clusters with $n = 2 - 25$, obtained by applying our further developed unbiased genetic algorithm. The functionality of the GA has been explained in detail. Starting with the GA developed by Joswig [220], we changed the mutating and mating procedures from cartesian coordinates to spherical ones. We implemented a MPI parallelization of the GA with an speedup up to 60% . Moreover an unbiased approach of the starting geometries has successfully been added.

The investigation of the clusters led to cluster structures, which are partly quite different

from the bulk structures. The obtained geometries are partly in agreement with structures for similar systems, like ZnO . Especially we note the planar structures for $(CdS)_3$ and $(CdS)_4$.

The structures has been evaluated by using commonly implemented analysis tools, i.e. similarity function, stability function, radial distribution, and shape analysis. The results are presented in detail.

In addition the electronic properties of the clusters are presented, i.e. band gaps.

It will be reasonable to investigate bigger cluster, i.e. being $n > 25$ in the future to figure out, at which size, the cluster behavior starts to converge to the bulk phase one.

8 Towards the universal Functional

8.1 Introduction

Electronic correlation is due to the interelectronic interaction within in the electronic structure of a quantum system. The Hartree-Fock method, where the wave function is approximated by a single Slater determinant, relies on averages. There is neither consideration of the instantaneous electrostatic interactions between electrons. The neglect of the Coulomb correlation leads to a total electronic energy different from the exact solution of the Schrödinger equation within the Born-Oppenheimer approximation. Therefore the Hartree-Fock limit is always above the exact energy [270]. Löwdin [271] introduced the term correlation energy for the difference.

There are many different ways of implementing density functional theory, originally introduced by Thomas [9] and Fermi [10, 272] in 1927, all requiring the formulation of density functionals for the kinetic, exchange and correlation energies. In 1934 Wigner [273] made the proposal, the total energy of a system can be determined by adding to the Hartree-Fock energy an estimate of the correlation energy, evaluated in terms of the density. Hohenberg and Kohn [11], Levy [274] and Lieb [275] made their contributions by establishing foundations, which led to the development of many computationally effective density functionals. The main way is the introduction of nonlocal effects in the exchange and correlation functionals via a density-gradient expansion. Kurth *et al.* [276] represent an extensive recent study on the development and testing of ever improved density functionals. Chakravorty *et al.* [277] and Jarzecki *et al.* [278] compared the exact and DFT correlation energies across the helium atomic isoelectronic sequence. Görling [279] included exact exchange methods, while Bartlett *et al.* [280] used ab initio density functional theory.

Katriel *et al.* [281] showed, that while several of the more recent density functionals reproduce the exact correlation energies of the helium isoelectronic sequence rather closely, none is satisfactory for Hooke's atom isoelectronic sequence. The aim of this work is to close

that gap and provide one step towards the universal correlation energy density functional.

8.2 Hooke's atom

The system known as Hooke's atom [282], hookium [283], harmonium [284], etc. is closely related to the helium atom. It consists of two charged particles with a Coulombic repulsion but the nuclear attraction is replaced by a harmonic potential.

The isoelectronic sequences of both systems, the Hookes one and the Helium one, do have a similarity between the angular correlation, which was first noted by White [285], who examined the asymptotic contributions of the large angular momentum terms to the energy in the second-order perturbation theory.

8.3 Nonuniversality of commonly used correlation-energy density functionals

As described in the introductory section, the ultimate correlation-energy density-functional, whose existence is guaranteed by the Hohenberg-Kohn theorem, remains elusive. Katriel *et al.* [281] evaluated the correlation energies of the helium isoelectronic sequence and of Hooke's atom isoelectronic sequence, using an assortment of local, gradient and metagradient density functionals. They compared the results with the exact correlation energies, showing that while several of the more recent density functionals reproduce the exact correlation energies of the helium isoelectronic sequence rather closely, none is satisfactory for Hooke's atom isoelectronic sequence. They showed that most density functionals fail to yield an adequate dependence of the correlation energy on the nuclear charge Z along isoelectronic sequences. Some of them are not too bad. But, none of that is true for Hooke's atom isoelectronic sequence. This suggests that the development of a universal density functional has not been attained, not even for spherically symmetric two-fermion systems.

8.4 Wigner's functional

In 1934 Eugene P. Wigner made his first exploration of the correlation-energy density as a means for estimating correlation energies in many-electron systems [273]. He assumed that the total correlation energy can be evaluated as the sum of local contributions, which are taken to be equal to the correlation energy per unit volume of a homogeneous electron gas.

Considering the Hamiltonian for a spherically symmetric N -electron system

$$\hat{H} = -\frac{1}{2} \sum_{i=1}^N \nabla_i^2 + \sum_{i=1}^N v(r_i) + \sum_{i<j}^N \frac{1}{r_{ij}}, \quad (8.4.1)$$

he proposed for the correlation energy [286] in 1938

$$E_c[\rho] = \int_0^\infty 4\pi\rho(r)\epsilon_c^W[\rho]r^2dr, \quad (8.4.2)$$

where the electron density $\rho(r)$ is normalized in such a way, that

$$\int_0^\infty 4\pi r^2 \rho(r) dr = N \quad (8.4.3)$$

with $r_s = \sqrt[3]{\frac{3}{4\pi\rho}}$ being the Wigner radius, i.e. the radius of a sphere containing a single particle with homogeneous density ρ , α an energy parameter and β a length parameter the correlation energy density is

$$\epsilon_c^W[\rho] = -\frac{\alpha}{1 + r_s/\beta}. \quad (8.4.4)$$

Over the years several parameterizations of Wigner's density functional have been reported. Some of them are presented in Table 8.4.1. They span an enormously broad range of values.

Source	α	β
Wigner 1938 [286]	0.056	5.1
Pines 1955 [287]	0.056	7.8
Gombás 1967 [288]	0.0035 7	11.04
McWeeny 1976 [289]	0.104	2.032
Brual and Rothstein 1978 [290]	0.102	0.284
Süle and Nagy 1994 [291, 292]	0.124 7	0.218 82
Colle and Salvetti 1975 [293]	0.049 18	1.777 5
Wilson and Levy 1990 [294]	0.207 90	3.600 73
Helium isoelectronic sequence [295]	0.023 26	13.14
Hooke's atom isoelectronic sequence [295]	0.024 88	8.04

Tab. 8.4.1: Parameters of Wigner-like correlation energy density functionals

8.5 Computational Notes

8.5.1 Hartree-Fock energies

The Hartree-Fock energies were obtained using the code by Thijssen [296]. Using a basis set of 16 reasonably well-optimized even-tempered Gaussians, we obtained a value of $E_{HF} = -2.86167953a.u.$ for the helium atom, which agrees to seven significant figures with the Hartree-Fock limit $-2.861\,679\,996\,a.u.$ [297]. For the Hooke atom we modify the expression for the matrix elements of the one-body attractive potential by replacing the expression

$$\int_0^\infty e^{-(\alpha_i+\alpha_j)r^2} \left(-\frac{Z}{r}\right) 4\pi r^2 dr = -\frac{2\pi Z}{\alpha_i + \alpha_j}, \quad (8.5.5)$$

with

$$\int_0^\infty e^{-(\alpha_i+\alpha_j)r^2} \left(\frac{k}{2}r^2\right) 4\pi r^2 dr = -\frac{3k\pi^{3/2}}{4(\alpha_i + \alpha_j)^{5/2}}. \quad (8.5.6)$$

Testing the convergence of this procedure for $k = \frac{1}{4}$ with a basis of 10 reasonably well-optimized even-tempered Gaussians yields to $E_{Hooke} = 2.0384389a.u.$ which is in well agreement with [283].

In our case we have

$$v(r) = \begin{cases} -Z/r, & \text{for the helium sequence} \\ \frac{1}{2}kr^2, & \text{for Hooke's atom.} \end{cases} \quad (8.5.7)$$

The correlation energy is given in terms of an expression of the form

$$E_c = \int_0^\infty 4\pi r^2 \rho(r) \epsilon_c[\rho] dr, \quad (8.5.8)$$

where $\epsilon_c[\rho]$ is a correlation-energy density whose value at r may depend on the values of $\rho, d\rho/dr$ as well as $d^2\rho/dr^2$ at r . The dependence of the various functionals on the density is usually expressed via the electron-gas parameter.

8.5.2 Radially correlated energies

Using a set of m even-tempered Gaussians

$$N - ie^{-\alpha_i r^2}, \alpha_i = \alpha_0 \epsilon_i, i = 1, 2, \dots, m \quad (8.5.9)$$

where $N_i = \left(\frac{2\alpha_i}{\pi}\right)^{3/4}$, we construct a set of $m(m+1)/2$ symmetry adapted pair functions

$$\phi_{i,j}(r_1, r_2) = N_i N_j [\exp(-\alpha_i r_1^2 - \alpha_j r_2^2) + \exp(-\alpha_j r_1^2 - \alpha_i r_2^2)]. \quad (8.5.10)$$

The wave function constructed in terms of this basis set provides an approximation to the spherical limit, i. e. the lowest-energy variational wave function depending only on the radial coordinates r_1 and r_2 . The latter can also be interesting as the exact ground-state wave function of the monopole Hamiltonian [298]

$$\hat{H}_r = -\frac{1}{2} (\nabla_{r,1}^2 + \nabla_{r,2}^2) + (v(r_1) + v(r_2)) + \frac{1}{r_>}, \quad (8.5.11)$$

where

$$r_> = \begin{cases} r_1 & \text{when } r_1 > r_2 \\ r_2 & \text{when } r_2 > r_1 \end{cases} \quad (8.5.12)$$

and $\nabla_{r,i}^2 = \delta^2/\delta r_i^2 + (2/r_i)(\delta/\delta r_i) \cdot 1/r_>$ is the leading term of the Neumann expansion. For a wave function that depends only on the radial coordinates r_1 and r_2 all other terms yield vanishing expectation values. To assess the accuracy of this procedure we note that for the heliumlike ions with $Z = 2, 5$, and 10 , the energies obtained with a basis

set of $m = 25$ optimized even-tempered Gaussians, are -2.8790284 , -22.0015128 and -93.875882 , compared to the best available radial limit energies [299] of -2.879928764 , -22.00151383 and -93.87588735 . For Hooke's atom with $k = \frac{1}{4}$ the value $2.0343348a.u.$ for the radial limit energy, obtained with a basis of 16 optimized even-tempered Gaussians, is stable to the number of digits presented with respect to increasing the basis size.

8.5.3 Exact energies

Kestner and Sinanogul [300] pointed out that Hooke's atom Hamiltonian is separable in the center of mass and relative coordinates. The center of mass equation for the relative coordinates can be further separated into a (standard) angular part and a radial part of the form

$$\left[-\frac{1}{2} \frac{d^2}{dr^2} + \frac{k}{8} r^2 + \frac{1}{2r} + \frac{l(l+1)}{2r^2} \right] u(r) = \epsilon u(r). \quad (8.5.13)$$

Kais *et al.* [301] have shown that for $k = \frac{1}{4}$ the ground state of 8.5.13 can be calculated exactly. Taut [302] has extended that result to an infinite sequence of values of the force constant, whose first few members are $k = \frac{1}{4}, \frac{1}{100}, 1.33497 \cdot 10^{-3}, 3.00891 \cdot 10^{-4}, \dots$. Ground-state energies for arbitrary force constants were obtained by Huang *et al.* [284] using a highly accurate two series solution. They presented results for $k = 1, 16, 100, 10000, 160000$ and 1000000 . An earlier numerical evaluation by Laufer *et al.* [303] yielded ground-state energies that are in agreement with those of Huang *et al.* [284] and Taut [302], albeit to fewer significant figures. The union of the two sets of exact ground-state energies samples the whole range of feasible values of $k(0 < k < \infty)$ sufficiently well.

8.5.4 Total and radial correlation energies

We calculated the Hartree-Fock and radial limit energies for Hooke's IS, for values of k for which exact energies were available.

8.5.5 Linear Potential

In order to calculate the one-body potentials $\nu(r) = r^\zeta$ the one-body matrix is modified as follows:

$$\int_0^\infty 4\pi\nu(r)e^{-\alpha r^2}r^2dr = 2\pi\mu\text{sgn}(\zeta)\frac{\Gamma((\zeta+3)/2)}{\alpha^{(\zeta+3)/2}}. \quad (8.5.14)$$

For $\zeta = -1$ and $\zeta = 2$, respectively, these expressions reduce to the familiar hydrogenic and harmonic matrix elements. Note that the linear potential ($\zeta = 1$) requires $\Gamma(2) = 1$, the square root potential ($\zeta = \frac{1}{2}$) needs $\Gamma(\frac{7}{4}) = 0.919062526848883$, and the reciprocal square root potential ($\zeta = -\frac{1}{2}$) calls for $\Gamma(\frac{5}{4}) = 0.906402477055477$.

Considering two-electron systems, the most accurate wave functions to use are those, that contain explicit dependence on both even and odd powers of the interelectronic distance. Although the most accurate wave functions for two-electron systems - those that contain explicit dependence on both even and odd powers of the interelectronic distance - not all properties of interest can be calculated in closed form for such Hylleraas-type wave functions. One appropriate alternative is to use Gaussian geminal build wave functions [304, 305], which depend only on even powers of the interelectronic distance. Wave functions of this type, with 50 terms or less, in the case that all nonlinear parameters are optimized, can lead to energies with errors of a few microhartrees and highly accurate values of most other properties (including all those of interest in this work, e. g.: recent work on the helium atom by Thakkar [306]. The optimization of a large number of nonlinear parameters is done computationally feasible by using a term-by-term procedure in which only rank-one matrix transformations are needed to update the Hamiltonian matrix [306].

8.6 Reparametrization of Wigner's Functional

Recently Katriel *et al.* [281] studied the isoelectronic sequences of the helium atom and of Hooke's atom. They suggested that none of the density functionals examined provides a satisfactory estimate of the corresponding correlation energies. We took the challenge

to choose parameters for the Wigner functional such that the correlation energies for the helium IS sequence are estimated adequately. These parameters were obtained by minimizing

$$f(\alpha, \beta) \equiv \sum_{Z=2}^{10} (E_c(Z) - E_c^W[\rho_Z; \alpha, \beta])^2 \quad (8.6.15)$$

with respect to α and β . We obtained the exact correlation energy $E_c(Z)$ by subtracting the Hartree-Fock energy from a highly accurate variational estimate of the ground state eigenvalue. $E_c^W[\rho_Z; \alpha, \beta]$ is the estimate of the correlation energy obtained for the Hartree-Fock electron density $\rho_Z(r)$, using a Wigner-like correlation energy density functional specified by the two parameters α and β . Z is the nuclear charge of the nuclei of the two-electron ionic systems. Since $E_c^w[\rho_Z; \alpha, \beta] = \alpha f_Z(\beta)$ where

$$f_Z(\beta) = - \int_0^\infty 4\pi \rho_Z(r) \frac{1}{1 + r_s/\beta} r^2 dr, \quad (8.6.16)$$

$f(\alpha, \beta)$ is a quadratic form in α and obtains its minimum at

$$\alpha = \frac{\sum_{Z=2}^{10} E_c(Z) f_Z(\beta)}{\sum_{Z=2}^{10} f_Z(\beta)^2}. \quad (8.6.17)$$

This reduces the parametrization problem to a minimization with respect to the single parameter β . For the optimal parameters $\alpha = 0.02326$ and $\beta = 13.13$ we obtained the correlation energies presented in Table 8.6.2 as well as the dimensionless combinations of expectation values R and S .

Z	E_c^{exact}	E_c^{W1}	$\langle r \rangle \langle 1/r \rangle$		$\langle r^2 \rangle / \langle r \rangle^2$	
			HF	Exact	HF	Exact
2	-0.042040	-0.04197	6.25473	6.27693	0.68787	0.69072
3	-0.043492	-0.04356	6.15274	6.15827	0.67966	0.68015
4	-0.044265	-0.04432	6.10846	6.11109	0.67584	0.67606
5	-0.044734	-0.04477	6.08404	6.08563	0.67376	0.67388
6	-0.045050	-0.04506	6.06855	6.06968	0.67244	0.67253
7	-0.045276	-0.04527	6.05781	6.05874	0.67154	0.67160
8	-0.045449	-0.04543	6.04988	6.05078	0.67088	0.67093
9	-0.045582	-0.04555	6.04376	6.04472	0.67038	0.67041
10	-0.045691	-0.04565	6.03886	6.03895	0.66998	0.67001

Tab. 8.6.2: Correlation energies (in a.u.) and expectation values for the helium isoelectronic sequence

$R = \langle r \rangle \langle 1/r \rangle$ and $S = \langle r^2 \rangle / \langle r \rangle^2$ evaluated for both the Hartree-Fock and the exact density. The correlated values of R and S differ marginal from their uncorrelated counterparts and are almost independent of the nuclear charge Z . This will be considered in the following sections in more detail.

The parameters for the Wigner functional are choosen in a similar way: i. e. so that the correlation energies for Hooke's atom isoelectronic sequence are estimated adequately. The force constant is chosen as $k = \left(\frac{1}{\pi^2}\right) \left(\frac{4Z}{3}\right)^4$. Making this choice, the same single Gaussian is found to be the optimized variational trial function for both the three dimensional harmonic oscillator and the hydrogenic atom with the nuclear charge Z . [307] By calculating the correlation energies for the corresponding Hooke's atoms with $Z = 2, 3, \dots, 10$, the optimized parameters $\alpha = 0.002488$ and $\beta = 8.03$ for the Wigner correlation energy density functional were obtained, yielding the results shown in Table 8.6.3. The correspondig combinations of expectation values are presented as well.

