

MASARYKOVA UNIVERZITA  
PŘÍRODOVĚDECKÁ FAKULTA  
DEPARTMENT OF CHEMISTRY

# Diplomová práce

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

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

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Podpis autora



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# 1 Introduction

## 1.1 Experiment X

The goal of the thesis was to verify experimental results provided by Mgr. Aleš Stýskalík, PhD. His work was focused on silicophosphates and hypervalent silicon. Concept of hypervalent molecules is a little bit confusing. It is possible to find a one signification for two different phenomenon. First, hypervalent molecule is a molecule with one or more element apparently bearing more than eight electrons in their valence shells. Otherwise .... doplním podle literatury

### 1.1.1 Silicophosphates

Silicophosphates are important advanced technology material consisting of Si-O-P group most often. Silicon and phosphorus are close together in periodic table of elements hence they have similar size. For this reason, silicon and phosphorus are easily exchangeable in compounds. Both elements occur in minerals and other oxidic materials, generally surrounded by four oxygen atoms in nature. Moreover, they have extraordinary physical properties like Brønsted acidity or high proton conductivity. In future they can be applied as catalysts, electrolytes, optical glasses, and biocompatible materials. Approximative form of silicophosphates is in the picture 1.1. [1] Groups of Si-O-P create pores with very variable sizes. On the other hand, it is hard to describe exact structure of silicophosphates because silicophosphates are amorphous structure.

### Hypervalent silicon

Silicon creates binary phases, halides, hydrides or metal organic and organometallic silicon compounds. Silicon in silicophosphates is 4-, 5- and 6- coordinated and occurs hypercoordination. Chemistry of higher-coordinated compounds called hypercoordinated or hypervalent compounds. On the other hand, detailed explanation of higher-coordinated compounds remain limited. Silicon is similar to carbon and both create fourfold coordinated in most cases. Silicon observes

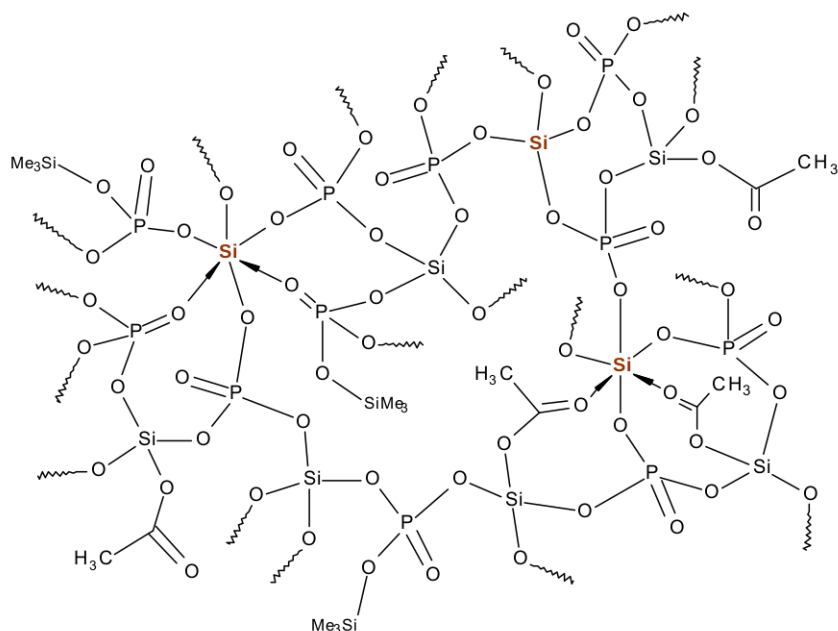


Figure 1.1: Silicophosphat's net [1].

in the third periods thus silicon has sufficient amount of orbital in order to create five or six bonds.  $(\text{SiF}_6)^{2-}$  and  $(\text{Si}(\text{NH}_2)_2\text{F}_3)^{2-}$  is long known silicon structure with six bonds. First structure were already known in the nineteenth centuries. In the twentieth centuries study of silicon's compound expanded, nevertheless advanced structures were developed in the last decade. Detailed analysis of acquired structures provided information and insight into structure and bonding in hypercoordinated silicon structures. [2]

### Physical and chemical properties

Silicophosphates have unusual physical and chemical properties and they could be used in an industry. There is a strong influence of donor electronegativity 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 fluorines. After that there was developed hexacoordinated structure with oxygen or nitrogen. In contrast, carbon is above silicon and it is capable of very different bonding characteristics.

