MASARYKOVA UNIVERZITA
PŘÍRODOVĚDECKÁ FAKULTA
DEPARTMENT OF CHEMISTRY

Diplomová práce

Brno 2018 Petra Hrozková

Masarykova univerzita
Přírodovědecká fakulta
Department of Chemistry

A DFT study of the Electronic Structure of Silicate Precursors for Phosphosilicates

Diplomová práce

Petra Hrozková

Vedoucí práce: doc. Markéta Munzarová Dr. rer. nat. **Brno 2018**

Bibliografický záznam

Autor: Petra Hrozková
Přírodovědecká fakulta, Masarykova univerzita
Department of Chemistry

Název práce: A DFT study of the Electronic Structure of Silicate Precursors for Phosphosilicates

Studijní program: Chemistry

Obor: Physical Chemistry

Vedoucí práce: doc. Markéta Munzarová Dr. rer. nat.

Akademický rok: 2017/2018

Počet stran: xiii + 13

Klíčová slova: klíčové slovo 1, klíčové slovo 2, …

Bibliographic record

Author:	Petra Hrozková Faculty of Science, Masaryk University Ústav chemie
Title of Thesis:	Studium elektronové struktury fosfosilikátů a jejich silikátových prekurzorů metodou DFT
Degree Programme:	Fyzikální chemie
Field of study:	Fyzikální chemie
Supervisor:	doc. Markéta Munzarová Dr. rer. nat.
Academic Year:	2017/2018
Number of Pages:	xiii + 13
Keywords:	kľúčové slovo 1, kľúčové slovo 2, ...

Abstrakt

This is the Czech abstract of my thesis, which can span multiple paragraphs.

Abstract

This is the abstract of my thesis, which can span multiple paragraphs.

Set the PDF document containing the official signed thesis assignment using the «assignment» key.

Poděkování

These are the acknowledgements for my thesis, which can span multiple paragraphs.

Prohlášení

Prohlašuji, že jsem svoji diplomovou práci vypracovala samostatně s využitím informačních zdrojů, které jsou v práci citovány.

Brno, 18. března 2018

Podpis autora

Contents

1 Introduction 1
1.1 *Experiment X* 1
  1.1.1 Silicophosphates 1
1.2 *Methods of quantum chemistry* 4
  1.2.1 Basis Sets 5
1.3 *Density functional theory (DFT)* 7
1.4 *Natural Bond Orbital* 8
1.5 *Hard and Soft Acid and Basis in theory* 9
1.6 *Výpočetní část* 10
  1.6.1 Struktury 10
  1.6.2 Vazby 11
  1.6.3 Spektroskopi 11

Bibliography 13

List of Tables

1.1 Global caption *12*
1.2 *12*
1.3 *12*

List of Figures

1.1 Silicophosphat’s net [1]. *2*
1.2 [3] *3*
1.3 *11*

1 Introduction

1.1 Experiment X

The goal of this thesis is to interpret experimental results obtained previously in our department for porous silicophosphate material.[1] In particular, our interest focuses on the presence or absence of hypervalent silicon atoms in the structures as well as on silicon cordination enviroment in terms of phosphate and "hosting" carbonyl esters. We present several models of both "pristine" silicoohosphate strucutres and their carboxyl-substituented analoges, desribe their bonding charaacteristics and compare quantum- chemically determined NMR parametrs with their experimental counterparts.

1.1.1 Silicophosphates

Silicophosphates are important advanced-technology materials with a porous structure constisting of repaiting Si-O-P-O sequences. Since they occur in minerals and other oxidic materials, generally surrounded by four oxygen atoms in nature. Silicophosphates have extraordinary physical properties like Brønsted acidity or high proton conductivity. In the future they could be applied as catalysts, electrolytes, optical glasses, and biocompatible materials. Approximative form of silicophosphates is shown in the figure 1.1. [1] Groups of Si-O-P create poors with very variable sizes. However, it is hard to describe the exact structure of silicophosphates because silicophosphates are amorphous structure.