Z	E_{HF}	E_{exact}	E_c^{exact}	$E_c^{W^2}$	$\langle r \rangle \langle r^{-1} \rangle$	$\langle r^2 \rangle / \langle r \rangle^2$
2	7.964047	7.920119	-0.043928	-0.04395	5.06762	0.58662
3	17.052132	17.006378	-0.045754	-0.04574	5.07663	0.58747
4	29.535713	29.489009	-0.046704	-0.04669	5.08094	0.58788
5	45.414678	45.367392	-0.047286	-0.04727	5.08346	0.58812
6	64.688987	64.641309	-0.047678	-0.04767	5.08511	0.58828
7	87.358625	87.310664	-0.047961	-0.04796	5.08627	0.58839
8	113.423583	113.375409	-0.048174	-0.04818	5.08713	0.58847
9	142.883856	142.835515	-0.048341	-0.04835	5.08780	0.58854
10	175.739443	175.690966	-0.048477	-0.04849	5.08833	0.58859

Tab. 8.6.3: Correlation energies (in a.u.) and expectation values for Hooke's isoelectronic sequence

Analyzing the numbers leads to the similar conclusions as for the helium isoelectronic sequence. The combined expectation values R and S are seen to be nearly independent of the nuclear charge Z for the Hooke isoelectronic sequence.

It is merely noted that for both the helium and Hooke's atom isoelectronic sequences

the agreement between the accurate correlation energies and the estimates based on the optimized Wigner density functional are remarkably good.

8.7 Correlation Energies for intermediate systems

As the α and particularly β parameters are quite different for the helium and Hooke's atom isoelectronic sequences, it is now examined how the parameters evolve as the one-body potential is varied smoothly from harmonic to Coulombic. Considering a one-body potential that linearly interpolates between the potentials for helium and Hooke's atom,

$$\nu(r) = \left(-\frac{Z}{r}\right)\eta + \left(\frac{k(Z)}{2}r^2\right)(1-\eta), \quad 0 \leq \eta \leq 1, \quad (8.7.18)$$

where η measures the relative amount of the Coulombic component. $\nu(r)$ as in the equation 8.7.18 is referred to as the Coulomb-Hooke potential. In the context of one-body problems, it can be thought of either as a spiked harmonic oscillator [308] with a Coulombic spike, or as a 'Coulombic plus power-law potential' [309] with the exponent being two. A literature search did not match any previous use of the Coulomb-Hooke potential for a two-body problem.

With regard to choosing the force constant k depending on η it is noted that the expectation value of the one-particle Hamiltonian with a Coulomb-Hooke potential using a Gaussian trial wave function

$$\left(\frac{2\gamma}{\pi}\right)^{3/4} e^{-\gamma r^2} \quad (8.7.19)$$

is

$$E = \frac{3\gamma}{2} - \eta 2Z \sqrt{\frac{2}{\pi}} \gamma^{1/2} + (1-\eta) \frac{3k}{8\gamma}. \quad (8.7.20)$$

Differentiating with respect to γ due to perform a variational optimization, yields to

$$\frac{\partial E}{\partial \gamma} = \frac{3}{2} - \frac{3k}{8\gamma^2} - \eta \left(Z \sqrt{\frac{2}{\pi}} \gamma^{-1/2} - \frac{3k}{8\gamma^2} \right). \quad (8.7.21)$$

As it can clearly be seen, the derivative above depends on all three potential parameters:

η , k and Z . The next step would be to identify a relationship between the harmonic force constant k and the nuclear charge Z in order to get an optimal Gaussian exponent γ , which is independent of the interpolation parameter η . Equating both the coefficient of η and the η -independent part to zero, leads to

$$\gamma = \left(\frac{3k}{8Z} \right)^{2/3} \left(\frac{\pi}{2} \right)^{1/3}, \quad (8.7.22)$$

$$\gamma = \frac{\sqrt{k}}{2}. \quad (8.7.23)$$

The consistency of the two equations above requires their right hand sides to be equal, which yields to

$$k = \frac{1}{\pi^2} \left(\frac{4Z}{3} \right)^4. \quad (8.7.24)$$

The connection of the nuclear charge Z and the force constant k as presented in equation 8.7.24 is identical with the relation derived by McWeeny [307] and presented in Section 8.6. This gives that the optimal Gaussian trial function corresponding to the Coulomb-Hooke potential, equation 8.7.18, is independent of η . The usage of more accurate wave functions will approximately maintain this independence of η as well.

The calculations were done to obtain the Hartree-Fock and exact ground state energies for two-particle systems as specified by equation 8.4.1, the Coulomb-Hooke one-body potential of equation 8.7.18 and McWeeny's force constant given by equation 8.7.24. The correlation energy being their difference, is presented in Table 8.7.4.

As described in section 8.6, the two parameters, which are specifying Wigner's correlation energy density functional, have been calculated by fitting the correlation energies for the nuclear charge range $Z = 2, 3, \dots, 10$ for each fixed η . Figure 8.7.1 and Table 8.7.5 presents those results.

Hence the overall dependence of the energy parameter α on η being weak, it exhibits a clear minimum at $\eta \approx 0.8$. As long as the Coulomb component of the potential remains small ($\eta \leq 0.8$), the length parameter β depends on η rather mildly. For larger ones ($\eta \geq 0.8$) β rises steeply as η increases.

Z	η							
	0.0	0.2	0.4	0.6	0.8	0.9	0.95	1.0
2	-0.043928	-0.042875	-0.041892	-0.041069	-0.040607	-0.040711	-0.041010	-0.042040
3	-0.045754	-0.044658	-0.043647	-0.042820	-0.042385	-0.042496	-0.042761	-0.043492
4	-0.046704	-0.045583	-0.044555	-0.043721	-0.043291	-0.043399	-0.043646	-0.044265
5	-0.047286	-0.046149	-0.045110	-0.044271	-0.043840	-0.043943	-0.044176	-0.044734
6	-0.047678	-0.046531	-0.045483	-0.044642	-0.044208	-0.044307	-0.044529	-0.045050
7	-0.047961	-0.046806	-0.045754	-0.044908	-0.044474	-0.044568	-0.044784	-0.045276
8	-0.048174	-0.047013	-0.045957	-0.045110	-0.044673	-0.044762	-0.044975	-0.045449
9	-0.048341	-0.047182	-0.046121	-0.045273	-0.044828	-0.044918	-0.045124	-0.045582
10	-0.048477	-0.047307	-0.046246	-0.045391	-0.044954	-0.045037	-0.045252	-0.045691
∞	-0.04970	-0.04850	-0.04741	-0.04654	-0.04608	-0.04614	-0.04632	-0.04669
-2α	-0.0498	-0.0485	-0.0475	-0.0466	-0.0461	-0.0462	-0.0464	-0.0465

Tab. 8.7.4: Correlation energies (in a.u.) for the Coulomb-Hooke potentials

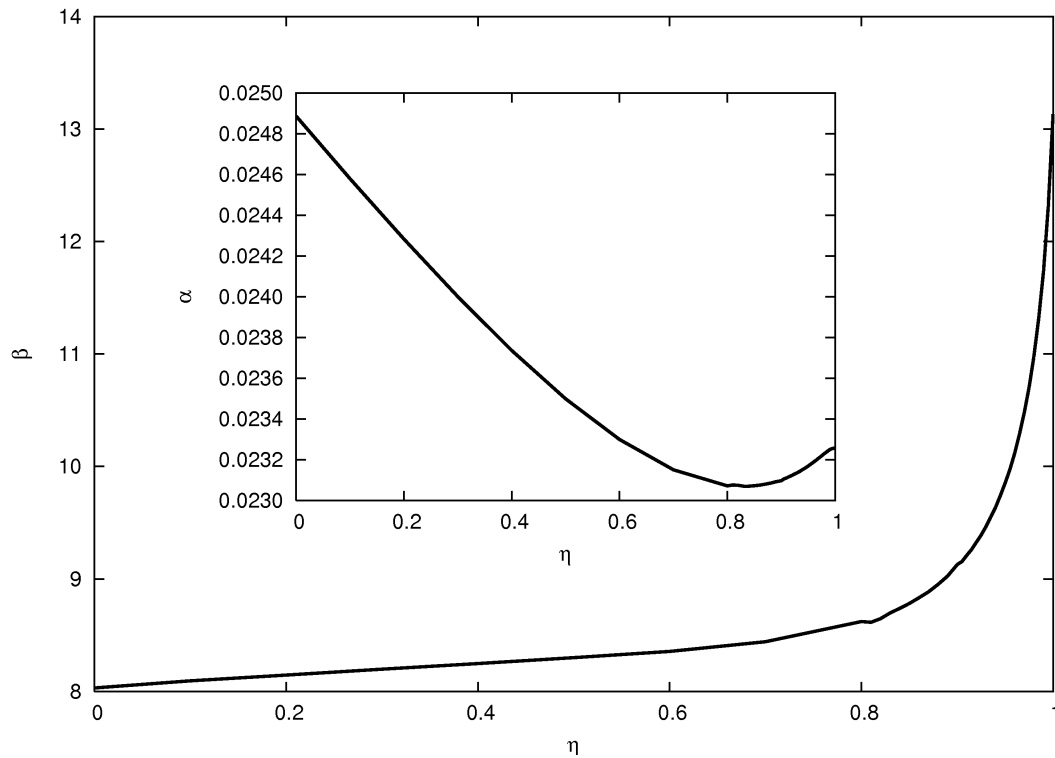


Fig. 8.7.1: Parameters of the optimized Wigner correlation energy density functional for the Coulomb-Hooke potential

Approximate E_0 for the asymptotic energies by least squares fits of the correlation energies for fixed η to expressions of the form $E_C \approx E_0 + E_1/Z + E_2/Z^2$ were first presented by White and Byers Brown [282]. Their results were confirmed by Gill and O'Neill [310] to be -0.049703 and -0.046663 , respectively, for Hooke's atom ($\eta = 0$) and the helium ($\eta = 1$) isoelectronic sequences. In the latter case, a better agreement (-0.046667) could

η	α	β	$\langle r \rangle \langle 1/r \rangle$		$\langle r^2 \rangle / \langle r \rangle^2$	
			$Z = 2$	$Z = 10$	$Z = 2$	$Z = 10$
1.00	0.02326	13.13	6.2547	6.0389	0.6879	0.6700
0.99	0.02325	11.74	6.1734	6.0057	0.6779	0.6658
0.98	0.02322	10.98	6.1134	5.9768	0.6710	0.6623
0.95	0.02318	9.85	5.9892	5.9052	0.6580	0.6544
0.90	0.02309	9.13	5.8556	5.8123	0.6455	0.6450
0.85	0.02308	8.78	5.7589	5.7368	0.6371	0.6380
0.80	0.02307	8.62	5.6806	5.6715	0.6307	0.6323
0.70	0.02315	8.44	5.5549	5.5603	0.6209	0.6231
0.60	0.02329	8.36	5.4537	5.4664	0.6133	0.6157
0.50	0.02351	8.30	5.3682	5.3846	0.6072	0.6095
0.40	0.02373	8.25	5.2941	5.3122	0.6020	0.6042
0.30	0.02399	8.20	5.2287	5.2475	0.5975	0.5996
0.20	0.02427	8.15	5.1705	5.1893	0.5935	0.5955
0.10	0.02460	8.09	5.1181	5.1365	0.5900	0.5919
0.00	0.02488	8.03	5.0707	5.0885	0.5869	0.5886

Tab. 8.7.5: Optimized Wigner functionals for the Coulomb-Hooke potentials

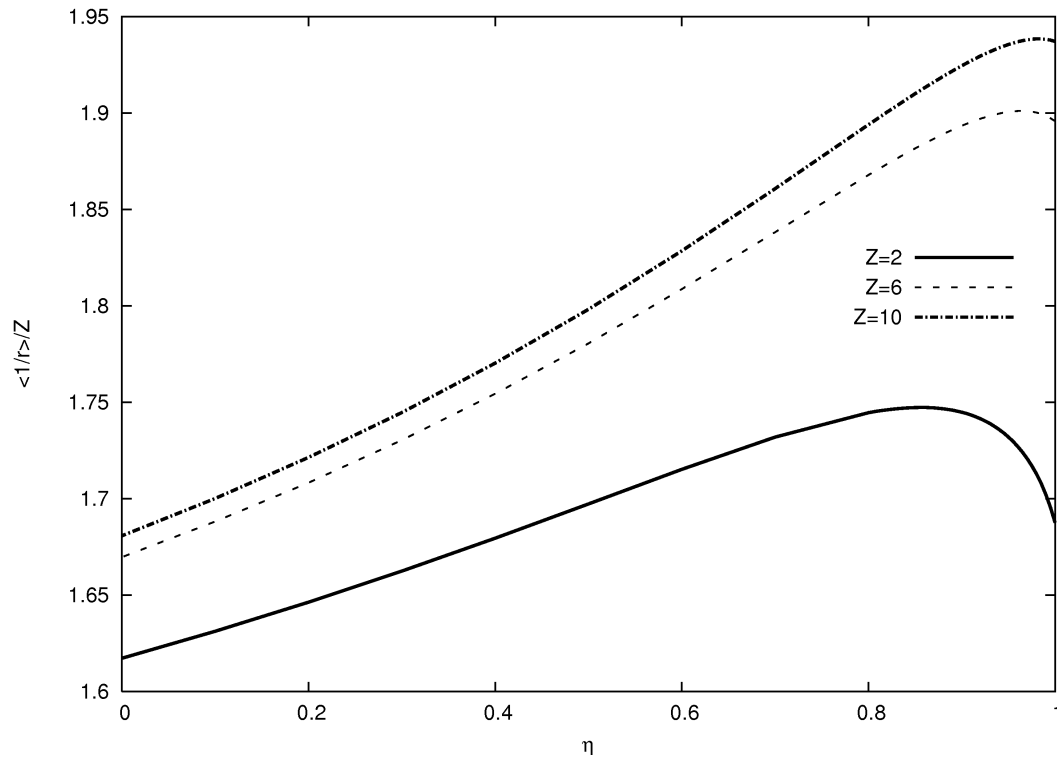
be achieved by dropping the $Z = 2$ correlation energy from the set of data fitted.

A comparison of the asymptotic correlation energies E_0 with the Wigner functional values of -2α is presented in the last two rows of table 8.7.4 and agreed to within less than 0.5%.

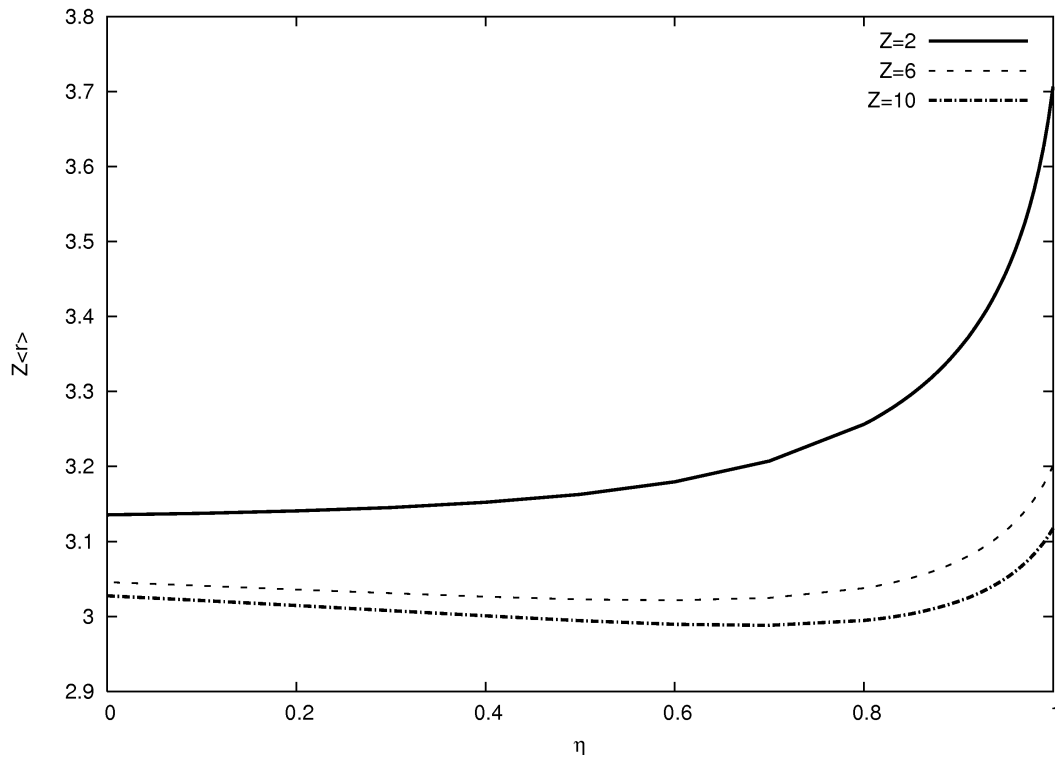
8.8 A Procedure to determine Wigner Parameters

After establishing the helium-Hooke's atom linear interpolation as described in Section 8.7 and deriving the parametrization of Wigner's density functional, a next step would be to transfer them to other types of external one-body potentials. Therefore a characterization of the potentials has to be done in such a way, that they can be defined universally. A good attempt to this characterization is the evaluation of the expectation values $\langle 1/r \rangle$, $\langle r \rangle$ and $\langle r^2 \rangle$ for both the exact and the Hartree-Fock ground states. Figures 8.8.2, 8.8.3, 8.8.4 show these expectation values, multiplied by powers of Z that account for the lowest order Z dependence.

