Review

of the materials submitted for participation in a competition for the academic position of "**Professor**" in the field of higher education 4. "Natural Sciences, Mathematics and Informatics", professional field 4.2. "Chemical Sciences" (**Theoretical Chemistry**), announced in State Gazette, issue 105 of 11.12.2020 for the needs of the Faculty of Chemistry and Pharmacy at Sofia University "St. Cl. Ohridski "

The only candidate in the current competition for the academic position (AD) "**Professor**" in a professional field 4.2. "Chemical Sciences" (**Theoretical Chemistry**) ***is Assoc. Prof. Dr. Petko Stoev Petkov*** (SCOPUS Author ID 57209563597; Web of Science ResearcherID: R-4168-2016). The documents submitted by the candidate are in compliance with the requirements of the Law for development of the academic staff in Republic of Bulgaria and the Regulations for its implementation, the Regulations for the terms and conditions for acquiring scientific degrees and holding academic positions at Sofia University "St. Cl. Ohridski", as well as with the Recommended Criteria of the Faculty of Chemistry and Pharmacy, Sofia University, for acquiring scientific degrees and holding academic positions for professional field 4.2 "Chemical Sciences". The reference for the fulfillment of the minimum national requirements under art. 2b (2) of the Law for development of the academic staff in Republic of Bulgaria, as well as with the Recommended Criteria of the Faculty of Chemistry and Pharmacy, Sofia University, in Professional field 4.2. "Chemical Sciences", for academic position "Professor", shows that Assoc. Prof. Dr. Petkov fulfills and significantly exceeds the required minimum in all indicators.

Assoc. Prof. Dr. Petkov graduated from the Faculty of Chemistry at Sofia University in 2004 with an average grade of excellent (6.00) and a professional qualification "Master of Computational Chemistry". In 2009 he acquired the educational and scientific degree "Doctor" in computational and theoretical chemistry. In the period 2009-2018 the candidate is assistant and chief assistant in the Faculty of Chemistry and Pharmacy, Sofia University, and in 2018 he was elected as "associate professor". Assoc. Prof. Dr. Petkov has repeatedly been a guest researcher at the Institute of Physical and Theoretical Chemistry, TU-Munich, Germany (2004, 2006), at the Jacobs University, Bremen (2009, 2010, 2011), post-PhD student at Jacobs University, Bremen (2014-2016), assistant/post-doctoral student at the Wilhelm-Ostwald Institute of the University of Leipzig (2016-2017). In 2018 he was a guest lecturer in the program "Go! Green Inter Applied Chemistry Program" at the Technical University, Gdansk, Poland. The list of research projects in which the candidate participates contains a total of 18 project topics. He is currently a team leader in the Bulgarian-French-Japanese consortium, funded by the EIG CONCERT-Japan program (MicroGreen project 2019-2022), research supervisor of a postdoctoral student in the program "Peter Beron and WE" (2021-2022) , visiting professor (Mercator Fellow) at universities in Germany (in the second stage of the project FOR 2433 "Switchable Metal-Organic Frameworks" (MOF-Switches, 2020-2022), the leader of a work package in a project from Operational Program

"Science and Education for Smart Growth" of the European Structural and Investment Funds of the EU (2017-2019).

The teaching activity of Assoc. Prof. Dr. Petko Petkov includes a number of lecture courses on the topic of the competition: Molecular modeling of materials, Hybrid QM/MM methods, Introduction to Linux programming, Quantum chemical modeling of organic systems, Organic chemistry, as well as practical classes (seminars and exercises) in Applied Quantum Chemistry, Molecular Modeling of Materials, Quantum Chemical Modeling of Organic Systems and Organic Chemistry I and II. Assoc. Prof. Dr. Petko Petkov is a successful supervisor of 4 diploma theses and co-supervisor of one post-doctoral student (2021-2022). He was a member of the organizing committees of a number of scientific forums: 1st to 17th "National Scientific Conference on Chemistry for students and PhD students", Faculty of Chemistry and Pharmacy, Sofia University, 1st to 4th "International Humboldt Conference on Computational Chemistry" and 7th FEZA Conference (2017) Sofia, Bulgaria.

Scientific publications. Assoc. Prof. Dr. Petko Petkov is a co-author of a total of 51 scientific publications, of which 49 (96%) are in journals with impact factor, 2 are in journals without impact factor and one chapter of a book. The scientific publications are very well cited, some of which have aroused a great interest in the world literature. When submitting the documents for participation in this competition, according to the Scopus database, the total number of citations of the candidate is 898. Assoc. Prof. Dr. Petko Petkov participated in the present competition for "Professor" with 20 scientific papers, all on the topic of the competition. They have been published in authoritative international journals with a high impact factor. 19 scientific articles (95%) have been published in Q1 journals, one - in Q2 journal. 235 citations were noticed during the preparation of the documents for the competition. According to Scopus, the Hirsch index of the candidate is 13. The scientific results described in the publications of Assoc. Prof. Dr. Petkov have been presented at more than 20 national and international forums as oral presentations or poster. Assoc. Professor Petkov has presented a Habilitation thesis on the topic: "Computational modeling of the framework flexibility and electronic properties of metal-organic frameworks".