Hypervalent silicon

First, hypervalent molecule is a molecule with one or more elements apparently bearing more than eight electrons in their valence shells. Otherwise .... doplním podle literatury Silicon in silicophosphates is 4-, 5- and 6- coordinated and displays hypercoordinacy. Chemistry calls higher-coordinated compouds either hypercoordinated or hypervalent compounds. In generally, an atom in a compounds is called hypervalent or hypercoordinated when it creates more bonds than is the number of its valence atomic orbitals. In the case of a p-element this means that it creates more than four, usually five or six, bonds. Silicophosphate strucutres can be thought of as arising from silicates by substituting some of silicon atoms with P-OH units. Silicon and phosphourus are namely exchangable in compounds. Silicon and phosphorus are namely exchangeable in compounds

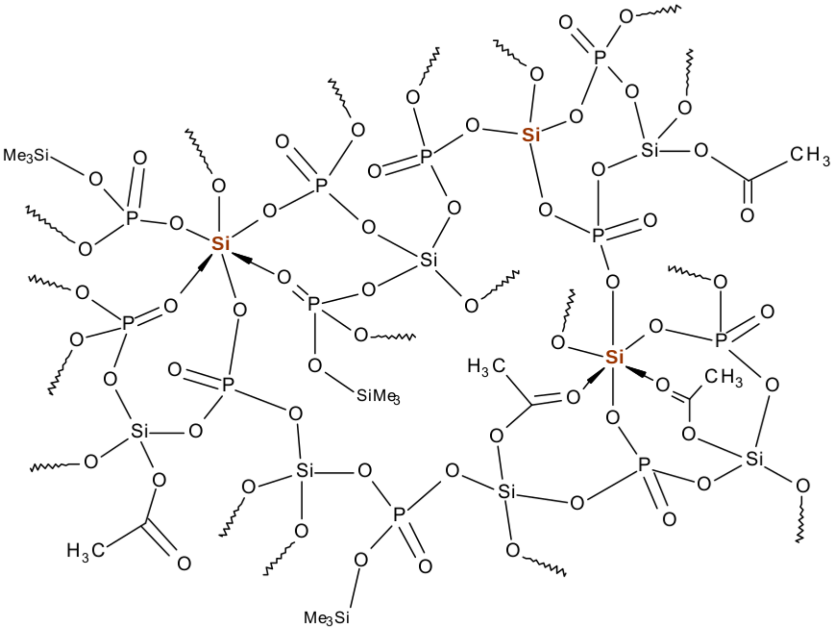


Figure 1.1: Silicophosphat's net [1].

Hypervalent silicon compounds with the most electronegative ligand possible, fluorine, have been known since nineteenth century. one of the first was $(SiF_6)^{2-}$ and $(Si(NH_2)_2F_3)^{2-}$. In the twentieth, century study of hypervalent silicon's compounds expanded, nevertheless advanced structures were developed mostly in the last decade. A detailed analysis of structures, bonding, and synthetic utility of hypervalent silicon compounds is given in e.g in ref [2].

Physical and chemical properties

Silicophosphates have unusual physical and chemical properties. An electronic characteristics of a Lewis acid is empty molecular orbital lying in energy sufficiently close to the occupied MO of a conjugated base. There is a strong influence of electro-negativity donors in bonds between silicon and donor's elements. Donors such as C, N, O, F and Cl support increasing coordination of Si. The strongest electronegative element is fluorine, hence first structure with hexacoordinated silicon contains six flurines. After that,ligands have been synthetised hexacoodinated structures with oxygen and/or nitrogen. In a tetracoordinated strucutre, silicon atom invests all of its valencce electrons in the bonding. Hence, upon increasing silicon coordination from four to five or six, silicon can offer only empty orbitals but no electrons, acting thius as a Lewis acid.
Bond between silicon and oxygens belong to a good lewis acids. Whereas the SiO_4 unit is empirically known to be sufficiently Lewis acidic to make silicon reactive towards Lewis base, upon substitution of oxygen by carbon, the ability to create five or six coordination is lost. Same phenomenom has been onserved in the experimental studies of Stýskalík et all **??**, leading to a hypothesis of decreased silicon Lewis acidity upon creating direct Si-C bond. Pentavalent silicon is better Lewis acid than fourcoordinated structure and supports hypervalency.[2]