The interelectronic repulsion becomes relatively insignificant in the high Z limit and

Fig. 8.8.2: $\langle 1/r \rangle / Z$ for the Coulomb-Hooke potential

the Z -scaled expectation values, $\langle r \rangle$, $\langle r^2 \rangle$ and $\langle 1/r \rangle$, approach appropriate (hydrogenic) constants. The nonmonotonicity of some of these expectation values as functions of η , is as well noted, as the strong residual dependence on Z . Most of this residual Z dependence can be taken care of by scaling with respect to screened Z values. Bartell and Gavin [311] showed a scaling by $Z - \sigma_S$ with $\sigma_S = 0.3$ to be accurate for correlated electron densities of the helium isoelectronic sequence, whereas Kellner, [312] determined a screening parameter of $\sigma_1 = 5/16$ for the helium sequence. Katriel *et al.* [281] found more recently $\sigma_0 = \sqrt{2}/16$ for Hooke's atom. The scaling performance with a screened Z was tested by evaluating $\langle 1/r \rangle / (Z - \sigma_\eta)$ with the previous mentioned scaling factors. This leads to the obtained the values 1.69197 and 1.69571 for $Z = 2$ and 10 for Hooke's atom, which are quite close to each other. For the helium sequence ($\eta = 1.0$) the corresponding values, 2.00008 and 1.99956, are even closer to each other. It clearly shows the sufficiency of the scaling with a screened Z for helium and hookium. This procedure has not been undertaken for the intermediate Coulomb-Hooke system, $0 < \eta < 1$.

Fig. 8.8.3: $\langle r \rangle Z$ for the Coulomb-Hooke potential

Figures 8.8.5, 8.8.6 are showing the Hartree-Fock values of the dimensionless combinations of the expectation values $R = \langle r \rangle \langle 1/r \rangle$ and $S = \langle r^2 \rangle / \langle r \rangle^2$. A rather weakly dependence on the nuclear charge Z is found, as well as a monotonic behavior on η throughout the relevant range $0 \leq \eta \leq 1$. This can be verified for $Z = 2$ and $Z = 10$ in Table 8.7.5. It gives the opportunity to work with characteristics that do not need Z scaling, which is clearly better to work with, at least in the high Z limit.

This would give a good starting point for different external potentials. In order to estimate correlation energies it would make sense to evaluate the combined and dimensionless expectation values R or S from the Hartree-Fock density, to choose the corresponding η in Table 8.7.5 to match that value for the Coulomb-Hooke potential and leads to the α and β parameters in Wigner's functional.

Under coordinate scaling the behavior of the density functional is not affected by the introduction of this dependence of the parameters in the scale-independent combinations of expectation values. This is seen to be an important criterion which should be satisfied by approximate density functionals. For sure, R and S are not the only quantities char-

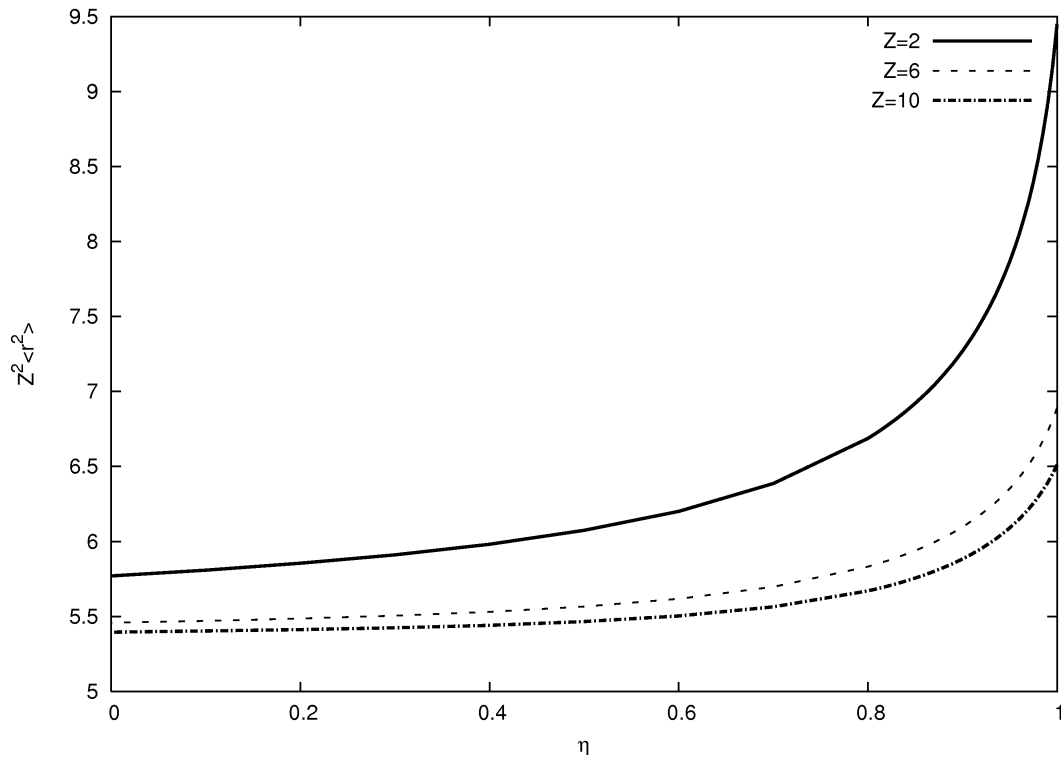
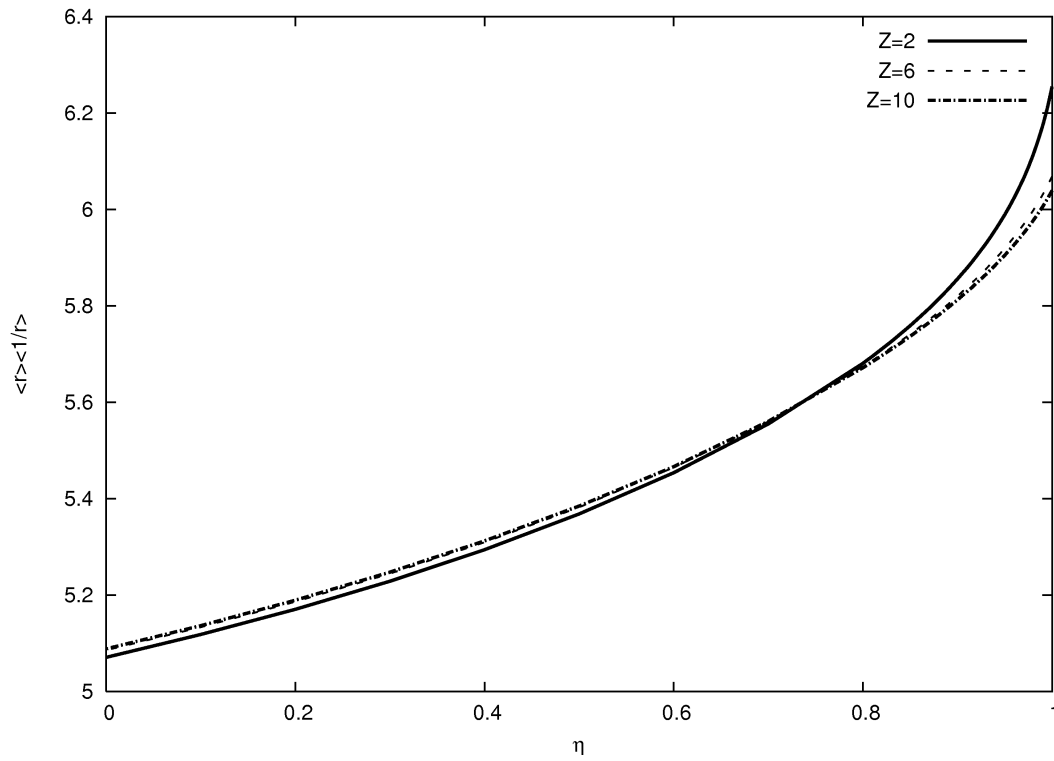


Fig. 8.8.4: $\langle r^2 \rangle Z^2$ for the Coulomb-Hooke potential

acterizing one-electron potentials. Another possibility is the examination the invariants due to the virial theorem. R and S , depending on ρ only, seemed to be the appropriate choice for the purposes of this work.

Table 8.7.5 and Figures 8.8.5, 8.8.6 allow to determine the parameters for the Wigner correlation energy functional. They may provide an advantage from a more application related point of view. This scheme is tested on two-electron systems with power-law one-body potentials, spanning the range from being Coulombic to harmonic, as described in the following section 8.9.

Fig. 8.8.5: $\langle r \rangle \langle 1/r \rangle$ for the Coulomb-Hooke potential

8.9 Tests on homogeneous power potentials

The homogeneous power potential

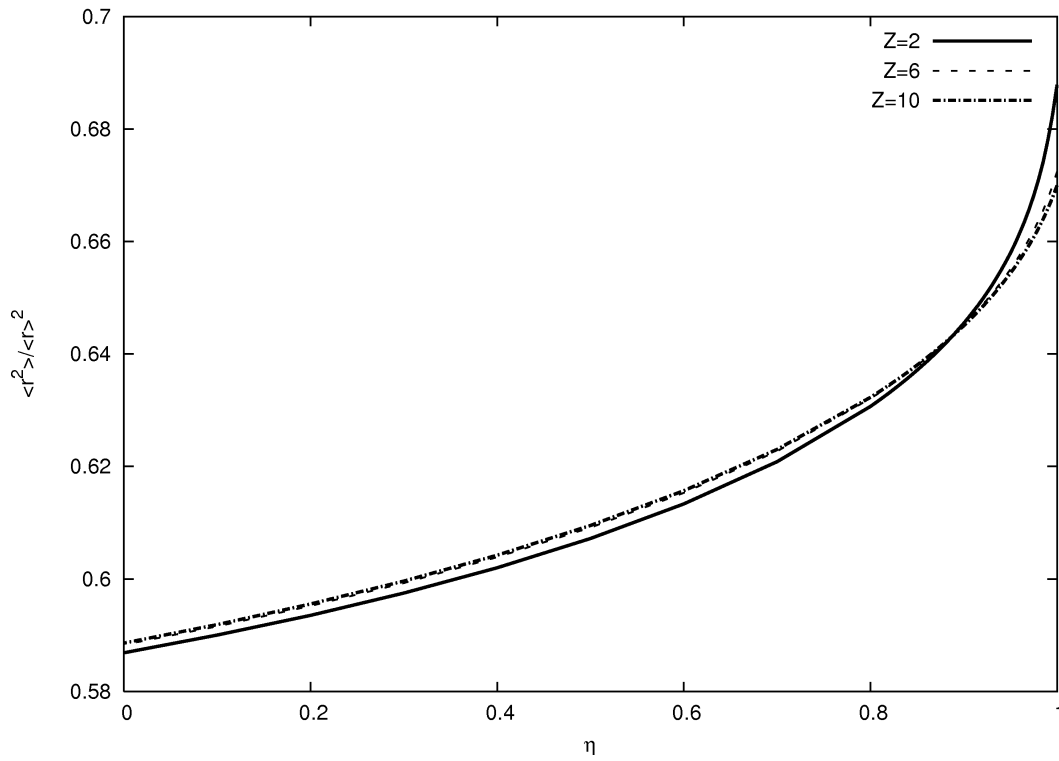
$$\nu(r) = \mu \operatorname{sgn}(\zeta) r^\zeta, \quad (8.9.25)$$

where

$$\operatorname{sgn}(\zeta) = \begin{cases} -1 & \text{if } \zeta < 0 \\ 1 & \text{if } \zeta > 0, \end{cases} \quad (8.9.26)$$

provides a nonlinear interpolation between the Coulomb ($\zeta = -1$) and harmonic ($\zeta = 2$) potentials. For $\zeta > 0$ these potentials are confining; i. e., they possess only a discrete spectrum, whereas for $\zeta < 0$ they possess a discrete spectrum of negative energies and a continuum of positive energies. However, the relevant ground state quantities on this context are continuous through $\zeta = 0$. [313]

To test the method proposed in Section 8.8, the usage of two-electron systems with one-

Fig. 8.8.6: $\langle r^2 \rangle / \langle r \rangle^2$ for the Coulomb-Hooke potential

body power potentials will be a good way. Tables 8.9.6, 8.9.7, 8.9.8 presents exact, Hartree-Fock and correlation energies for $\zeta = 1, 1/2, -1/2$, each for a small selection of μ values.

μ	E_{HF}	E_{exact}	E_C^{exact}	E_C^W
1	4.408399	4.369322	-0.039077	-0.0393
2	6.778100	6.737337	-0.040763	-0.0409
5	12.067514	12.024936	-0.042578	-0.0427
10	18.766928	18.723272	-0.043656	-0.0437
20	29.295407	29.250870	-0.044537	-0.0446
50	53.030371	52.984854	-0.045517	-0.0455

Tab. 8.9.6: Correlation energies for the linear potential. For the calculation of E_C^W in the fifth column we used the parameters $\alpha = 0.0241$; $\beta = 8.18$.

Concerning the linear potential $\nu(r) = \mu r$, giving $R = \langle r \rangle \langle 1/r \rangle \approx 5.19$ and $S = \langle r^2 \rangle / \langle r \rangle^2 \approx 0.598$, being almost independent on μ . Using Figures 8.8.5, 8.8.6, shows the value of R corresponds to $\eta \approx 0.2$ whereas the S value corresponds to

μ	E_{HF}	E_{exact}	E_C^{exact}	E_C^W
1	3.678135	3.643034	-0.03510	-0.0355
2	6.211108	6.173427	-0.03768	-0.0379
5	12.527748	12.487380	-0.04037	-0.0405
10	21.420304	21.378367	-0.04194	-0.0420
20	36.768647	36.725490	-0.04316	-0.0431
50	75.461544	75.417170	-0.04437	-0.0443

Tab. 8.9.7: Correlation energies for the square root potential. For the calculation of E_C^W in the fifth column we used the parameters $\alpha = 0.0236$; $\beta = 8.27$.

μ	E_{HF}	E_{exact}	E_C^{exact}	E_C^W	E_C^W
1	-0.779682	-0.809695	-0.03001	-0.0313	-0.0291
2	-2.227916	-2.263105	-0.03519	-0.0368	-0.0348
5	-8.359331	-8.399157	-0.03983	-0.0410	-0.0395
10	-22.027467	-22.069458	-0.04199	-0.0430	-0.0416
20	-57.097970	-57.141359	-0.04339	-0.0442	-0.0430
50	-198.055331	-198.099824	-0.04493	-0.0452	-0.0441

Tab. 8.9.8: Correlation energies for the inverse square root potential. For the calculation of E_C^W in the fifth column we used the parameters $\alpha = 0.0232$; $\beta = 10.4$. For the calculation of E_C^W in the sixth column we used the parameters $\alpha = 0.023$; $\beta = 8.8$.

$\eta \approx 0.3$. Using Figure 8.7.1 indicates that the α and β parameters are rather similar for both these values of η and have been chosen to typical values for α and β , i. e. $\alpha = 0.0241$ and $\beta = 8.18$. Table 8.9.6 contains a comparison between the exact correlation energies and those estimated by means of Wigner's functional with the parameters just proposed, giving deviations, which amount to less than 0.25%. Varying α and β within realistic limits changed at most the last significant figure in the table by 1 or 2.

For the square root potential, $\nu(r) = \mu\sqrt{r}$, it is found that $R \approx 5.30$ almost independent of μ . Examining Figure 8.8.5, suggests $\eta \approx 0.4$. Similarly, $S \approx 0.608$ suggests $\eta \approx 0.5$. Again, Figure 8.7.1 indicates that the α and β parameters are rather similar for both these values of η and have been chosen to $\alpha = 0.0236$ and $\beta = 8.27$ for Wigner's functional. Table 8.9.7 presents a comparison of the exact and estimated correlation energies. The deviations decrease from about 2% for the lowest value of $\mu = 1$ to less than 1% for the highest $\mu = 50$. Also here, realistic variations in the values for α and β led to only minor changes in our results.

For the inverse square root potential, $\nu(r) = -\mu/\sqrt{r}$, it is found that R and S depend on μ . Therefore a choice of the parameters predicted for the two extreme values of μ has been done.

- $\mu = 1$. Here, $R = 6.02$ suggesting that $\eta \approx 0.95$, and $S = 0.668$ suggesting $\eta \approx 0.98$. These values of η correspond to the parameters $\alpha = 0.0232$ and $\beta = 10.4$ in Wigner's functional.
- $\mu = 50$. Here, $R = 5.65$ suggesting that $\eta \approx 0.8$, and $S = 0.639$ suggesting that $\eta \approx 0.87$. These values of η correspond to the parameters $\alpha = 0.0231$ and $\beta = 8.8$, but at this range of η the steep dependence of α and β on η makes the estimate less robust.

The two sets of parameters may be hoped to yield lower and upper bounds to the 'true' values of the correlation energies. The second case is expected to be more relevant because most of the range is closer to it. Table 8.9.8 presents the results. The exact correlation energies are indeed lower and higher than the Wigner predictions in Cases I and II, with deviations being of the order of 2%.

8.10 Conclusions

The great promise embodied in the Hohenberg-Kohn theorem, the existence of the ultimate correlation-energy density functional, already has an enormous impact in the computational practices widely employed in chemistry, solid state physics, and, more recently, biology [314]. In this chapter, the formulation of a universal correlation energy density functional has been undertaken, but not been achieved. Nevertheless it provides one of several possible steps towards it.

Instead of pursuing the gradient expansion paradigm, as it is done so often, this work retains the simple framework of Wigner's local density functional, as proposed in 1938. It allows the parameters that specify it, to depend on the system investigated. The systems

under investigation have only been explored via a scale-invariant combination of expectation values of local one-body operators, which will give functionals to become maximally nonlocal. Despite this, more general dependencies can be allowed. In particular, characterization in terms of expectation values involving gradients or higher derivatives of the Hartree-Fock density should be of interest. Moreover, replacing Wigner's functional as the starting point of the reparametrization can be replaced by gradient-corrected functionals. This allows the reparametrization of a larger number of coefficients and might result in better results. Also the method described in this chapter looks adequate for confining and relatively flat-bottom potentials, whereas it gets less robust when approaching Coulomb-like system. But especially these systems are certainly the most highly relevant for the majority of applications.

9 Summary and Conclusions

A more detailed conclusion section is presented for each of the three parts. Nevertheless, we give a small summary to the different parts.