Creating of hexacoordinated structure determines lewis acidity. Good lewis acid has a vacant orbital, thus structure has enough space to create another bonds. Bond between silicon and oxygens belongs to a good lewis acids. In contrast, bond between silicon and carbon is little acidic thus creation hexacoordinated structure is disabled. Pentavalency silicon is better Lewis acid than fourcoordinated structure and support hypervalency.[2]

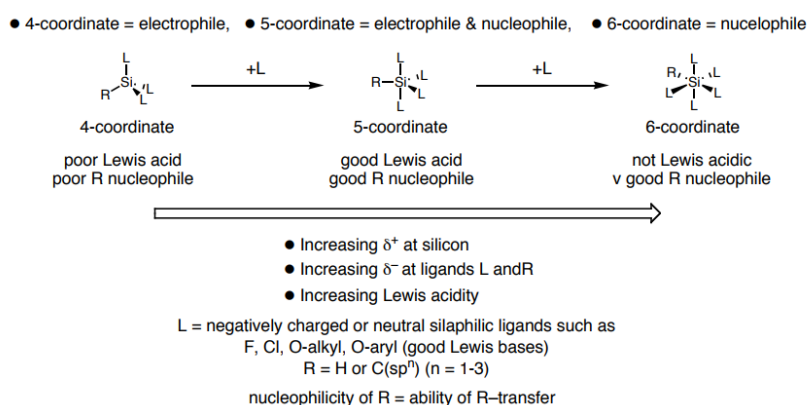


Figure 1.2: [3]

Explanation of penta- and hexavalency was frequently discussed. First explanation of hypervalent coordination was with sp<sup>3</sup>d<sup>2</sup> hybridization. Disadvantages of this claim is high energy of the sp<sup>3</sup>d<sup>2</sup> hybridization. Energy of 3d orbital is relatively high thus it is accepted that role of 3d orbital is not significant. Permission pentavalency determines 3c-4e bonds, picture .... . Hypervalent compounds is more Lewis acids because of d<sup>+</sup> effect at the central silicon. The reason is transformation all of the electron density on 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 interpretation of hypercoordination is subsection name-based on the higher ionicity of the silicon bonds than in the corresponding tetrahedral species. Moreover, behaviour and properties of Si-E compounds strongly depends on atom E and steric and electronic constraints. Behaviour 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 am interested in molecular orbitals, which could give us a lot of information about molecules, bonds, structure, acidity etc. Analysis was 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 determined by electrons. Behavior of electrons is described by Schrödinger equation. This is a second-order differential equation and exact solution exists only for system with two particles. Therefore, it is necessary to use an approximation in chemical applications. The basis are Born-Oppenheimer approximation and Slater's 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. Furthermore, nuclei are fixed in a certain configuration, obviously the equilibrium configuration. In the second step we get potential energy surface for each geometry and Schrödinger equation depends only on 3N spatial coordinates of electrons.

$$\Psi_{total} = \Psi_{electronic} \cdot \Psi_{nuclear} \quad (1.1)$$

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

$$\Psi_{total} = \Psi_{electronic} \cdot \Psi_{nuclear} \quad (1.2)$$

Slater determinant is one way to write the Schrödinger equation. Slater determinant consists of atomic orbitals as a product of  $N$  one-electron wavefunctions. Atomic orbitals must be orthogonal and orthonormal.

$$S_{ii} = \int \psi_i^* \psi_i dx dy dz = 1 \wedge S_{ij} = \int \psi_i^* \psi_j dx dy dz = 0 \quad (1.3)$$

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

The next step is Hartree-Fock method (HF), sometimes it is called self-consistent method. HF uses the principles from the simple Hartree method. Hartree method calculates the final field from the average field of electrons. Fock's equations give the antisymmetry of wavefunction, thus Hartree-Fock methods. It doesn't contain correlation of electron's movements. Extension of HF methods are Many-Body Perturbation 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 principle.

### 1.2.1 Basis Sets

Experimental data helps to select computational methods. One of these approaches is a model of basis sets. Molecular orbitals are searched for as a combination of basis functions' set. According to a quantum mechanics postulate on the completeness of hermitian operator eigenvalue set, any molecular orbitals can be expressed as a linear combination of atomic orbitals (LCAO). The atomic orbitals are conventionally expressed as linear combinations of GTOs and STOs. However, a complete basis set consists of an infinite number of functions which makes the solution of the problem unachievable. Thus, suitable finite basis sets have been developed which, via a proper balance in error cancellation, provide

sufficiently accurate results at a reasonable price. Each of the available electron correlation methods has a different computational scaling with the number of electrons (determining the number of occupied MOs) and basis sets (determining 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, Slater's 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 described by the many electrons wavefunction. The three ways of describing electron correlations are to be discussed in section 1.2. Here I would just say that the traditional ab initio ways of including electron correlation have two basic disadvantages: computational requirements and conceptual complexity.



Density functional theory<sup>1</sup> 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  $\rho$ . 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

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

term.[5][6] Slater determinant corresponds to interacting electrons. Exact kinetic energy is connected with natural orbitals.

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

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

Tomas-Fermi model lose accurac because it uses an electron density alone. Kohn-Sham indirect approach to the kinetic energy  $T[\rho]$  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 best 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 one 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  $\rho(r)$ . 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.

$$f_A^+ = P_A(N+1) - P_A(N) \quad (1.6)$$

Nucleophilicity of atom A in molecule M with N electrons

$$f_A^- = P - A(N) - P_A(N-1) \quad (1.7)$$

## 1. INTRODUCTION

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

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

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

### 1.6 •

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