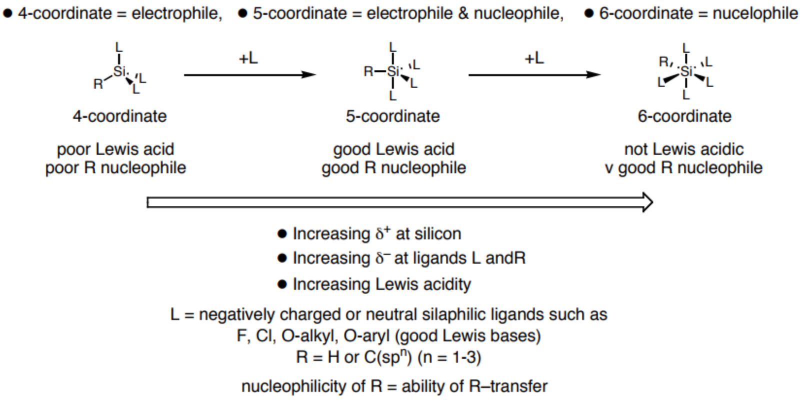

● 4-coordinate = electrophile, ● 5-coordinate = electrophile & nucleophile, ● 6-coordinate = nucelophile
+L
+L
4-coordinate
poor Lewis acid
poor R nucleophile
5-coordinate
good Lewis acid
good R nucleophile
6-coordinate
not Lewis acidic
v good R nucleophile
● Increasing δ^+ at silicon
● Increasing δ^- at ligands L andR
● Increasing Lewis acidity
L = negatively charged or neutral silaphilic ligands such as
F, Cl, O-alkyl, O-aryl (good Lewis bases)
R = H or C(sp^n) (n = 1-3)
nucleophilicity of R = ability of R–transfer

Figure 1.2: [3]

Explanation of penta- and hexavalency was frequently discussed. First explanation of hypervalent coordination was using sp3d2 hybridization. Disadvantages of this claim is high energy of the sp3d2 hybridization. Energy of 3d orbitals is relatively high thus it is accepted that role of 3d orbital is not significant. Permission of pentavalency is determined by 3c-4e bonds, show in figure .... . Hypervalent compounds are more lewis acids because of d+ effect at the central silicon. The reason is transformation of the electron density to the ligands atoms because of non-bonding MO. This electron density distribution stabilizes structure. For this reason electronegative elements occurs in hypervalents compounds. Explanation of this phenomenon gives Ben's rule: "Electronegative elements prefer bonds with more p-character".[3]

Another intepretation of hypercoordination is subsubsection namebased on the higher ionicity of the silicon bonds than in the corresponding tetrahedral species. Moreover, behavior and properties of Si-E compounds strongly depend on atom E and steric and electronis constraints. Behavior of silicon bonds can be divided into ionic, sigma bonds and dative interactions. [2]
For this reason we decided to compare Lewis acidity in order to determine stability of parts of silicon. Moreover we wanted to find the parameter, which determines the size of pores. I was interested in molecular orbitals, which could give us a lot of information about molecules, bonds, structure, acidity e.g. Analysis were made by density functional theory, which ranks among quantum chemistry methods. In addition, similar analysis was based on natural bond orbitals, which gets better practical view on chemical bond. Natural bond orbitals help with a transformation from a number to a chemical sense.

1.2 Methods of quantum chemistry

Chemical properties are obviously determine by electrons. Behavior of electrons is desribed by Schrödiger equation. This is a second-order differential equation and exact solution exists only for system with two particles. Therefor, it is nessesary to use an aproximation in chemical applications. The basis are Born-Oppenheimer aproximation and

Slaters determinant. Born-Oppenheimer approximation assumes, that movement of nuclei and electrons can be separated. Wavefunctions is broken into two parts, electronic and nuclear 1.1. The solution reduces to 3N spatial coordinates. Furtheremore, nuclei are fixed in a certain configuration, obviously the equilibrium configuration. In the second step we get potencial energy surface for each geometry and Schrödinger equation depends only on 3N spatial coordinates of electrons.

$$\Psi_{total} = \Psi_{electronic} \cdot \Psi_{nuclear} \tag{1.1}$$

Results are energies and configuration of electrons for each geometry of nuclei.

$$\Psi_{total} = \Psi_{electronic} \cdot \Psi_{nuclear} \tag{1.2}$$

Slater determinat is one ways to write the Schrödinger equation. Slater determinat consists of atoms orbitals as a product of N one-electron wavefunction. Atoms orbitals must be orthogonal and orthonormal.

$$S_{ii} = \int \psi_i * \psi_i dxdydz = 1 \ \wedge \ S_{ij} = \int \psi_i * \psi_j dxdydz = 0 \tag{1.3}$$

$$\psi = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_1(1)\alpha(1) & \psi_1(1)\beta(1) & \dots & \psi_{n/2}(1)\beta(1) \\ \psi_1(2)\alpha(2) & \psi_1(2)\beta(2) & \dots & \psi_{n/2}(2)\beta(2) \\ \vdots & \vdots & \ddots & \vdots \\ \psi_1(n)\alpha(n) & \psi_1(n)\beta(n) & \dots & \psi_{n/2}(n)\beta(n) \end{vmatrix} \tag{1.4}$$