We showed that modelling of the adhesion of polymers on an oxidized metal surface within an *ab-initio* framework is a challenge, especially for the desired informations within this scientific problem. We showed that the programs we used did not provide the favored informations. Moreover, we could show that at the current development state, the properties are not computable. Neither the periodic boundary conditions approach, nor the cluster method yielded satisfactory results. Nevertheless, for sure further improvement of the codes will be done, so that it might be hoped that the investigation can be done one day.

In the second part we presented the results of our geometry optimization of stoichiometric $(CdS)_n$ clusters with $n = 2 - 25$, applying an unbiased genetic algorithm within density-functional tight-binding framework. The new obtained structures, which are different from cutouts of the infinite bulk phase structures, are shown. Structural and electronic properties are presented, i. e. stability function, similarity function, radial distribution function, Mulliken gross population, etc.

We successfully implemented the program code in a MPI parallelization.

For further support of the investigations, analyzing clusters bigger than $n = 25$ would be useful.

In the third and last part the formulation of an universal correlation energy density functional has been undertaken, but not been achieved. Despite this fact, it provides one of several possible steps towards it. This work retains the simple framework of a

1938 local density functional. It has been successfully applied to different test systems by reparametrizing the original density functional. The results are presented in detail.

Table of figures

6.1.1	Symbolic Adhesion of polymers on a surface	17
6.2.2	Structure of the rocksalt-type: Mg atoms in green color, oxygen in grey color. The octahedral coordination can easily be seen by the implemented octahedrons.	19
6.2.3	Charge distribution of the 6x6 atoms monolayer MgO cluster at the B3LYP,3-21G level	21
6.2.4	Illustration of the eight layer 8x6 atoms MgO cluster	22
6.2.5	Mulliken charges for a 4x4x4 MgO cluster plotted against the radial distance to the cluster center. Lower part represents the negatively charged oxygen atoms, whereas the upper part is the positive charge of the magnesium atoms.	24
6.2.6	HOMO, LUMO and HOMO-LUMO gap for a 4x4x4 MgO-Cluster in different external point charge field	25
6.2.7	Unit Cell of MgO	26
6.2.8	Illustration of the Mulliken Charges obtained by a HF,3-21g calculation using the PBC as implemented in the <i>Gaussian</i> G03 B03 [28] program suite. The color range illustrates the charge range from -3.947 (red color) located on a Mg atom up to +6.961 (green color) located on a oxygen atom.	27
6.2.9	Illustration of the Mulliken Charges obtained by a B3LYP,STO-3G [97, 98] calculation using the PBC as implemented in the <i>Gaussian G03</i> B03 [29] program suite. The color range illustrates the charge range from -0.617 (red color) located on a O atom up to +0.617 (green color) located on a Mg atom.	28
6.3.10	Structure of the monomeric DGEBA	30

6.3.11	Structure of the energy minimized DGEBA	31
6.3.12	HOMO of the energy minimized DGEBA	32
6.3.13	LUMO of the energy minimized DGEBA	33
6.3.14	Charge distribution of the energy minimized DGEBA. The more red color indicates the more negatively distributed charge.	34
6.3.15	Structure of the DETA	35
6.3.16	Structure of the energy minimized DETA	35
6.3.17	HOMO of the energy minimized DETA	36
6.3.18	LUMO of the energy minimized DETA monomer	36
6.3.19	Charge distribution of the energy minimized DETA	37
7.2.1	3D-model of the wurtzite CdS structure	43
7.2.2	Wurtzite unit cell	44
7.2.3	Wurtzite structure	45
7.2.4	Sphalerite unit cell	46
7.3.5	Simplified flowchart for creating the unbiased initial cluster structures from scratch. Each single step is described in Section 7.3.3.	50
7.3.6	Simplified flowchart for creating the unbiased initial cluster structures from a previously relaxed structure. Each single step is described in Section 7.3.3.	51
7.3.7	Illustration of a spherical coordinate system.	53
7.3.8	Amdahl's Law, illustrating the maximum speedup on parallelizing a computer program for different amount of sequential program code . . .	57
7.3.9	Simplified flowchart of the GA	60
7.3.10	Routine ONEPAR	63
7.3.11	Routine TWOPAR	64
7.3.12	Routine TWOPAR Pasting Problem	66
7.4.13	Structure of (CdS_4) cluster	69
7.4.14	Radial Distribution Function for the CdS cluster.	70
7.4.15	Similarity Function interatomic distances	72
7.4.16	Similarity Function radial distances	73

7.4.17	Relative total energy per <i>CdS</i> unit.	75
7.4.18	Total energy per <i>CdS</i> unit (cutout).	76
7.4.19	Stability Function for the <i>CdS</i> cluster.	77
7.4.20	Shape Analysis for the <i>CdS</i> clusters.	79
7.5.21	HOMO energy and gap for the <i>CdS</i> clusters.	85
7.5.22	LUMO energy and gap for the <i>CdS</i> clusters.	86
7.5.23	Relative total energy and gap for the <i>CdS</i> clusters.	87
8.7.1	Parameters of the optimized Wigner correlation energy density func- tional for the Coulomb-Hooke potential	100
8.8.2	$\langle 1/r \rangle / Z$ for the Coulomb-Hooke potential	102
8.8.3	$\langle r \rangle Z$ for the Coulomb-Hooke potential	103
8.8.4	$\langle r^2 \rangle Z^2$ for the Coulomb-Hooke potential	104
8.8.5	$\langle r \rangle \langle 1/r \rangle$ for the Coulomb-Hooke potential	105
8.8.6	$\langle r^2 \rangle \langle r \rangle^2$ for the Coulomb-Hooke potential	106

List of Tables

3.0.1 Table of used abbreviations	VI
6.2.1 Monolayer MgO clusters at B3LYP,3-21G of the <i>Gaussian</i> program suite [28]	21
6.2.2 Multilayer MgO clusters at B3LYP,3-21G of the <i>Gaussian</i> program suite [28]	22
6.2.3 Energies and Mulliken Charges at different TV for MgO at HF,3-21G level by <i>Gaussian G03</i> B.03	25
6.2.4 Molecular Orbitals for MgO Single-Point calculation at B3LYP,STO-3G level by <i>Gaussian G03</i> E.03	28
6.2.5 Molecular Orbitals for the relaxed MgO supercell at B3LYP,STO-3G level by <i>Gaussian G03</i> E.03	29
6.2.6 Molecular Orbitals for the relaxed MgO supercell at B3LYP,STO-3G level by <i>Gaussian G03</i> E.03	29
7.4.1 Obtained relative total energies for $(CdS)_n$ clusters, $n = 2-25$. All energies are given in eV.	68
8.4.1 Parameters of Wigner-like correlation energy density functionals	92
8.6.2 Correlation energies (in a.u.) and expectation values for the helium isoelectronic sequence	96
8.6.3 Correlation energies (in a.u.) and expectation values for Hooke's isoelectronic sequence	97
8.7.4 Correlation energies (in a.u.) for the Coulomb-Hooke potentials	100
8.7.5 Optimized Wigner functionals for the Coulomb-Hooke potentials	101
8.9.6 Correlation energies for the linear potential.	106
8.9.7 Correlation energies for the square root potential	107
8.9.8 Correlation energies for the inverse square root potential	107

A.1.1	Chosen physical, chemical and technical data of DGEBA [43]	XVI
A.2.2	Chosen physical, chemical and technical data of DETA [43]	XVII
C.1.1	Hartree-Fock and exact energies and Wigner Correlation energies for $Z = 2$ for Coluomb-Hooke-Potential	XXV
C.2.2	Hartree-Fock and exact energies and Wigner Correlation energies for $Z = 3$ for Coluomb-Hooke-Potential	XXVII
C.3.3	Hartree-Fock and exact energies and Wigner Correlation energies for $Z = 4$ for Coluomb-Hooke-Potential	XXIX
C.4.4	Hartree-Fock and exact energies and Wigner Correlation energies for $Z = 5$ for Coluomb-Hooke-Potential	XXXI
C.5.5	Hartree-Fock and exact energies and Wigner Correlation energies for $Z = 6$ for Coluomb-Hooke-Potential	XXXIII
C.6.6	Hartree-Fock and exact energies and Wigner Correlation energies for $Z = 7$ for Coluomb-Hooke-Potential	XXXV
C.7.7	Hartree-Fock and exact energies and Wigner Correlation energies for $Z = 8$ for Coluomb-Hooke-Potential	XXXVII
C.8.8	Hartree-Fock and exact energies and Wigner Correlation energies for $Z = 9$ for Coluomb-Hooke-Potential	XXXIX
C.9.9	Hartree-Fock and exact energies and Wigner Correlation energies for $Z =$ 10 for Coluomb-Hooke-Potential	XLI
D.1.1	Expectation Values for the Coluomb-Hooke potential for $Z = 2$	XLIII
D.2.2	Expectation Values for the Coluomb-Hooke potential for $Z = 3$	XLV
D.3.3	Expectation Values for the Coluomb-Hooke potential for $Z = 4$	XLVII
D.4.4	Expectation Values for the Coluomb-Hooke potential for $Z = 5$	XLIX
D.5.5	Expectation Values for the Coluomb-Hooke potential for $Z = 6$	LI
D.6.6	Expectation Values for the Coluomb-Hooke potential for $Z = 7$	LIII
D.7.7	Expectation Values for the Coluomb-Hooke potential for $Z = 8$	LV
D.8.8	Expectation Values for the Coluomb-Hooke potential for $Z = 9$	LVII
D.9.9	Expectation Values for the Coluomb-Hooke potential for $Z = 10$	LIX

A Technical Data

A.1 Technical Data of the epoxide DGEBA

Producer	Dow
product title	D.E.R. [®] 332
product typ	difunctional epoxide, typ: Bisphenol A
molar mass	$340 \frac{g}{mol}$
Density ρ (Pyknometry)	$1.5688 \pm 0.0001 \frac{g}{cm^3}$ ($T = 23 \pm 1^\circ C$)
Viscosity η (at $T = 25^\circ C$)	$4000 - 6000 mPa \cdot s$
Water content	$\leq 700 ppm$
Chlorine content (hydrolysable)	$\leq 300 ppm$
Epichlorohydrin content	$\leq 5 ppm$
Oxiranegroup content	$57^0 - 5850 \frac{mmol}{kg}$
Epoxide equivalent weight	$171 - 175 g$
Melting temperarute T_m	$42^\circ C$

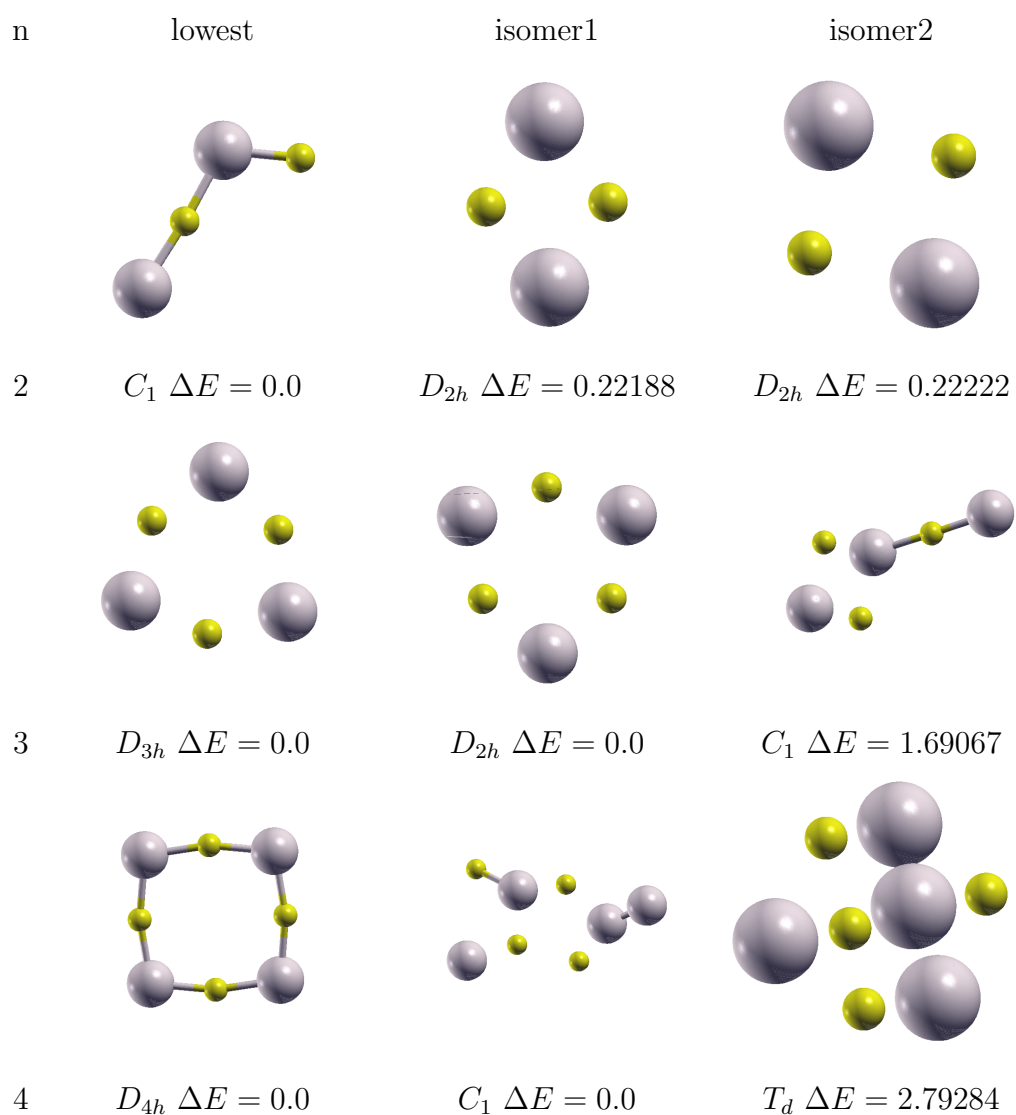
Tab. A.1.1: Chosen physical, chemical and technical data of DGEBA [43]

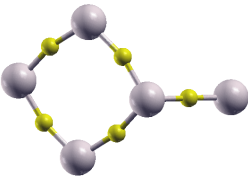
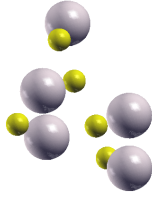
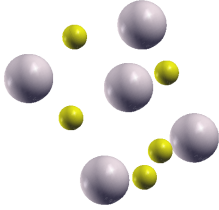
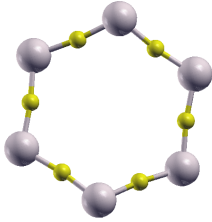
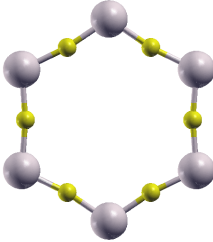
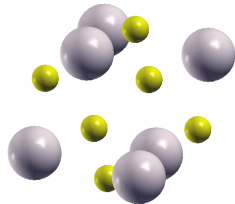
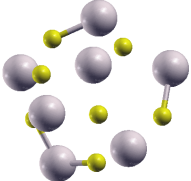
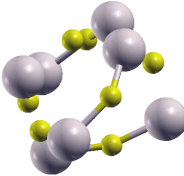
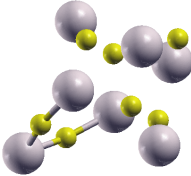
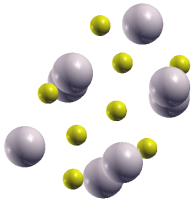
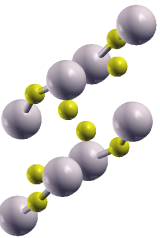
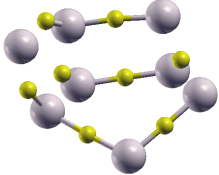
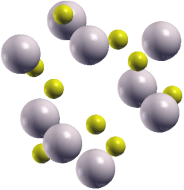
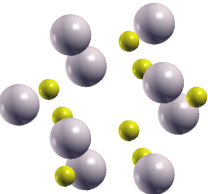
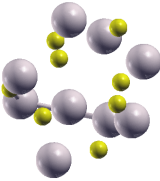
A.2 Technical Data of the DETA

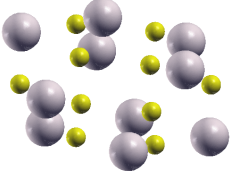
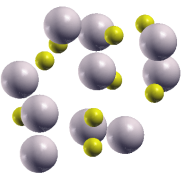
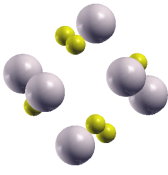
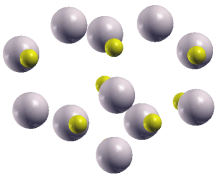
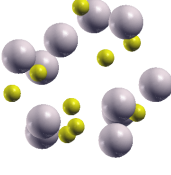
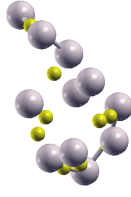
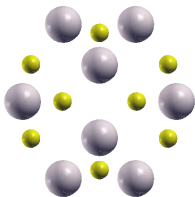
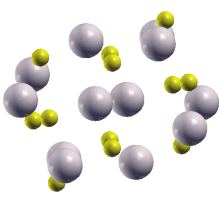
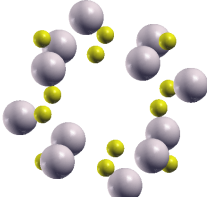
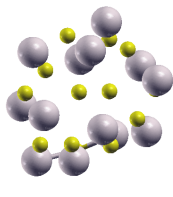
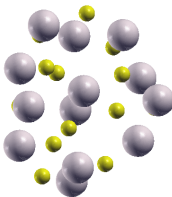
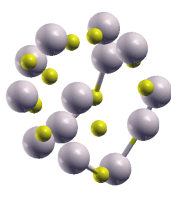
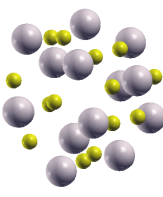
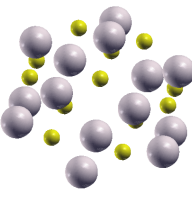
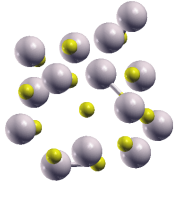
Producer	Dow
product title	D.E.H. [®] 20
product typ	aliphatic Polyamine Hardener
molar mass	$103 \frac{g}{mol}$
Refraction index n_D (Abbe-Refraktometrie, $\lambda = 598,3nm$)	1.4822 ± 0.0001 ($T = 23 \pm 1^\circ C$)
Density ρ (Pyknometry)	$0.9482 \pm 0.0005 \frac{g}{cm^3}$ ($T = 21 \pm 1^\circ C$)
Purity (GC)	purum $> 97\%$
CAS-No.	111-40-0
Viscosity η (at $T = 25^\circ C$)	$5.5 - 8.5 mPa \cdot s$
Water content	$\leq 5000 ppm$
Melting temperarute T_M	$42^\circ C$
Boiling temperature T_B	$199 - 209^\circ C$
Vapor pressure at $T = 20^\circ C$	$0.08 mmHg$

