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Department of Chemistry

Diplomová práce

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

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Abstrakt

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Abstract

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Poděkování

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s využitím informačních zdrojů, které jsou v práci citovány.

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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 moleculs 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 ....

1.1.1 Silicophosphates

Silicophoshates consist of Si-O-P group. Silicon and phosphorus are close together in periodic table. For this reason, silicon and phoshopurs have similar size, therefore they are easily exchangeable. Silicophosphates are advamced technology material. Both elements occure in minerals and other oxidic materials, generally surrounded by four oxygen atoms in nature. Moreover, they have extraordinary parthysical 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] Si-O-P create poors with very different size. On the other hand, it is hard to desribe exact structure of silicophosphates. Silicon in silicophosphates is 4-, 5- and 6- coordinated. For this reason it is observed different poors.

Hypervalent silicon

Silicon is similar to carbon and both create fourfold coortinated in most cases.Silicon observes in the third periods thus slicon has sufficiant amount of orbital in order to creates five or six bonds. $(SiF_6)^{2-}$ and $(Si(NH_2)_2F_3)^{2-}$ is long known strucutre with sixs bonds. First structure were known in the nineteeth centuries. Study about silicon expanded in the twentieth centuries, nevethlesess advances strucutre weren developed in the last decade. Obtained strucutre were analyzed

and details information about structure provided detail insight into strucutre and bonding in hypercoordinated silicons strucutres. Silicon creates also binary phases, halides, hydrides or metal organic and organometallic silicon compounds. Chemistry of higher-coordinated compouds called hypercoordinated or hypervalent compounds. On the other hand, detailed explanation of higher-coordintaed compounds remain limited. (clanek Higher-Coordinated Molecular Silicon Compounds, Kroke)

Physical and chemical properties

There is a strong influence of donors electronegativity. Donor such as C, N, O, F and Cl increase coordination of Si. First structure with hexacoordinated silicon contains fluor with the the strongest electronegativity. After that there was developed hexacoodinated structure with oxygen. Parametrs to determine ability of creating hexacoordinated structre Creating of hexacoordinated strucutre determines lewis acidity. Good lewis acid has a vacant orbital, thus strucutre has enough orbital to create another bonds. Bond Si-O belongs to a good lewis acid. In contrast, bond Si-C is little acidic thus creation hexacoodinated strucutre is disabled. Pentavalency silicon

Explanation of hexacoordinates was frequentally discussed. First explanation was with sp3d2 hybridization. Disadvantages of this claim is energy of the 3d hybridization. Energy of 3d orbitaly is relatively high thus it is accepted that role of 3d orbital is not significant. Another intepretation of hypercoordination is subsubsection namebased on the higer 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 electronis constraints. Behaviour of silicon bonds can be divided into ionic, sigma bonds and dative interactions.

Physical and chemical properties

Silicon can adopt 4-,5- and 6- coordinate complexes, picture 1.2. Degree of cordination determines chemical properties.
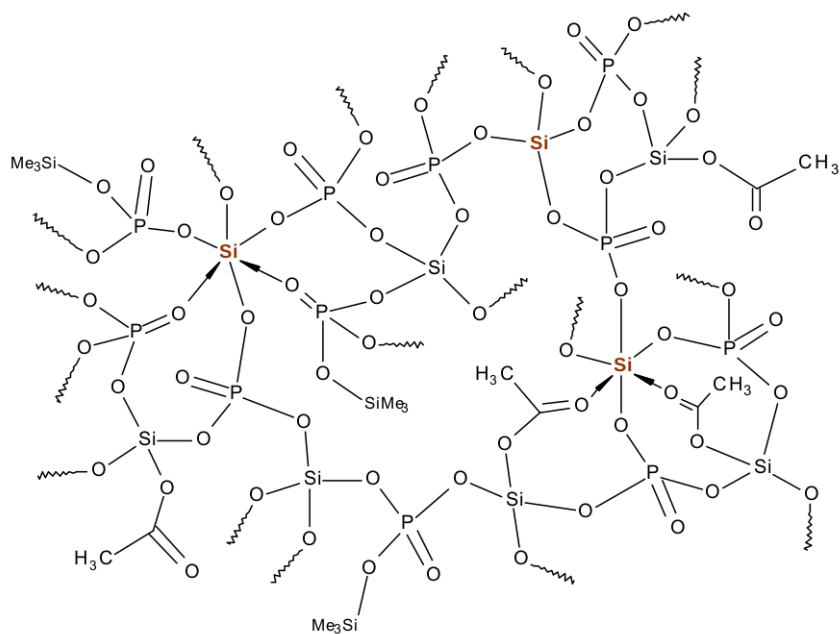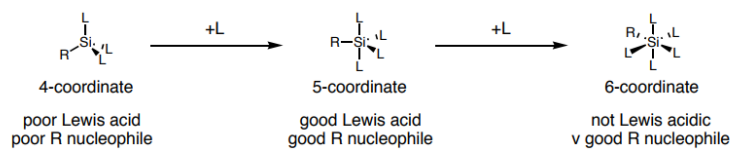
Figure 1.1: Silicophosphat's net [1].

- 4-coordinate = electrophile,   - 5-coordinate = electrophile & nucleophile,   - 6-coordinate = nucelophile

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: [2]

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.[3] 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.[4]

Contemporary DFT methods were born in 1964 as the result of two theorems. It took almost 40 years from Thomas-Fermi models.

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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.

The first Hohenberg-Kohn theorems(H-K) speaks about ground state. The external potential $V_e xt$ 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.[4][5] 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.

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

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. [6]

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.[4]

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 $\varrho(r)$. 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 •

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