The next step is Hartre-Fock method (HF), sometimes it is called self-consisted method. HF use the principles from simply Harrtre method. Harrtree method calculates the final field from the average field of electrons. Focks equations gives the antisymmetry of wavefunction, thus Hartree-Fock methods. It doesn't contain correlation of electron's movements. Extension of HF methods are Many-Body Pertrubation theory (MBPT), Configuration Interaction (CI), Coupled Cluster methods (CC). Time complexity of those methods is shown in the picture. Advantage of methods is accuracy. The most suitable energy is minimal energy. Minimal energy can be found using a variation principe.

1.2.1 Basis Sets

Experimental data helps to select computational methods. One of this approach is a model of basis sets. Molecular orbitals are searched for as a combination of basis function's set. According to a qantum mechanics postulate on the completencess of hermitian operator eigenvalue set, any molecular orbitals can be expressed as na linear combination of atoms orbitals (LCAO). The atom orbitals are concentionally expressed as linear combinations of GTOs and STOs. However, a complete basis set consists of an infinite number of function which makes the solution of the problem unachievable. Thus, suitable finite basis sets have been developed which, via a proper blance in error cancellation, provide sufficienty accurate results at a reasonable price. Each of the available electron correlation methods has a differennt computational scaling with the number of electrons (determing the number of occupied MOs) and basis sets (determing the number of virtual MOs).

Minimum basis set contains electrons in a ground state. On the other side, expanding basis set consists polarizations functions or diffuse function. Basic types of basis set for atoms orbitals are hydrogen function, Slaters function and Gaussian function. The disadvantage of hydrogen function is duration. STO does not have any radial nodes and it scales not linearly. An appropriate approximation is Gaussians orbitals. Advantages are sum of GTO is also GTO. On the contrary, it misinterpreted behaviour on the nuclei.[4] Atomic Natural Orbitals Basis Sets is an example of contraction basis. Natural orbitals diagonalize the density matrix. The number of electrons in an orbital is an orbital occupation number.

Effective Core Potential Basis Sets

A system with a large number of core electrons, obviously after the third period, is time-consuming. From the point of view of chemical bonding, explicit inclusion of core electrons is much less important. The same situation occurs with too many atoms in the system. Simply, system or molecules are too large. In both cases, core electrons are modelled by a suitable function. ECP has four major steps. First, all electron wave function is generated for an atom with Hartree-Fock calculation. Valence orbitals are replaced by a set of nodeless pseudo-orbitals.

1.3 Density functional theory (DFT)

The electronic structure of any system of chemical interest is desribed by the many electrons wavefunction. The three way of describing electron correlations are to be discussed in section 1.2. Here I would just say that the traditional ab inito ways of including elctron correlation have two basis disadvantages: computational requirements and conceptual complexity.

Density functional theory[1] attempts to provide a solution for larger systems. The concept DFT is ingenious in looking at the electron structure from a completely different perspective. DFT is a quantum mechanical modelling used in chemistry, physics and materials science. Between electrons density of system and energy exists correspondence. Advantages of DFT include, that it is a function of three variables, independent on the number of electrons thus a number of variables are independent of the system size. Correlation energy is part of the result from DFT. Energy is determined as a functional of electronic density. Exact functional between energy and electron density is not known yet. Functional could be divided into three parts, as a wavefunction. Kinetic energy, an attraction between the nuclei and electrons and electron-electron repulsion. E-E repulsion consists of Coulomb part and Exchange part. This model is an approximation for electron gas, for this reason, it is inapplicable in chemistry. On the other hand, it is an appropriate method to start.

The disadvantage is a non-interacting uniform electron. Error in total energy is 15-50%. Molecules and bonds don't exist in this model.[5]

Contemporary DFT methods were born in 1964 as the result of two theorems. It took almost 40 years from Thomas-Fermi models. The first Hohenberg-Kohn theorems(H-K) speaks about ground state. The external potential V_ext is a unique functional of ϱ. All properties of the ground state of many electrons system are determined by an electronic density. On the other hand, it must be said, that density determines just ground state. The density of excited state cannot be used. It depends only on three spatial coordinates and due to it is better for larger systems. Electron density is provided by the second theorem. Moreover, the second theorem proves, that founded density is the only one right. It uses variation principle to determine electron density without wavefunction. Right electron's density must have lowest and the most exact energy. The energy of exact ground state must be lower than energy of others electron's density. Weakness is the kinetic energy of electrons, correlations and exchange effects. For computational chemistry are much better Kohn-Sham's orbital. Kinetic energy is split into two parts. One exacts part and correction term.[5][6] Slater determinant corresponds to interacting electrons. Exact kinetic energy is connected with natural orbitals.