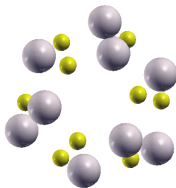
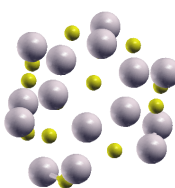
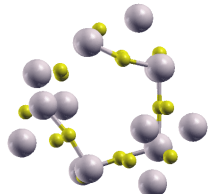
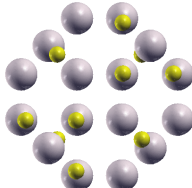
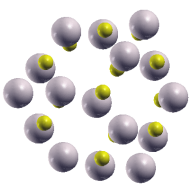
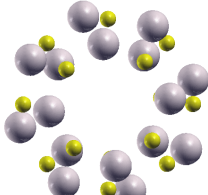
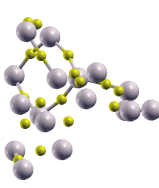
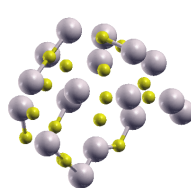
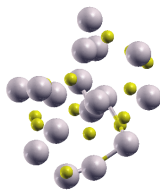
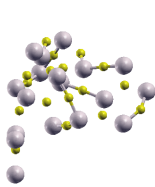
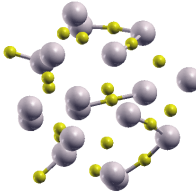
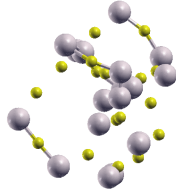
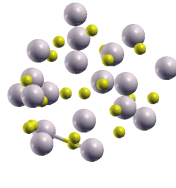
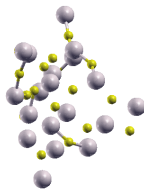
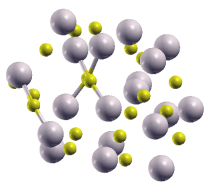
Tab. A.2.2: Chosen physical, chemical and technical data of DETA [43]

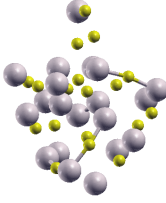
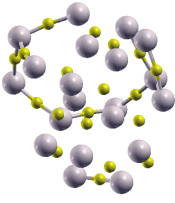
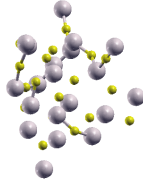
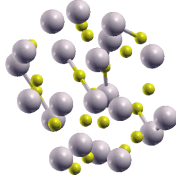
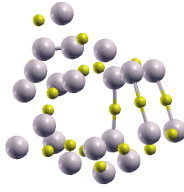
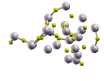
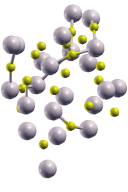
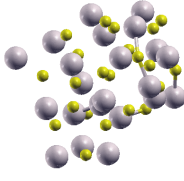
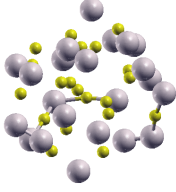
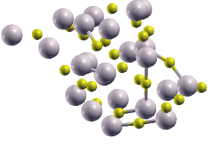
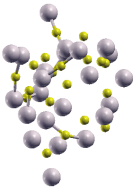
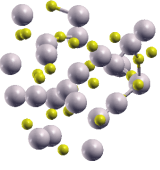
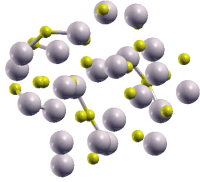
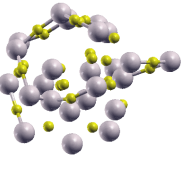
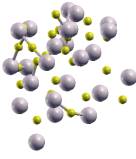
B Structures of stoichiometric $(CdS)_n$ clusters for $n = 2 - 25$

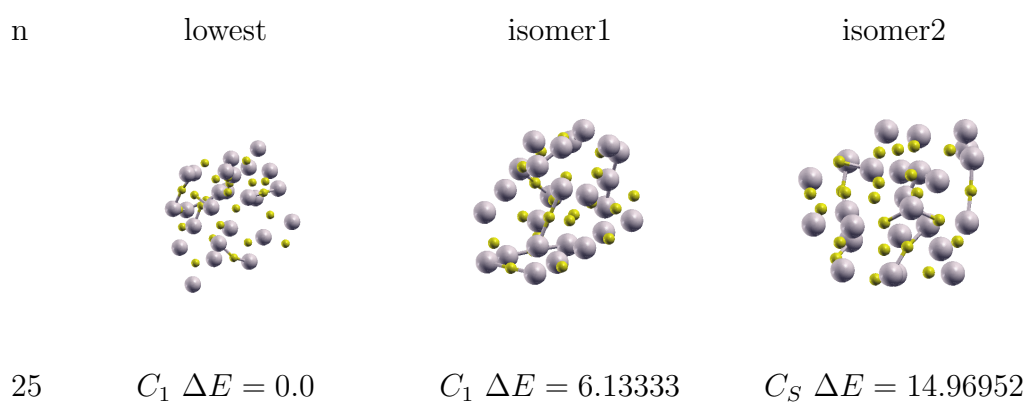


n	lowest	isomer1	isomer2
5	 $C_2 \Delta E = 0.0$	 $C_S \Delta E = 1.03209$	 $D_S \Delta E = 1.87284$
6	 $D_{6h} \Delta E = 0.0$	 $D_{6h} \Delta E = 0.00484$	 $D_{3d} \Delta E = 0.79772$
7	 $C_1 \Delta E = 0.0$	 $C_S \Delta E = 0.06490$	 $C_1 \Delta E = 0.17152$
8	 $S_4 \Delta E = 0.0$	 $C_{2h} \Delta E = 0.03781$	 $C_{2h} \Delta E = 0.61620$
9	 $C_{3h} \Delta E = 0.0$	 $D_{3h} \Delta E = 0.14987$	 $C_1 \Delta E = 0.44037$

n	lowest	isomer1	isomer2
			
10	$C_2 \Delta E = 0.0$	$C_2 \Delta E = 0.45206$	$C_{2h} \Delta E = 0.79968$
			
11	$C_S \Delta E = 0.0$	$C_1 \Delta E = 0.65878$	$C_1 \Delta E = 2.17573$
			
12	$T_h \Delta E = 0.0$	$D_{3d} \Delta E = 3.01920$	$D_{4h} \Delta E = 3.09291$
			
13	$C_1 \Delta E = 0.0$	$C_1 \Delta E = 0.30518$	$C_1 \Delta E = 0.76214$
			
14	$C_S \Delta E = 0.0$	$C_{2v} \Delta E = 0.80050$	$C_1 \Delta E = 1.95786$

n	lowest	isomer1	isomer2
15	 $C_{3h} \Delta E = 0.0$	 $C_1 \Delta E = 1.48594$	 $D_{5h} \Delta E = 3.65514$
16	 $T_d \Delta E = 0.0$	 $C_{3v} \Delta E = 0.44526$	 $S_8 \Delta E = 2.20320$
17	 $C_1 \Delta E = 0.0$	 $C_{2v} \Delta E = 1.35917$	 $C_1 \Delta E = 2.79724$
18	 $C_1 \Delta E = 0.0$	 $C_1 \Delta E = 2.01740$	 $C_1 \Delta E = 7.44751$
19	 $C_1 \Delta E = 0.0$	 $C_1 \Delta E = 0.13593$	 $C_1 \Delta E = 0.72434$

n	lowest	isomer1	isomer2
20	 $C_S \Delta E = 0.0$	 $C_S \Delta E = 0.63403$	 $C_1 \Delta E = 0.85490$
21	 $C_S \Delta E = 0.0$	 $C_S \Delta E = 5.05893$	 $C_1 \Delta E = 7.61029$
22	 $C_1 \Delta E = 0.0$	 $C_1 \Delta E = 4.96590$	 $C_1 \Delta E = 13.73736$
23	 $C_{2v} \Delta E = 0.0$	 $C_1 \Delta E = 1.66110$	 $C_1 \Delta E = 9.95546$
24	 $C_S \Delta E = 0.0$	 $C_1 \Delta E = 0.33810$	 $C_1 \Delta E = 1.09371$



C Hartree-Fock, exact energies and Wigner Correlation energies for the Coluomb-Hooke-Potential

C.1 Hartree-Fock, exact energies and Wigner Correlation energies for $Z = 2$ for the Coluomb-Hooke-Potential

Z	η	E_{HF}	E_{exact}	E_{corr}^W
2	0.000	-7.96404700	-7.92011900	-0.04392800
2	0.100	-6.94367900	-6.90028300	-0.04339600
2	0.200	-5.91478300	-5.87190800	-0.04287500
2	0.300	-4.87638300	-4.83401200	-0.04237100
2	0.400	-3.82729500	-3.78540300	-0.04189200
2	0.500	-2.76604000	-2.72458800	-0.04145200
2	0.600	-1.69068400	-1.64961500	-0.04106900
2	0.700	-0.59851000	-0.55773900	-0.04077100
2	0.800	0.51479700	0.55540400	-0.04060700
2	0.810	0.62755100	0.66815300	-0.04060200
2	0.820	0.74060500	0.78120400	-0.04059900
2	0.830	0.85397100	0.89457100	-0.04060000
2	0.840	0.96766500	1.00826800	-0.04060300
2	0.850	1.08170300	1.12231300	-0.04061000
2	0.860	1.19610500	1.23672600	-0.04062100
2	0.870	1.31089200	1.35152700	-0.04063500
2	0.880	1.42608700	1.46674300	-0.04065600
2	0.890	1.54172100	1.58240100	-0.04068000
2	0.900	1.65782500	1.69853600	-0.04071100
2	0.905	1.71606500	1.75679500	-0.04073000
2	0.910	1.77443900	1.81518900	-0.04075000

2	0.915	1.83295100	1.87372300	-0.04077200
2	0.920	1.89160900	1.93240600	-0.04079700
2	0.925	1.95042100	1.99124500	-0.04082400
2	0.930	2.00939400	2.05024800	-0.04085400
2	0.935	2.06853800	2.10942500	-0.04088700
2	0.940	2.12786300	2.16878700	-0.04092400
2	0.945	2.18738200	2.22834700	-0.04096500
2	0.950	2.24710800	2.28811800	-0.04101000
2	0.955	2.30705800	2.34811700	-0.04105900
2	0.960	2.36724800	2.40836400	-0.04111600
2	0.965	2.42770300	2.46888200	-0.04117900
2	0.970	2.48844700	2.52969800	-0.04125100
2	0.975	2.54951400	2.59084600	-0.04133200
2	0.980	2.61094400	2.65237000	-0.04142600
2	0.985	2.67278800	2.71432500	-0.04153700
2	0.990	2.73511600	2.77678500	-0.04166900
2	0.995	2.79802900	2.83986000	-0.04183100
2	1.000	2.86168000	2.90372000	-0.04204000

Tab. C.1.1: Hartree-Fock and exact energies and Wigner Correlation energies for $Z = 2$ for Coluomb-Hooke-Potential

C.2 Hartree-Fock, exact energies and Wigner Correlation energies for $Z = 3$ for the Coluomb-Hooke-Potential

Z	η	E_{HF}	E_{exact}	E_{corr}^W
3	0.000	-17.05213200	-17.00637800	-0.04575400
3	0.100	-14.75563100	-14.71043200	-0.04519900
3	0.200	-12.43993500	-12.39527700	-0.04465800
3	0.300	-10.10291600	-10.05877900	-0.04413700
3	0.400	-7.74203800	-7.69839100	-0.04364700
3	0.500	-5.35419800	-5.31099600	-0.04320200
3	0.600	-2.93546500	-2.89264500	-0.04282000
3	0.700	-0.48055200	-0.43802100	-0.04253100
3	0.800	2.01844100	2.06082600	-0.04238500
3	0.810	2.27121800	2.31359900	-0.04238100
3	0.820	2.52458500	2.56696500	-0.04238000
3	0.830	2.77856400	2.82094600	-0.04238200
3	0.840	3.03317900	3.07556500	-0.04238600
3	0.850	3.28845600	3.33085100	-0.04239500
3	0.860	3.54442500	3.58683200	-0.04240700
3	0.870	3.80111900	3.84354100	-0.04242200
3	0.880	4.05857500	4.10101700	-0.04244200
3	0.890	4.31683600	4.35930200	-0.04246600
3	0.900	4.57595100	4.61844700	-0.04249600
3	0.905	4.70584600	4.74835800	-0.04251200
3	0.910	4.83597600	4.87850800	-0.04253200
3	0.915	4.96635100	5.00890300	-0.04255200
3	0.920	5.09697900	5.13955400	-0.04257500
3	0.925	5.22787200	5.27047100	-0.04259900
3	0.930	5.35904000	5.40166600	-0.04262600
3	0.935	5.49049700	5.53315300	-0.04265600
3	0.940	5.62225700	5.66494400	-0.04268700
3	0.945	5.75433500	5.79705800	-0.04272300
3	0.950	5.88675100	5.92951200	-0.04276100
3	0.955	6.01952400	6.06232600	-0.04280200

3	0.960	6.15267700	6.19552600	-0.04284900
3	0.965	6.28623900	6.32913900	-0.04290000
3	0.970	6.42024100	6.46319700	-0.04295600
3	0.975	6.55472100	6.59774000	-0.04301900
3	0.980	6.68972600	6.73281500	-0.04308900
3	0.985	6.82531200	6.86848100	-0.04316900
3	0.990	6.96155100	7.00481200	-0.04326100
3	0.995	7.09854100	7.14190700	-0.04336600
3	1.000	7.23641500	7.27990700	-0.04349200

Tab. C.2.2: Hartree-Fock and exact energies and Wigner Correlation energies for $Z = 3$ for Coluomb-Hooke-Potential

C.3 Hartree-Fock, exact energies and Wigner Correlation energies for $Z = 4$ for the Coluomb-Hooke-Potential

Z	η	E_{HF}	E_{exact}	E_{corr}^W
4	0.000	-29.53571300	-29.48900900	-0.04670400
4	0.100	-25.45175600	-25.40562100	-0.04613500
4	0.200	-21.33355400	-21.28797100	-0.04558300
4	0.300	-17.17736100	-17.13230800	-0.04505300
4	0.400	-12.97873600	-12.93418100	-0.04455500
4	0.500	-8.73230900	-8.68820400	-0.04410500
4	0.600	-4.43137100	-4.38765000	-0.04372100
4	0.700	-0.06709800	-0.02366400	-0.04343400
4	0.800	4.37326200	4.41655300	-0.04329100
4	0.810	4.82219200	4.86548000	-0.04328800
4	0.820	5.27211400	5.31540100	-0.04328700
4	0.830	5.72306100	5.76635000	-0.04328900
4	0.840	6.17506800	6.21836200	-0.04329400
4	0.850	6.62817400	6.67147700	-0.04330300
4	0.860	7.08242400	7.12573800	-0.04331400
4	0.870	7.53786400	7.58119300	-0.04332900
4	0.880	7.99454900	8.03789700	-0.04334800
4	0.890	8.45254100	8.49591200	-0.04337100
4	0.900	8.91190800	8.95530700	-0.04339900
4	0.905	9.14213100	9.18554800	-0.04341700
4	0.910	9.37273100	9.41616500	-0.04343400
4	0.915	9.60371700	9.64717000	-0.04345300
4	0.920	9.83510300	9.87857800	-0.04347500
4	0.925	10.06690500	10.11040200	-0.04349700
4	0.930	10.29913700	10.34265900	-0.04352200
4	0.935	10.53181700	10.57536700	-0.04355000
4	0.940	10.76496500	10.80854300	-0.04357800
4	0.945	10.99860100	11.04221200	-0.04361100
4	0.950	11.23275000	11.27639600	-0.04364600
4	0.955	11.46743900	11.51112200	-0.04368300

4	0.960	11.70269900	11.74642300	-0.04372400
4	0.965	11.93856500	11.98233400	-0.04376900
4	0.970	12.17507700	12.21889700	-0.04382000
4	0.975	12.41228500	12.45615900	-0.04387400
4	0.980	12.65024500	12.69417900	-0.04393400
4	0.985	12.88902600	12.93302900	-0.04400300
4	0.990	13.12871600	13.17279400	-0.04407800
4	0.995	13.36942400	13.41358900	-0.04416500
4	1.000	13.61129900	13.65556400	-0.04426500

Tab. C.3.3: Hartree-Fock and exact energies and Wigner Correlation energies for $Z = 4$ for Coluomb-Hooke-Potential

C.4 Hartree-Fock, exact energies and Wigner Correlation energies for $Z = 5$ for the Coluomb-Hooke-Potential

Z	η	E_{HF}	E_{exact}	E_{corr}^W
5	0.000	-45.41467800	-45.36739200	-0.04728600
5	0.100	-39.03192700	-38.98521800	-0.04670900
5	0.200	-32.59549700	-32.54934800	-0.04614900
5	0.300	-26.09955200	-26.05393900	-0.04561300
5	0.400	-19.53720000	-19.49209000	-0.04511000
5	0.500	-12.90015100	-12.85549500	-0.04465600
5	0.600	-6.17814300	-6.13387200	-0.04427100
5	0.700	0.64215300	0.68613600	-0.04398300
5	0.800	7.57961200	7.62345200	-0.04384000
5	0.810	8.28083000	8.32466800	-0.04383800
5	0.820	8.98355400	9.02739100	-0.04383700
5	0.830	9.68782900	9.73166700	-0.04383800
5	0.840	10.39370500	10.43754700	-0.04384200
5	0.850	11.10123500	11.14508500	-0.04385000
5	0.860	11.81048200	11.85434300	-0.04386100
5	0.870	12.52151100	12.56538600	-0.04387500
5	0.880	13.23439700	13.27829000	-0.04389300
5	0.890	13.94922300	13.99313900	-0.04391600
5	0.900	14.66608600	14.71002900	-0.04394300
5	0.905	15.02531300	15.06927200	-0.04395900
5	0.910	15.38509200	15.42906800	-0.04397600
5	0.915	15.74543800	15.78943300	-0.04399500
5	0.920	16.10636900	16.15038400	-0.04401500
5	0.925	16.46790500	16.51194200	-0.04403700
5	0.930	16.83006600	16.87412600	-0.04406000
5	0.935	17.19287600	17.23696100	-0.04408500
5	0.940	17.55635900	17.60047300	-0.04411400
5	0.945	17.92054500	17.96468800	-0.04414300
5	0.950	18.28546400	18.32964000	-0.04417600
5	0.955	18.65115200	18.69536300	-0.04421100

5	0.960	19.01764800	19.06189700	-0.04424900
5	0.965	19.38499800	19.42928900	-0.04429100
5	0.970	19.75325400	19.79759100	-0.04433700
5	0.975	20.12247700	20.16686300	-0.04438600
5	0.980	20.49273800	20.53718000	-0.04444200
5	0.985	20.86412400	20.90862600	-0.04450200
5	0.990	21.23673900	21.28131000	-0.04457100
5	0.995	21.61071800	21.65536500	-0.04464700
5	1.000	21.98623400	22.03096800	-0.04473400

Tab. C.4.4: Hartree-Fock and exact energies and Wigner Correlation energies for $Z = 5$ for Coluomb-Hooke-Potential

C.5 Hartree-Fock, exact energies and Wigner Correlation energies for $Z = 6$ for the Coluomb-Hooke-Potential

Z	η	E_{HF}	E_{exact}	E_{corr}^W
6	0.000	-64.68898700	-64.64130900	-0.04767800
6	0.100	-55.49609900	-55.44900300	-0.04709600
6	0.200	-46.22571300	-46.17918200	-0.04653100
6	0.300	-36.86943100	-36.82344200	-0.04598900
6	0.400	-27.41736200	-27.37187900	-0.04548300
6	0.500	-17.85765000	-17.81262200	-0.04502800
6	0.600	-8.17569400	-8.13105200	-0.04464200
6	0.700	1.64730300	1.69165700	-0.04435400
6	0.800	11.63761100	11.68181900	-0.04420800
6	0.810	12.64725400	12.69146000	-0.04420600
6	0.820	13.65902800	13.70323300	-0.04420500
6	0.830	14.67299100	14.71719700	-0.04420600
6	0.840	15.68921100	15.73342200	-0.04421100
6	0.850	16.70776200	16.75198000	-0.04421800
6	0.860	17.72872300	17.77295200	-0.04422900
6	0.870	18.75218400	18.79642600	-0.04424200
6	0.880	19.77824200	19.82250300	-0.04426100
6	0.890	20.80700900	20.85129100	-0.04428200
6	0.900	21.83861000	21.88291700	-0.04430700
6	0.905	22.35551500	22.39983900	-0.04432400
6	0.910	22.87318400	22.91752400	-0.04434000
6	0.915	23.39163900	23.43599600	-0.04435700
6	0.920	23.91090100	23.95527700	-0.04437600
6	0.925	24.43099500	24.47539200	-0.04439700
6	0.930	24.95195000	24.99636900	-0.04441900
6	0.935	25.47379400	25.51823700	-0.04444300
6	0.940	25.99655900	26.04102900	-0.04447000
6	0.945	26.52028300	26.56478100	-0.04449800
6	0.950	27.04500500	27.08953400	-0.04452900
6	0.955	27.57077000	27.61533300	-0.04456300

6	0.960	28.09762800	28.14222700	-0.04459900
6	0.965	28.62563700	28.67027600	-0.04463900
6	0.970	29.15486200	29.19954400	-0.04468200
6	0.975	29.68537800	29.73010700	-0.04472900
6	0.980	30.21727500	30.26205600	-0.04478100
6	0.985	30.75065900	30.79549600	-0.04483700
6	0.990	31.28565800	31.33055800	-0.04490000
6	0.995	31.82243300	31.86740400	-0.04497100
6	1.000	32.36119200	32.40624200	-0.04505000

Tab. C.5.5: Hartree-Fock and exact energies and Wigner Correlation energies for $Z = 6$ for Coluomb-Hooke-Potential

C.6 Hartree-Fock, exact energies and Wigner Correlation energies for $Z = 7$ for the Coluomb-Hooke-Potential

Z	η	E_{HF}	E_{exact}	E_{corr}^W
7	0.000	-87.35862500	-87.31066400	-0.04796100
7	0.100	-74.84425400	-74.79687900	-0.04737500
7	0.200	-62.22418200	-62.17737600	-0.04680600
7	0.300	-49.48697700	-49.44071500	-0.04626200
7	0.400	-36.61919700	-36.57344300	-0.04575400
7	0.500	-23.60477000	-23.55947400	-0.04529600
7	0.600	-10.42398200	-10.37907400	-0.04490800
7	0.700	2.94840100	2.99301900	-0.04461800
7	0.800	16.54730600	16.59178000	-0.04447400
7	0.810	17.92151000	17.96598500	-0.04447500
7	0.820	19.29858100	19.34305500	-0.04447400
7	0.830	20.67859900	20.72307000	-0.04447100
7	0.840	22.06164300	22.10611700	-0.04447400
7	0.850	23.44780900	23.49229100	-0.04448200
7	0.860	24.83720400	24.88169500	-0.04449100
7	0.870	26.22993900	26.27444400	-0.04450500
7	0.880	27.62614200	27.67066500	-0.04452300
7	0.890	29.02595400	29.07049800	-0.04454400
7	0.900	30.42953600	30.47410400	-0.04456800
7	0.905	31.13279300	31.17737700	-0.04458400
7	0.910	31.83706400	31.88166300	-0.04459900
7	0.915	32.54237300	32.58699000	-0.04461700
7	0.920	33.24875000	33.29338600	-0.04463600
7	0.925	33.95622700	34.00088300	-0.04465600
7	0.930	34.66483700	34.70951500	-0.04467800
7	0.935	35.37461800	35.41932000	-0.04470200
7	0.940	36.08561100	36.13033800	-0.04472700
7	0.945	36.79786100	36.84261500	-0.04475400
7	0.950	37.51141700	37.55620100	-0.04478400
7	0.955	38.22633600	38.27115300	-0.04481700

7	0.960	38.94268000	38.98753100	-0.04485100
7	0.965	39.66051900	39.70540900	-0.04489000
7	0.970	40.37993600	40.42486500	-0.04492900
7	0.975	41.10102200	41.14599500	-0.04497300
7	0.980	41.82388500	41.86890700	-0.04502200
7	0.985	42.54865400	42.59373100	-0.04507700
7	0.990	43.27548600	43.32062300	-0.04513700
7	0.995	44.00457400	44.04977600	-0.04520200
7	1.000	44.73616300	44.78143900	-0.04527600

Tab. C.6.6: Hartree-Fock and exact energies and Wigner Correlation energies for $Z = 7$ for Coluomb-Hooke-Potential

C.7 Hartree-Fock, exact energies and Wigner Correlation energies for $Z = 8$ for the Coluomb-Hooke-Potential

Z	η	E_{HF}	E_{exact}	E_{corr}^W
8	0.000	-113.42358300	-113.37540900	-0.04817400
8	0.100	-97.07638300	-97.02879800	-0.04758500
8	0.200	-80.59089100	-80.54387800	-0.04701300
8	0.300	-63.95217300	-63.90570600	-0.04646700
8	0.400	-47.14268700	-47.09673000	-0.04595700
8	0.500	-30.14149600	-30.09599900	-0.04549700
8	0.600	-12.92299200	-12.87788200	-0.04511000
8	0.700	4.54546600	4.59028400	-0.04481800
8	0.800	22.30872600	22.35339900	-0.04467300
8	0.810	24.10363100	24.14830600	-0.04467500
8	0.820	25.90224900	25.94692300	-0.04467400
8	0.830	27.70467500	27.74935000	-0.04467500
8	0.840	29.51101900	29.55569700	-0.04467800
8	0.850	31.32139800	31.36608400	-0.04468600
8	0.860	33.13594300	33.18063900	-0.04469600
8	0.870	34.95479700	34.99950500	-0.04470800
8	0.880	36.77811700	36.82284200	-0.04472500
8	0.890	38.60608400	38.65082500	-0.04474100
8	0.900	40.43889000	40.48365200	-0.04476200
8	0.905	41.35717200	41.40195200	-0.04478000
8	0.910	42.27675400	42.32155000	-0.04479600
8	0.915	43.19766600	43.24247800	-0.04481200
8	0.920	44.11994400	44.16477400	-0.04483000
8	0.925	45.04362700	45.08847700	-0.04485000
8	0.930	45.96875600	46.01362700	-0.04487100
8	0.935	46.89537800	46.94027200	-0.04489400
8	0.940	47.82354200	47.86846100	-0.04491900
8	0.945	48.75330500	48.79825100	-0.04494600
8	0.950	49.68472600	49.72970100	-0.04497500
8	0.955	50.61787500	50.66288100	-0.04500600

8	0.960	51.55282600	51.59786700	-0.04504100
8	0.965	52.48966700	52.53474400	-0.04507700
8	0.970	53.42849400	53.47361100	-0.04511700
8	0.975	54.36942100	54.41458100	-0.04516000
8	0.980	55.31257700	55.35778400	-0.04520700
8	0.985	56.25811800	56.30337700	-0.04525900
8	0.990	57.20622900	57.25154500	-0.04531600
8	0.995	58.15714000	58.20251900	-0.04537900
8	1.000	59.11114100	59.15659000	-0.04544900

Tab. C.7.7: Hartree-Fock and exact energies and Wigner Correlation energies for $Z = 8$ for Coluomb-Hooke-Potential

C.8 Hartree-Fock, exact energies and Wigner Correlation energies for $Z = 9$ for the Coluomb-Hooke-Potential

Z	η	E_{HF}	E_{exact}	E_{corr}^W
9	0.000	-142.88385600	-142.83551500	-0.04834100
9	0.100	-122.19248000	-122.14473000	-0.04775000
9	0.200	-101.32584200	-101.27866000	-0.04718200
9	0.300	-80.26502300	-80.21838700	-0.04663600
9	0.400	-58.98783100	-58.94171000	-0.04612100
9	0.500	-37.46782100	-37.42216300	-0.04565800
9	0.600	-15.67271600	-15.62744300	-0.04527300
9	0.700	6.43850300	6.48348500	-0.04498200
9	0.800	28.92188400	28.96671200	-0.04482800
9	0.810	31.19362700	31.23846000	-0.04483300
9	0.820	33.47004100	33.51487200	-0.04483100
9	0.830	35.75124100	35.79607300	-0.04483200
9	0.840	38.03736300	38.08219800	-0.04483500
9	0.850	40.32855100	40.37339300	-0.04484200
9	0.860	42.62496600	42.66981700	-0.04485100
9	0.870	44.92678200	44.97164500	-0.04486300
9	0.880	47.23419100	47.27907100	-0.04488000
9	0.890	49.54740800	49.59230800	-0.04490000
9	0.900	51.86668200	51.91160000	-0.04491800
9	0.905	53.02866100	53.07360000	-0.04493900
9	0.910	54.19226400	54.23721800	-0.04495400
9	0.915	55.35752600	55.40249600	-0.04497000
9	0.920	56.52448900	56.56947700	-0.04498800
9	0.925	57.69320000	57.73820800	-0.04500800
9	0.930	58.86371500	58.90874000	-0.04502500
9	0.935	60.03608100	60.08112700	-0.04504600
9	0.940	61.21036200	61.25543200	-0.04507000
9	0.945	62.38662500	62.43172000	-0.04509500
9	0.950	63.56494200	63.61006600	-0.04512400
9	0.955	64.74539600	64.79055000	-0.04515400

9	0.960	65.92807700	65.97326400	-0.04518700
9	0.965	67.11308900	67.15831100	-0.04522200
9	0.970	68.30054700	68.34580900	-0.04526200
9	0.975	69.49058700	69.53589000	-0.04530300
9	0.980	70.68336300	70.72871200	-0.04534900
9	0.985	71.87905800	71.92445800	-0.04540000
9	0.990	73.07789200	73.12334700	-0.04545500
9	0.995	74.28013300	74.32564900	-0.04551600
9	1.000	75.48612400	75.53170600	-0.04558200

Tab. C.8.8: Hartree-Fock and exact energies and Wigner Correlation energies for $Z = 9$ for Coluomb-Hooke-Potential

C.9 Hartree-Fock, exact energies and Wigner Correlation energies for $Z = 10$ for the Coluomb-Hooke-Potential

Z	η	E_{HF}	E_{exact}	E_{corr}^W
10	0.000	-175.73944300	-175.69096600	-0.04847700
10	0.100	-150.19254200	-150.14466000	-0.04788200
10	0.200	-124.42901300	-124.38170600	-0.04730700
10	0.300	-98.42549900	-98.37874100	-0.04675800
10	0.400	-72.15461000	-72.10836400	-0.04624600
10	0.500	-45.58373200	-45.53794900	-0.04578300
10	0.600	-18.67312700	-18.62773600	-0.04539100
10	0.700	8.62754300	8.67264400	-0.04510100
10	0.800	36.38678800	36.43174200	-0.04495400
10	0.810	39.19148900	39.23646800	-0.04497900
10	0.820	42.00194700	42.04692400	-0.04497700
10	0.830	44.81830300	44.86326200	-0.04495900
10	0.840	47.64068100	47.68564300	-0.04496200
10	0.850	50.46927500	50.51424300	-0.04496800
10	0.860	53.30427700	53.34925400	-0.04497700
10	0.870	56.14589700	56.19088700	-0.04499000
10	0.880	58.99436700	59.03937300	-0.04500600
10	0.890	61.84994500	61.89497100	-0.04502600
10	0.900	64.71293100	64.75796800	-0.04503700
10	0.905	66.14727800	66.19234200	-0.04506400
10	0.910	67.58361400	67.62869200	-0.04507800
10	0.915	69.02197200	69.06706700	-0.04509500
10	0.920	70.46240500	70.50751700	-0.04511200
10	0.925	71.90496800	71.95010000	-0.04513200
10	0.930	73.34972300	73.39487500	-0.04515200
10	0.935	74.79673400	74.84190800	-0.04517400
10	0.940	76.24607500	76.29127300	-0.04519800
10	0.945	77.69782300	77.74304600	-0.04522300
10	0.950	79.15206500	79.19731700	-0.04525200
10	0.955	80.60889900	80.65418000	-0.04528100

10	0.960	82.06843500	82.11374500	-0.04531000
10	0.965	83.53078900	83.57613200	-0.04534300
10	0.970	84.99609900	85.04147900	-0.04538000
10	0.975	86.46452400	86.50994400	-0.04542000
10	0.980	87.93624400	87.98170900	-0.04546500
10	0.985	89.41147600	89.45699000	-0.04551400
10	0.990	90.89047600	90.93604300	-0.04556700
10	0.995	92.37355500	92.41918200	-0.04562700
10	1.000	93.86111000	93.90680100	-0.04569100

Tab. C.9.9: Hartree-Fock and exact energies and Wigner Correlation energies for $Z = 10$ for Coluomb-Hooke-Potential

D Expectation Values for the Coluomb-Hooke potential

D.1 Expectation Values for the Coluomb-Hooke potential for $Z = 2$

Z	η	$\langle r \rangle$	$\langle r^2 \rangle$	$\langle 1/r \rangle$	$\langle r \rangle \langle 1/r \rangle$	$\langle r^2 \rangle / \langle r \rangle^2$
2	0.000	1.56776154	1.44243729	3.23436856	5.07071864	0.58686327
2	0.100	1.56880820	1.45213437	3.26240420	5.11808646	0.59002050
2	0.200	1.57034552	1.46365666	3.29256058	5.17045776	0.59353834
2	0.300	1.57263756	1.47771358	3.32481456	5.22872825	0.59749322
2	0.400	1.57609916	1.49540758	3.35898876	5.29409936	0.60199447
2	0.500	1.58142948	1.51854467	3.39454889	5.36823970	0.60719462
2	0.600	1.58983946	1.55028176	3.43035507	5.45371385	0.61334396
2	0.700	1.60366678	1.59671402	3.46386838	5.55489066	0.62086742
2	0.800	1.62806618	1.67167938	3.48918843	5.68062969	0.63067973
2	0.810	1.63148367	1.68184125	3.49080968	5.69519900	0.63185807
2	0.820	1.63515520	1.69269609	3.49219537	5.71028142	0.63308355
2	0.830	1.63910437	1.70431983	3.49329925	5.72588205	0.63436306
2	0.840	1.64336121	1.71680105	3.49409151	5.74205446	0.63570248
2	0.850	1.64796317	1.73025048	3.49454379	5.75887945	0.63710935
2	0.860	1.65295565	1.74479020	3.49460530	5.77642758	0.63858808
2	0.870	1.65838397	1.76057100	3.49421048	5.79474263	0.64015238
2	0.880	1.66431487	1.77777827	3.49330974	5.81396733	0.64181019
2	0.890	1.67081904	1.79663372	3.49182868	5.83421386	0.64357729
2	0.900	1.67798495	1.81741190	3.48968005	5.85563062	0.64547176
2	0.905	1.68185079	1.82863021	3.48831463	5.86682472	0.64647385
2	0.910	1.68592405	1.84046531	3.48674536	5.87838787	0.64751767
2	0.915	1.69022906	1.85297859	3.48494625	5.89035742	0.64860348
2	0.920	1.69478381	1.86624205	3.48289776	5.90275872	0.64973963
2	0.925	1.69961143	1.88032770	3.48057890	5.91563166	0.65092996
2	0.930	1.70474303	1.89533556	3.47796321	5.92903353	0.65218118