---

[1] In mathematical analysis, it refers to a mapping from a vector space V into a field such as the real or complex numbers.

Minimum of the energy functional represents the ground state of many-electron system.

$$E[\varrho] = \int \varrho(r)v(r)dr + F[\varrho] \quad F[\varrho] = T[\varrho] + V_{ee}[\varrho] \tag{1.5}$$

Tomas-Fermi model lose accurac because it uses an electron density alone. Kohn-Sham indirect approach to the kinetic energy $T[\varrho]$ is ingenious and turn density functional theory into a practical tool for rigorous calculations. [7]

1.4 Natural Bond Orbital

There are many types of analysis molecular wavefunction. SCHE provides energy for each wavefunction. Wavefunction describes position of electrons and nuclei. It is possible to determine whether two atoms are bonded? A good example of parameters which could provide molecular properties is an atomic charge. Common methods for assigning a charge to a given electron is an analysis based on basics function, electrostatic potential, wavefunction, localized orbitals or natural bond orbitals. The first excess uses MO and DS(density matrix) and Mulliken Population Analysis. Mathematical it is hard to indicate the bests result. Set of population charges does not correspond to real multipole moments,... The charge could be much better described with electrostatic potential. The charge is deeply rooted in force field method. Non-bonded interaction is described in term of electrostatic interaction. the mathematically accurate method is AIM (atoms in the molecule). Electron density could be analyzed as a normal function - maxima, minima or saddle points. The border between two atoms in three-dimensional space is spacious with two dimensions. Another approach is Localized Orbitals. The last on is Natural Orbitals (NO). The first-order density matrix is diagonalized and its eigenvectors are called Natural orbitals. Eigenvalues are occupation number. Natural orbitals provide the fastest convergence. Natural bond may describe distribution of electron and derive atomic charge and molecular bonds.[5]

Natural Orbitals are theoretical approximation which determines electron density in atoms. This approach corresponds with Lewis structures. Natural Orbitals were introduced in 1955 by Per-Olov Lödwin. Orbitals could be created from Slaters determinant. Obviously, Kohn-Sham orbitals do not have physical meaning and there is a problem with interpretation. Although, HF and K-S orbitals could be used for a better set of orbitals, called natural bond orbital. Natural orbitals are created by diagonalising the distance matrix. (NBO program)

Better set orbitals are called 'natural' and they are able to describe correlation ϱ(r). Natural orbitals have maximum occupancy and they are determined from wavefunction itself.

1.5 Hard and Soft Acid and Basis in theory

Chemical hardness and softness are significant for experimental chemistry. Stability of reaction product could be predicted by hardness and softness of molecule. It is observed that hard molecule with hard molecule should give the stable product as well as a soft molecule with the soft molecule. Global softness and global hardness are both used for the whole molecule. Individual atoms have local softness and hardness. It could be interpreted as a local charge. Those parameters can be indirectly obtained from ab initio calculation. Global properties come from energies of HOMO and LUMO orbitals. Local properties are a little bit difficult. Local properties are dealing with calculated Fukui equation. Fukui functions describe which atoms in a molecule will lose or accept an electron. It is something like reactivity indices. Chemical interpretations are the ability of a nucleophile or an electrophilic attack. As well as it tells us behaviour in external electric

field and polarization. This is connected with electron density and DFT methods.

Electrophilicity of atom A in molecule M with N electrons.

$$f_A^+ = P_A(N+1) - P_A(N) \tag{1.6}$$

Nucleophilicity of atom A in molecule M with N electrons

$$f_A^- = P - A(N) - P_A(N-1) \tag{1.7}$$

Radical attack susceptibility of atom A in molecule M with N electrons.

$$f_A^0 = \frac{1}{2}[P_{(}N+1) - P_A(N-1)] \tag{1.8}$$

Finding occupation number on each atom is really sensitive to the selection of basis sets. A large basis set gives wrong results.