2	0.935	1.71020675	1.91136742	3.47502446	5.94301028	0.65350204
2	0.940	1.71604836	1.92855525	3.47172761	5.95765247	0.65489706
2	0.945	1.72230804	1.94705117	3.46803069	5.97301714	0.65638056
2	0.950	1.72904241	1.96704102	3.46389008	5.98921285	0.65796399
2	0.955	1.73631477	1.98876083	3.45925140	6.00634932	0.65966833
2	0.960	1.74421442	2.01249337	3.45404196	6.02458978	0.66150741
2	0.965	1.75283909	2.03860903	3.44819546	6.04413178	0.66351362
2	0.970	1.76231980	2.06758189	3.44159484	6.06519074	0.66572256
2	0.975	1.77283120	2.10004640	3.43412113	6.08811709	0.66818099
2	0.980	1.78460109	2.13686585	3.42561364	6.11335385	0.67095741
2	0.985	1.79795039	2.17924953	3.41582918	6.14149140	0.67414226
2	0.990	1.81332469	2.22895503	3.40449023	6.17344620	0.67787584
2	0.995	1.83139312	2.28860950	3.39113855	6.21050783	0.68235211
2	1.000	1.85317707	2.36234236	3.37513781	6.25472799	0.68787417

Tab. D.1.1: Expectation Values for the Coluomb-Hooke potential for $Z = 2$

D.2 Expectation Values for the Coluomb-Hooke potential for $Z = 3$

Z	η	$\langle r \rangle$	$\langle r^2 \rangle$	$\langle 1/r \rangle$	$\langle r \rangle \langle 1/r \rangle$	$\langle r^2 \rangle / \langle r \rangle^2$
3	0.000	1.03030813	0.62373233	4.92865801	5.07803640	0.58757594
3	0.100	1.02985597	0.62659448	4.97711325	5.12570977	0.59079062
3	0.200	1.02954221	0.63000453	5.02971840	5.17830738	0.59436791
3	0.300	1.02948391	0.63418895	5.08668184	5.23665713	0.59838340
3	0.400	1.02987731	0.63950396	5.14804649	5.30185625	0.60293745
3	0.500	1.03104985	0.64653599	5.21350574	5.37538430	0.60818175
3	0.600	1.03359842	0.65631586	5.28201056	5.45947778	0.61434061
3	0.700	1.03866374	0.67083567	5.35096598	5.55785436	0.62182217
3	0.800	1.04876053	0.69451898	5.41383457	5.67781603	0.63143907
3	0.810	1.05023766	0.69773334	5.41927910	5.69153098	0.63257832
3	0.820	1.05183387	0.70116341	5.42447710	5.70564873	0.63376017
3	0.830	1.05356026	0.70483375	5.42939520	5.72019500	0.63499153
3	0.840	1.05543303	0.70877045	5.43400574	5.73522917	0.63627409
3	0.850	1.05746782	0.71300417	5.43825388	5.75077847	0.63761386
3	0.860	1.05968475	0.71757239	5.44209814	5.76690843	0.63901691
3	0.870	1.06210506	0.72251767	5.44547176	5.78366311	0.64049172
3	0.880	1.06475616	0.72789246	5.44831610	5.80112810	0.64204712
3	0.890	1.06767035	0.73376024	5.45054960	5.81939018	0.64369452
3	0.900	1.07088566	0.74019706	5.45207596	5.83854995	0.64544784
3	0.905	1.07262218	0.74365813	5.45254231	5.84851781	0.64636790
3	0.910	1.07445180	0.74729937	5.45277834	5.85874752	0.64732255
3	0.915	1.07638371	0.75113660	5.45278549	5.86928948	0.64831294
3	0.920	1.07842684	0.75518876	5.45251942	5.88014327	0.64934297
3	0.925	1.08059013	0.75947493	5.45197439	5.89134971	0.65041635
3	0.930	1.08288658	0.76402038	5.45112515	5.90295025	0.65153688
3	0.935	1.08532751	0.76885206	5.44993496	5.91496432	0.65271134
3	0.940	1.08792901	0.77400213	5.44836950	5.92743924	0.65394473
3	0.945	1.09071124	0.77950823	5.44639778	5.94044726	0.65524110
3	0.950	1.09368968	0.78541595	5.44396114	5.95400412	0.65661604
3	0.955	1.09689271	0.79177880	5.44103289	5.96822933	0.65807526
3	0.960	1.10034966	0.79866236	5.43752670	5.98318068	0.65963211
3	0.965	1.10409498	0.80614907	5.43338108	5.99896879	0.66130603

3	0.970	1.10817552	0.81433988	5.42850399	6.01573521	0.66311462
3	0.975	1.11264527	0.82336783	5.42279243	6.03364434	0.66509004
3	0.980	1.11758137	0.83340693	5.41610289	6.05293567	0.66726570
3	0.985	1.12307882	0.84469807	5.40825605	6.07389784	0.66970112
3	0.990	1.12927926	0.85758555	5.39901638	6.09699720	0.67247285
3	0.995	1.13638604	0.87259859	5.38803911	6.12289241	0.67571371
3	1.000	1.14473569	0.89064562	5.37481117	6.15273820	0.67966435

Tab. D.2.2: Expectation Values for the Coluomb-Hooke potential for $Z = 3$

D.3 Expectation Values for the Coluomb-Hooke potential for $Z = 4$

Z	η	$\langle r \rangle$	$\langle r^2 \rangle$	$\langle 1/r \rangle$	$\langle r \rangle \langle 1/r \rangle$	$\langle r^2 \rangle / \langle r \rangle^2$
4	0.000	0.76710796	0.34597540	6.62454939	5.08174459	0.58793896
4	0.100	0.76633096	0.34717777	6.69363832	5.12954227	0.59117924
4	0.200	0.76558620	0.34861565	6.76896286	5.18222454	0.59478319
4	0.300	0.76494217	0.35039404	6.85094118	5.24057381	0.59882442
4	0.400	0.76451540	0.35268006	6.93986702	5.30563521	0.60340434
4	0.500	0.76450819	0.35574904	7.03563595	5.37880129	0.60866658
4	0.600	0.76528978	0.36008748	7.13735056	5.46214146	0.61483162
4	0.700	0.76757610	0.36663020	7.24229717	5.55901421	0.62227929
4	0.800	0.77293724	0.37744066	7.34335423	5.67595193	0.63177178
4	0.810	0.77376062	0.37891403	7.35266876	5.68920552	0.63288885
4	0.820	0.77465743	0.38048744	7.36176014	5.70284218	0.63404626
4	0.830	0.77563488	0.38217115	7.37054348	5.71685064	0.63524790
4	0.840	0.77670145	0.38397732	7.37902260	5.73129755	0.63649844
4	0.850	0.77786809	0.38591954	7.38712263	5.74620699	0.63780050
4	0.860	0.77914578	0.38801482	7.39480591	5.76163180	0.63916189
4	0.870	0.78054631	0.39028212	7.40198898	5.77759517	0.64059171
4	0.880	0.78208911	0.39274400	7.40862322	5.79420357	0.64209174
4	0.890	0.78379178	0.39542833	7.41457605	5.81148377	0.64367460
4	0.900	0.78567654	0.39836860	7.41980648	5.82956787	0.64535329
4	0.905	0.78669614	0.39994684	7.42209578	5.83893407	0.64623166
4	0.910	0.78777176	0.40160567	7.42413902	5.84852707	0.64714115
4	0.915	0.78890860	0.40335143	7.42593193	5.85838157	0.64808238
4	0.920	0.79011190	0.40519178	7.42744493	5.86851263	0.64905787
4	0.925	0.79138768	0.40713546	7.42865086	5.87894275	0.65007035
4	0.930	0.79274130	0.40919220	7.42953348	5.88969802	0.65112502
4	0.935	0.79418033	0.41137394	7.43004274	5.90079382	0.65222662
4	0.940	0.79571396	0.41369358	7.43015337	5.91227677	0.65337847
4	0.945	0.79735231	0.41616651	7.42982531	5.92418840	0.65458585
4	0.950	0.79910624	0.41881108	7.42902088	5.93657695	0.65585694
4	0.955	0.80098814	0.42164880	7.42767429	5.94947900	0.65720173
4	0.960	0.80301589	0.42470562	7.42572737	5.96297705	0.65862731
4	0.965	0.80520731	0.42801312	7.42310667	5.97713977	0.66014853

4	0.970	0.80758834	0.43161073	7.41971684	5.99207679	0.66177774
4	0.975	0.81018418	0.43554792	7.41546679	6.00789388	0.66354201
4	0.980	0.81303519	0.43988884	7.41020870	6.02476044	0.66546352
4	0.985	0.81618911	0.44471997	7.40378523	6.04288888	0.66758265
4	0.990	0.81971169	0.45015901	7.39595795	6.06255315	0.66995202
4	0.995	0.82369590	0.45638171	7.38644791	6.08418684	0.67265817
4	1.000	0.82828522	0.46366575	7.37482166	6.10845576	0.67584203

Tab. D.3.3: Expectation Values for the Coluomb-Hooke potential for $Z = 4$

D.4 Expectation Values for the Coluomb-Hooke potential for $Z = 5$

Z	η	$\langle r \rangle$	$\langle r^2 \rangle$	$\langle 1/r \rangle$	$\langle r \rangle \langle 1/r \rangle$	$\langle r^2 \rangle / \langle r \rangle^2$
5	0.000	0.61096960	0.21955098	8.32116318	5.08397776	0.58816094
5	0.100	0.61013907	0.22016700	8.41096497	5.13185836	0.59141801
5	0.200	0.60930002	0.22090529	8.50907707	5.18458081	0.59503667
5	0.300	0.60849726	0.22182544	8.61619663	5.24293206	0.59909278
5	0.400	0.60780972	0.22302096	8.73281956	5.30789263	0.60368500
5	0.500	0.60737908	0.22464943	8.85906696	5.38081193	0.60895565
5	0.600	0.60746664	0.22698846	8.99417686	5.46366238	0.61511869
5	0.700	0.60858077	0.23057218	9.13534355	5.55959440	0.62254458
5	0.800	0.61183882	0.23657057	9.27478409	5.67467293	0.63195573
5	0.810	0.61236602	0.23739193	9.28800106	5.68765625	0.63305842
5	0.820	0.61294460	0.23826964	9.30097675	5.70098350	0.63420003
5	0.830	0.61357993	0.23920946	9.31366634	5.71467873	0.63538368
5	0.840	0.61427814	0.24021801	9.32602406	5.72877269	0.63661293
5	0.850	0.61504591	0.24130304	9.33800316	5.74330060	0.63789285
5	0.860	0.61589122	0.24247365	9.34952354	5.75828945	0.63922908
5	0.870	0.61682433	0.24374059	9.36053562	5.77380610	0.64062645
5	0.880	0.61785543	0.24511603	9.37093544	5.78988334	0.64209305
5	0.890	0.61899745	0.24661523	9.38065243	5.80659998	0.64363873
5	0.900	0.62026799	0.24825634	9.38955688	5.82404155	0.64527021
5	0.905	0.62095594	0.24913678	9.39366817	5.83305409	0.64612458
5	0.910	0.62168390	0.25006166	9.39750481	5.84227740	0.64700536
5	0.915	0.62245375	0.25103429	9.40108204	5.85173876	0.64791625
5	0.920	0.62326896	0.25205889	9.40434170	5.86143429	0.64886003
5	0.925	0.62413466	0.25314033	9.40729332	5.87141782	0.64983746
5	0.930	0.62505442	0.25428337	9.40986538	5.88167794	0.65085208
5	0.935	0.62603319	0.25549454	9.41206741	5.89226656	0.65190889
5	0.940	0.62707573	0.25678071	9.41382027	5.90317823	0.65301388
5	0.945	0.62818992	0.25814986	9.41510296	5.91447279	0.65416901
5	0.950	0.62938315	0.25961125	9.41587067	5.92619031	0.65538016
5	0.955	0.63066345	0.26117659	9.41605568	5.93836220	0.65665750
5	0.960	0.63204199	0.26285848	9.41559315	5.95105024	0.65800642
5	0.965	0.63352954	0.26467347	9.41440678	5.96430483	0.65944210

5	0.970	0.63514423	0.26664147	9.41240788	5.97823659	0.66097186
5	0.975	0.63690180	0.26878703	9.40947819	5.99291356	0.66261819
5	0.980	0.63882667	0.27114189	9.40550709	6.00848876	0.66440140
5	0.985	0.64094871	0.27374744	9.40029430	6.02510653	0.66635171
5	0.990	0.64330834	0.27666017	9.39363384	6.04300301	0.66851057
5	0.995	0.64596051	0.27996147	9.38523960	6.06249416	0.67094408
5	1.000	0.64898622	0.28377458	9.37468815	6.08404343	0.67375584

Tab. D.4.4: Expectation Values for the Coluomb-Hooke potential for $Z = 5$

D.5 Expectation Values for the Coluomb-Hooke potential for $Z = 6$

Z	η	$\langle r \rangle$	$\langle r^2 \rangle$	$\langle 1/r \rangle$	$\langle r \rangle \langle 1/r \rangle$	$\langle r^2 \rangle / \langle r \rangle^2$
6	0.000	0.50763160	0.15160184	10.01809311	5.08550063	0.58831126
6	0.100	0.50682217	0.15195748	10.12862968	5.13341406	0.59157646
6	0.200	0.50598603	0.15238538	10.24959850	5.18615371	0.59520456
6	0.300	0.50515532	0.15292262	10.38192844	5.24448644	0.59926905
6	0.400	0.50438911	0.15362942	10.52633762	5.30937004	0.60386937
6	0.500	0.50379491	0.15460689	10.68314838	5.38211576	0.60914587
6	0.600	0.50357139	0.15603274	10.85174370	5.46462767	0.61530953
6	0.700	0.50410903	0.15824865	11.02921867	5.55992867	0.62271749
6	0.800	0.50626165	0.16200043	11.20713902	5.67374465	0.63207137
6	0.810	0.50662911	0.16251655	11.22426319	5.68653846	0.63316560
6	0.820	0.50703657	0.16306835	11.24114227	5.69967018	0.63429476
6	0.830	0.50748676	0.16365957	11.25772953	5.71314869	0.63546550
6	0.840	0.50798440	0.16429442	11.27397537	5.72700361	0.63668126
6	0.850	0.50853491	0.16497773	11.28981876	5.74126695	0.63794580
6	0.860	0.50914425	0.16571541	11.30519295	5.75597395	0.63926543
6	0.870	0.50982028	0.16651362	11.32002258	5.77117711	0.64064221
6	0.880	0.51057172	0.16738084	11.33421135	5.78692776	0.64208457
6	0.890	0.51140630	0.16832581	11.34766579	5.80326780	0.64360375
6	0.900	0.51233763	0.16935997	11.36023140	5.82027397	0.64520579
6	0.905	0.51284355	0.16991486	11.36615276	5.82905813	0.64604320
6	0.910	0.51337951	0.17049734	11.37179470	5.83804644	0.64690506
6	0.915	0.51394719	0.17110980	11.37713242	5.84724522	0.64779543
6	0.920	0.51454932	0.17175484	11.38214684	5.85667586	0.64871654
6	0.925	0.51518840	0.17243516	11.38681316	5.86635401	0.64967131
6	0.930	0.51586837	0.17315401	11.39107800	5.87629679	0.65066098
6	0.935	0.51659280	0.17391518	11.39493465	5.88654121	0.65168959
6	0.940	0.51736528	0.17472264	11.39831352	5.89709163	0.65276165
6	0.945	0.51819110	0.17558162	11.40119076	5.90799557	0.65388165
6	0.950	0.51907563	0.17649767	11.40349102	5.91927431	0.65505488
6	0.955	0.52002466	0.17747742	11.40519047	5.93098026	0.65628916
6	0.960	0.52104729	0.17852901	11.40616989	5.94315396	0.65758895
6	0.965	0.52215034	0.17966153	11.40637875	5.95584451	0.65896745

6	0.970	0.52334583	0.18088713	11.40571690	5.96913435	0.66043509
6	0.975	0.52464736	0.18222053	11.40407276	5.98311661	0.66200663
6	0.980	0.52607059	0.18367971	11.40128231	5.99787937	0.66370202
6	0.985	0.52763623	0.18528865	11.39718437	6.01356739	0.66554834
6	0.990	0.52937329	0.18707953	11.39155960	6.03038736	0.66757833
6	0.995	0.53131825	0.18909764	11.38411140	6.04858612	0.66984860
6	1.000	0.53352618	0.19141063	11.37442303	6.06855249	0.67244161