1.6 Výpočetní část

Výpočetní část byla rozdělena do tří částí. První část se zabývá stukturami, druhá část dává podrobnější pohled na vazby ve zvolených strukturách a třetí, poslední, část se zaměřuje na spektroskopii. Cílem strukturní bylo modelovat části struktur silikofosfátů metodami DFT. Struktura silikofosfátu byla rozdělena do tři skupin, aby co nejlépe popsala jevy, které se tam objevují. Vazby byly analyzovány metodou NBO a analýzou složení kanonických orbitalů. Poslední část, která se věnuje spektroskopii, dává pohled na NMR parametry.

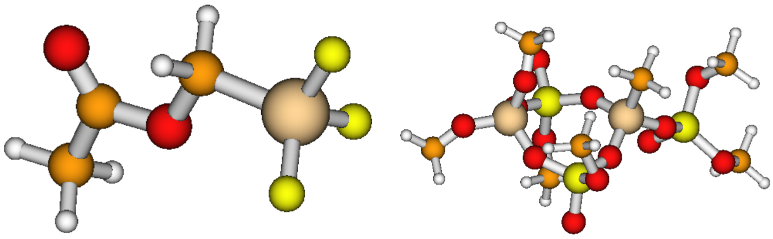
1.6.1 Struktury

Struktury pro teoretickou část jsou rozděleny podle velikosti a zároveň podle stupně koordinace křemíku.

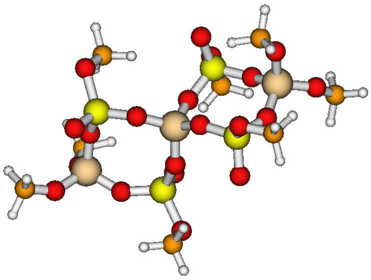
Malé modely

Středně velké modely

Tato část se věňuje nejmenším možným modelům, které již tvoří uvnitř svých struktur cyklus. Jako referenční molekula byl použita



(a) (acetylmethoxyl)trifluorsilan (b)



(c)

Figure 1.3:

(acetylmethoxyl)trifluorsilan z článku **??**. Strutktura (acetylmethoxyl)trifluorsilan slouží jako model křemíku v koordinaci čtyři, který má ve svém okolí vysoce elektronegativní atomy

Velké modely

1.6.2 Vazby

1.6.3 Spektroskopi

Table 1.2: Bar

si_model_orezany	si_model_methy	acetylmethyltrifluorsilan	
struktura			
E_homo	-0.29772	-0.28758	
E_lumo	-0.00217	0.04007	
Si s	65,16 %	191	63 %
C s	-	120	44 %
O s	65,28 %	66	10 %
Si p	0,94 %	12	89 %
C p		1	84 %
O p	13,20 %	19	28 % height

Bibliography

1. STÝSKALÍK, Aleš. *Synthesis of metallophosphate materials by non-hydrolytic methods [online]*. 2015 [cit. 2016-05-01]. Available also from: http://is.muni.cz/th/211138/prif_d/. Disertační práce. Masarykova univerzita, Přírodovědecká fakulta, Brno. Supervised by Jiří PINKAS.
2. WAGLER, Jörg; BÖHME, Uwe; KROKE, Edwin. Higher-Coordinated Molecular Silicon Compounds. In: *Functional Molecular Silicon Compounds I: Regular Oxidation States*. Ed. by SCHESCHKEWITZ, David. Cham: Springer International Publishing, 2014, pp. 29–105. ISBN 978-3-319-03620-5. Available from DOI: 10.1007/430_2013_118.
3. STORER, Ian. *Hypervalent Silicon: Bonding, Properties and Synthetic Utility*. MacMillan Group Meeting, 20th July, 2005.
4. LOWE, J.P.; PETERSON, K. *Quantum Chemistry*. Elsevier Science, 2011. ISBN 9780080470788. Available also from: https://books.google.cz/books?id=OOmGAwAAQBAJ.
5. JENSEN, F. *Introduction to Computational Chemistry*. Wiley, 2007. ISBN 9780470058046. Available also from: https://books.google.cz/books?id=RDIG48UcZfYC.
6. KOCH, Wolfram; HOLTHAUSEN, Max C. *A chemist's guide to density functional theory*. John Wiley & Sons, 2000.
7. PARR, R.G.; WEITAO, Y. *Density-Functional Theory of Atoms and Molecules*. Oxford University Press, 1994. International Series of Monographs on Chemistry. ISBN 9780195357738. Available also from: https://books.google.cz/books?id=mGOpScSIwU4C.