Tab. D.5.5: Expectation Values for the Coluomb-Hooke potential for $Z = 6$

D.6 Expectation Values for the Coluomb-Hooke potential for $Z = 7$

Z	η	$\langle r \rangle$	$\langle r^2 \rangle$	$\langle 1/r \rangle$	$\langle r \rangle \langle 1/r \rangle$	$\langle r^2 \rangle / \langle r \rangle^2$
7	0.000	0.43418318	0.11092448	11.71519566	5.08654091	0.58841186
7	0.100	0.43341643	0.11114767	11.84655190	5.13449019	0.59168374
7	0.200	0.43261573	0.11141800	11.99043560	5.18725102	0.59532039
7	0.300	0.43180543	0.11176070	12.14798832	5.24556734	0.59939471
7	0.400	0.43103296	0.11221725	12.32019043	5.31040809	0.60400243
7	0.500	0.43038151	0.11285672	12.50759411	5.38303720	0.60928461
7	0.600	0.43001056	0.11380151	12.70969296	5.46530215	0.61544576
7	0.700	0.43023306	0.11528777	12.92350960	5.56012110	0.62283880
7	0.800	0.43173802	0.11783139	13.13995934	5.67302001	0.63215041
7	0.810	0.43201038	0.11818282	13.16098595	5.68568257	0.63323658
7	0.820	0.43231401	0.11855888	13.18177986	5.69866809	0.63435951
7	0.830	0.43265224	0.11896190	13.20224762	5.71198194	0.63552112
7	0.840	0.43302915	0.11939502	13.22239113	5.72568073	0.63672507
7	0.850	0.43344760	0.11986145	13.24211025	5.73976090	0.63797893
7	0.860	0.43391359	0.12036511	13.26132870	5.75427072	0.63928443
7	0.870	0.43443269	0.12091032	13.27998161	5.76925807	0.64064641
7	0.880	0.43501118	0.12150275	13.29793262	5.78474934	0.64207428
7	0.890	0.43565708	0.12214842	13.31511784	5.80082541	0.64357369
7	0.900	0.43637994	0.12285504	13.33135319	5.81753509	0.64515407
7	0.905	0.43677321	0.12323401	13.33907413	5.82615024	0.64597929
7	0.910	0.43719083	0.12363202	13.34649849	5.83496676	0.64682810
7	0.915	0.43763384	0.12405033	13.35361767	5.84399501	0.64770331
7	0.920	0.43810356	0.12449069	13.36036587	5.85322380	0.64860953
7	0.925	0.43860364	0.12495511	13.36673832	5.86270008	0.64954547
7	0.930	0.43913546	0.12544578	13.37268448	5.87241998	0.65051760
7	0.935	0.43970230	0.12596504	13.37818336	5.88241802	0.65152722
7	0.940	0.44030735	0.12651560	13.38318825	5.89271614	0.65257766
7	0.945	0.44095510	0.12710099	13.38762569	5.90334186	0.65367246
7	0.950	0.44164851	0.12772492	13.39146042	5.91431858	0.65482022
7	0.955	0.44239360	0.12839156	13.39463329	5.92570006	0.65602262
7	0.960	0.44319573	0.12910646	13.39705086	5.93751574	0.65728973
7	0.965	0.44406253	0.12987573	13.39862251	5.94982622	0.65862734

7	0.970	0.44500077	0.13070710	13.39924622	5.96267485	0.66005125
7	0.975	0.44602120	0.13160996	13.39883995	5.97616666	0.66157298
7	0.980	0.44713682	0.13259628	13.39719963	5.99038123	0.66320912
7	0.985	0.44836360	0.13368134	13.39417648	6.00546122	0.66498232
7	0.990	0.44972110	0.13488545	13.38950825	6.02154435	0.66692741
7	0.995	0.45123869	0.13623735	13.38290405	6.03888412	0.66908845
7	1.000	0.45295510	0.13777836	13.37396908	6.05780746	0.67153816

Tab. D.6.6: Expectation Values for the Coluomb-Hooke potential for $Z = 7$

D.7 Expectation Values for the Coluomb-Hooke potential for $Z = 8$

Z	η	$\langle r \rangle$	$\langle r^2 \rangle$	$\langle 1/r \rangle$	$\langle r \rangle \langle 1/r \rangle$	$\langle r^2 \rangle / \langle r \rangle^2$
8	0.000	0.37929872	0.08466551	13.41251850	5.08735106	0.58849639
8	0.100	0.37858251	0.08481564	13.56463814	5.13533472	0.59177258
8	0.200	0.37782791	0.08499774	13.73140049	5.18810638	0.59541438
8	0.300	0.37705526	0.08523014	13.91415977	5.24640710	0.59949175
8	0.400	0.37630147	0.08554260	14.11420250	5.31119511	0.60410246
8	0.500	0.37563697	0.08598595	14.33222198	5.38371237	0.60938373
8	0.600	0.37519336	0.08665027	14.56785870	5.46576382	0.61554479
8	0.700	0.37523314	0.08770827	14.81805038	5.56022363	0.62292846
8	0.800	0.37633017	0.08953630	15.07300949	5.67242818	0.63220960
8	0.810	0.37654108	0.08978972	15.09795094	5.68499872	0.63328891
8	0.820	0.37677771	0.09006107	15.12262535	5.69786813	0.63440514
8	0.830	0.37704319	0.09035217	15.14700985	5.71107688	0.63555976
8	0.840	0.37733981	0.09066508	15.17101574	5.72462820	0.63675856
8	0.850	0.37767196	0.09100214	15.19460678	5.73857688	0.63800210
8	0.860	0.37804300	0.09136627	15.21765995	5.75292976	0.63929822
8	0.870	0.37845835	0.09176058	15.24012947	5.76775427	0.64064869
8	0.880	0.37892273	0.09218908	15.26187420	5.78307105	0.64206378
8	0.890	0.37944326	0.09265626	15.28276253	5.79894120	0.64354822
8	0.900	0.38002709	0.09316761	15.30265808	5.81542455	0.64511309
8	0.905	0.38034600	0.09344184	15.31218719	5.82392915	0.64592738
8	0.910	0.38068432	0.09372976	15.32137871	5.83260858	0.64676651
8	0.915	0.38104331	0.09403248	15.33025074	5.84148956	0.64763335
8	0.920	0.38142535	0.09435111	15.33873272	5.85058151	0.64852679
8	0.925	0.38183165	0.09468704	15.34681606	5.85990004	0.64945150
8	0.930	0.38226473	0.09504181	15.35443878	5.86946045	0.65040855
8	0.935	0.38272667	0.09541728	15.36157990	5.87928631	0.65140276
8	0.940	0.38322046	0.09581541	15.36817265	5.88939825	0.65243606
8	0.945	0.38374856	0.09623829	15.37417221	5.89981646	0.65351319
8	0.950	0.38431451	0.09668886	15.37952995	5.91057647	0.65464051
8	0.955	0.38492292	0.09717003	15.38416767	5.92171877	0.65582017
8	0.960	0.38557804	0.09768567	15.38798332	5.93326839	0.65706192
8	0.965	0.38628554	0.09824017	15.39088917	5.94527799	0.65837326

8	0.970	0.38705224	0.09883890	15.39281082	5.95782188	0.65976421
8	0.975	0.38788596	0.09948825	15.39359951	5.97096109	0.66124695
8	0.980	0.38879693	0.10019685	15.39307499	5.98478023	0.66283959
8	0.985	0.38979772	0.10097499	15.39107513	5.99940595	0.66456160
8	0.990	0.39090478	0.10183681	15.38732719	6.01497982	0.66644269
8	0.995	0.39213923	0.10280170	15.38152027	6.03169746	0.66852816
8	1.000	0.39353272	0.10389785	15.37324810	6.04987619	0.67088005

Tab. D.7.7: Expectation Values for the Coluomb-Hooke potential for $Z = 8$

D.8 Expectation Values for the Coluomb-Hooke potential for $Z = 9$

Z	η	$\langle r \rangle$	$\langle r^2 \rangle$	$\langle 1/r \rangle$	$\langle r \rangle \langle 1/r \rangle$	$\langle r^2 \rangle / \langle r \rangle^2$
9	0.000	0.33673191	0.06673507	15.10984516	5.08796703	0.58855296
9	0.100	0.33606157	0.06684005	15.28277493	5.13595329	0.59183281
9	0.200	0.33535221	0.06696836	15.47247219	5.18872778	0.59548017
9	0.300	0.33462095	0.06713377	15.68050289	5.24702481	0.59956293
9	0.400	0.33389798	0.06735902	15.90835762	5.31176844	0.60418251
9	0.500	0.33324406	0.06768209	16.15697289	5.38421517	0.60946528
9	0.600	0.33276939	0.06817140	16.42612839	5.46611279	0.61562386
9	0.700	0.33269820	0.06895836	16.71266937	5.56027495	0.62299708
9	0.800	0.33352226	0.07032976	17.00611305	5.67191726	0.63225090
9	0.810	0.33369070	0.07052055	17.03495789	5.68440707	0.63332623
9	0.820	0.33388111	0.07072495	17.06353951	5.69719351	0.63443765
9	0.830	0.33409584	0.07094438	17.09181404	5.71030390	0.63558830
9	0.840	0.33433756	0.07118030	17.11971092	5.72376242	0.63678007
9	0.850	0.33460945	0.07143456	17.14715576	5.73760034	0.63801664
9	0.860	0.33491442	0.07170942	17.17405128	5.75183736	0.63930560
9	0.870	0.33525699	0.07200716	17.20031357	5.76652542	0.64064873
9	0.880	0.33564177	0.07233062	17.22579765	5.78169724	0.64205193
9	0.890	0.33607388	0.07268350	17.25042343	5.79741665	0.64352632
9	0.900	0.33656049	0.07306983	17.27395439	5.81373051	0.64507738
9	0.905	0.33682600	0.07327695	17.28529167	5.82213559	0.64588647
9	0.910	0.33710858	0.07349441	17.29626465	5.83071925	0.64671763
9	0.915	0.33740896	0.07372308	17.30686951	5.83949284	0.64757524
9	0.920	0.33772850	0.07396377	17.31707573	5.84847002	0.64846062
9	0.925	0.33806884	0.07421745	17.32684517	5.85766650	0.64937522
9	0.930	0.33843207	0.07448544	17.33614349	5.86710699	0.65032183
9	0.935	0.33881944	0.07476880	17.34490585	5.87679136	0.65130399
9	0.940	0.33923405	0.07506923	17.35309410	5.88676046	0.65232361
9	0.945	0.33967739	0.07538841	17.36064339	5.89701809	0.65338821
9	0.950	0.34015298	0.07572824	17.36750793	5.90760956	0.65449946
9	0.955	0.34066439	0.07609113	17.37359238	5.91856419	0.65566279
9	0.960	0.34121564	0.07647979	17.37878799	5.92991427	0.65688418
9	0.965	0.34181061	0.07689745	17.38306046	5.94171457	0.65817419

9	0.970	0.34245551	0.07734813	17.38624191	5.95401428	0.65954055
9	0.975	0.34315708	0.07783658	17.38818550	5.96687901	0.66099445
9	0.980	0.34392294	0.07836895	17.38877678	5.98039928	0.66255473
9	0.985	0.34476468	0.07895290	17.38776588	5.99468754	0.66423623
9	0.990	0.34569436	0.07959874	17.38490486	6.00986361	0.66607264
9	0.995	0.34673062	0.08032028	17.37987137	6.02613357	0.66809897
9	1.000	0.34789848	0.08113781	17.37220192	6.04376270	0.67037559

Tab. D.8.8: Expectation Values for the Coluomb-Hooke potential for $Z = 9$

D.9 Expectation Values for the Coluomb-Hooke potential for $Z = 10$

Z	η	$\langle r \rangle$	$\langle r^2 \rangle$	$\langle 1/r \rangle$	$\langle r \rangle \langle 1/r \rangle$	$\langle r^2 \rangle / \langle r \rangle^2$
10	0.000	0.30275533	0.05395215	16.80724335	5.08848244	0.58860666
10	0.100	0.30212867	0.05402891	17.00095558	5.13647614	0.59189175
10	0.200	0.30146322	0.05412273	17.21354675	5.18925117	0.59554019
10	0.300	0.30077267	0.05424448	17.44683647	5.24753153	0.59962379
10	0.400	0.30008379	0.05441204	17.70251656	5.31223819	0.60424067
10	0.500	0.29944775	0.05465559	17.98177338	5.38460149	0.60952631
10	0.600	0.29896221	0.05502891	18.28446007	5.46636251	0.61568468
10	0.700	0.29882213	0.05563524	18.60732079	5.56027932	0.62305216
10	0.800	0.29945675	0.05669963	18.93919754	5.67147046	0.63228380
10	0.810	0.29959464	0.05684815	18.97192764	5.68388785	0.63335657
10	0.820	0.29975206	0.05700735	19.00440598	5.69660978	0.63446331
10	0.830	0.29993033	0.05717824	19.03655243	5.70963953	0.63560895
10	0.840	0.30013224	0.05736210	19.06832123	5.72301805	0.63679510
10	0.850	0.30036002	0.05756038	19.09961510	5.73676085	0.63802754
10	0.860	0.30061686	0.05777478	19.13034439	5.75090407	0.63931018
10	0.870	0.30090654	0.05800702	19.16038895	5.76548632	0.64064484
10	0.880	0.30123264	0.05825955	19.18964195	5.78054643	0.64204144
10	0.890	0.30159983	0.05853495	19.21797371	5.79613761	0.64350669
10	0.900	0.30201429	0.05883651	19.24512482	5.81230273	0.64504781
10	0.905	0.30224130	0.05899829	19.25825119	5.82063879	0.64585028
10	0.910	0.30248258	0.05916811	19.27098274	5.82913649	0.64667636
10	0.915	0.30273956	0.05934662	19.28335190	5.83783348	0.64752663
10	0.920	0.30301312	0.05953452	19.29526711	5.84671901	0.64840451
10	0.925	0.30330470	0.05973266	19.30673981	5.85582496	0.64931222
10	0.930	0.30361590	0.05994175	19.31766701	5.86515081	0.65025006
10	0.935	0.30394831	0.06016300	19.32806969	5.87473417	0.65122345
10	0.940	0.30430377	0.06039745	19.33782578	5.88457320	0.65223481
10	0.945	0.30468512	0.06064650	19.34693527	5.89472321	0.65328587
10	0.950	0.30509385	0.06091163	19.35526657	5.90517289	0.65438494
10	0.955	0.30553362	0.06119464	19.36280060	5.91598652	0.65553419
10	0.960	0.30600730	0.06149763	19.36939621	5.92717656	0.65674206
10	0.965	0.30651933	0.06182315	19.37497520	5.93880441	0.65801438

10	0.970	0.30707446	0.06217412	19.37940025	5.95091882	0.65935948
10	0.975	0.30767781	0.06255433	19.38251877	5.96357084	0.66079239
10	0.980	0.30833662	0.06296836	19.38417053	5.97684954	0.66232656
10	0.985	0.30906060	0.06342211	19.38413811	5.99087342	0.66397750
10	0.990	0.30985996	0.06392331	19.38212967	6.00574595	0.66577627
10	0.995	0.31074998	0.06448248	19.37781715	6.02165625	0.66775865
10	1.000	0.31175184	0.06511468	19.37072945	6.03886060	0.66997845

Tab. D.9.9: Expectation Values for the Coluomb-Hooke potential for $Z = 10$

E Papers, Talks and Posters

E.1 Papers

J. Katriel, M. Bauer, M. Springborg, S. P. McCarthy and A. J. Thakkar (2007) ”‘Nonlocal Wigner-like correlation energy density functional: Parametrization and tests on two-electron systems’” The Journal of Chemical Physics, **127**, 024101

O. Clemens, M. Basters, M. Wild, S. Wilbrand, Chr. Reichert, M. Bauer, M. Springborg, and G. Jung (2008) ”‘Solvent effects on the absorption / emission spectra of an organic chromophore: a theoretical study’” Molecular Structure THEOCHEM, **866**, 15-20

N. Kunkel, J. Sander, N. Louis, Y. Pang, L.-M. Dejon, F. Wagener, Y. N. Zang, A. Sayede, M. Bauer, M. Springborg and H. Kohlmann (2010) ” ‘Theoretical investigation of the hydrogenation induced atomic rearrangements in palladium rich intermetallic compounds MPd_3 (M=Mg, In, Tl) ’ ” submitted

M. Bauer and M. Springborg (2010) ” ‘Structural and electronic properties of stoichiometric $(CdS)_n$ clusters, $n = 2 - 25$: A GA-DFTB approach’ ” in preparation

E.2 Talks

M. Bauer, J. Katriel and M. Springborg, *Towards a universal electron correlation density-functional*, Technical University Dresden, 2007

M. Bauer and M. Springborg, *Chemistry with computers*, Doktorandentag, Saarland University, 2007

M. Bauer and M. Springborg, *Clusters in theoretical chemistry*, Doktorandentag, Saarland University, 2008

E.3 Posters and Conferences

Symposium for Theoretical Chemistry 2001, Bad Herrenalb, Germany

XIth International Congress of Quantum Chemistry, Bonn, Germany, 2003

M. Bauer and M. Springborg, *Unbiased study of properties of stoichiometric (CdS)_n-Cluster*, S3C 2005, Brand, Austria

M. Bauer and M. Springborg, *MgO Clusters: A DFT Approach*, Bunsentagung 2005, Frankfurt, Germany

M. Bauer and M. Springborg, *MgO Clusters: A DFT Approach*, 37th Spring School of the Institute of Solid State Research: Computational Condensed Matter Physics, Forschungszentrum Jülich, 2006

M. Bauer and M. Springborg, *MgO Clusters: A DFT Approach*, Symposium for Theoretical Chemistry 2006, Erkner, Germany

M. Bauer and M. Springborg, *Unbiased study of properties of stoichiometric (CdS)_n-Cluster*, Programming Parallel Computers, John von Neumann Institute for Computing (NIC), Forschungszentrum Jülich, 2007

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F Eidesstattliche Erklärung

Hiermit versichere ich an Eides statt, dass ich die vorliegende Arbeit selbständig und ohne Benutzung anderer als der angegebenen Hilfsmittel angefertigt habe. Die aus anderen Quellen oder indirekt übernommenen Daten und Konzepte sind unter Angabe der Quelle gekennzeichnet. Die Arbeit wurde bisher weder im In- noch Ausland in gleicher oder ähnlicher Form in einem Verfahren zur Erlangung eines akademischen Grades vorgelegt.

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