Scientific contributions. The author's reference of Dr. Petkov is comprehensive, correctly reflects the specific motivation and the course of the research, presents the most important results and conclusions and his own contributions. They consist in the development of theoretical models for quantum chemical studies of the spatial and electronic structure of coordination and organic polymers, to study the interaction of drug molecules with mesoporous materials and biopolymers, to study the spectral characteristics of molecules or clusters in different environments and for the study of the dynamics of ions with *ab initio* molecular dynamics. Dr. Petkov is skillful at application of many computational methods and techniques. As required by the good standards of computer modeling of (inorganic) periodic structures and clusters, the calculations are performed with a combination of appropriate and proven in terms of reliability and accuracy computational methods, approximations and codes, always closely related to data from advanced experiments, which draws correct and convincing conclusions. The calculations of the periodic models were

performed using the QUICKSTEP module in CP2K program code, with PBE functional, Goedecker–Teter–Hutter (GTH) pseudopotentials incorporating scalar-relativistic core corrections, Gaussian basis sets of DZVP quality and Grimme's DFT-D3 dispersion correction. Born-Oppenheimer molecular dynamics (BOMD) and well-tempered meta-dynamics (WTMetaD) have been applied to study dynamic processes. DFT(GGA+U)/PBE-D2/PAW method (VASP code) was applied to study the structure and electronic properties of 2D MOFs ($Fe_3(THT)_2(NH_4)_3$ and K_3Fe_2[PcFe–O_8]). Electronic band structure and density of states were calculated with PBE0 hybrid functional with POB-TZVP basis set and program code CRYSTAL17. The adsorption of N_2 gas was simulated by the Grand Canonical Monte Carlo (GCMC) simulations included in the MuSiC program code. The optimization of the clusters was performed with program code NWchem 6.3 at DFT level with PBE0 functional and TZVP basis.

Specific scientific contributions, results and conclusions.

1. Modeling the structure and electronic properties of coordination and organic polymers.

The research of Assoc. Prof. Dr. Petkov on the structure and properties of "breathing" metal-organic frames with pronounced structural flexibility of the crystal lattice have aroused indisputable interest and positive evaluation in the specialized literature. These studies are the basis of the Habilitation work of the candidate, which covers seven scientific publications. Through the theoretical research on the topic, Dr. Petkov added a significant part of data and conclusions about the studied systems and fenomena, which were missing and cannot be obtained from the conducted broad-spectrum experiments. The candidate's contributions consist in the development of theoretical models, and especially distinctly, in the selection of suitable computational methods, used to clarify the role of nonlinear ligands and the influence of metal ion type on the "breathing" MOFs 3D structure and properties.

- Through DFT modeling of a series of three-dimensional periodic structures, Dr. Petkov proved that the collective flexibility ("breathing") of DUT-8(Ni) is controlled by the conformation of the ligands, whereas the interligand interactions compensated the strain energy required to close the pores in the lattice. The possibility of rotation of the ligands relative to each other was studied by the method of meta-dynamics. The free energy to rotate the ligand, estimated of 20 kJ mol^{-1} per unit cell, predicted possible conformational transformation. As expected, the "flexible" form of DUT-8(Ni) was associated with a conformation in which the overlap between the ligands is energetically the most efficient.

- Analogs of DUT-8(Ni) with longer ligands were studied with *ab initio* molecular dynamics: anthracene dicarboxylic acid (nonlinear ligand) and 4,4'-biphenyl dicarboxylic acid (linear ligand). Calculations of MOFs with a nonlinear ligand showed a more efficient interaction between the ligands in the transition of the structure from open to closed form of the pores. The conclusions made are important in the structural design of MOFs with high flexibility of the crystal lattice.

- The crystal lattice dynamics of DUT-8(Ni) in "rigid" and "flexible" forms was studied by Born-Oppenheimer molecular dynamic simulations and Raman spectroscopy. The results showed that the open and closed phases of the pores can be uniquely identified by the bands of the "breathing" vibrational modes in the Raman spectra at 23 cm^{-1} and 60 cm^{-1}.

- The influence of the metal ion type (Ni^{2+}, Co^{2+}, Zn^{2+}) on the (local) structure and properties of "breathing" metal-organic lattices has been evaluated. The modeling of the three-dimensional structure of DUT-8(Co) was performed correctly in the Hubbard approximation with a mixed basis of plane waves and Gaussian functions, and with a parameter (U - J) = 2.2 eV, optimized by the candidate in the course of the calculations. The dependence of the deformation of the three-dimensional structure on the Co-ions spin state has been established. A higher stability of the closed-pore structure of DUT-8(Co) was demonstrated as compared to that of DUT-8(Ni), which is in agreement with available experimental data. The possibility to control the "breathing" ability of MOFs containing both Ni^{2+} and Co^{2+} ions was evaluated by periodic quantum chemical calculations. *Ab initio* MD simulations of an open-pore DUT-8(Zn) structure, in relation with experimental data, predicted longer Zn-Zn and some Zn-O distances, and much lower deformation energy in the closed phase than that of DUT-8(Ni) and DUT-8(Co). Therefore, DUT-8(Zn) lattice remains closed at much higher pressures during absorption of various gases and solvents.

- DFT calculations in GGA+U approximation were performed to prove the structure and the way of stacking of 2D layered MOFs, to determine the change in the electronic structure and the magnetic state in different ways of stacking and to determine the effective mass of the charge carriers.

- Data from DFT calculations, in agreement with X-ray data for the most stable 3D structure of $Fe_3(THT)_2(NH_4)_3$ confirmed the inclined AA way of stacking of the two-dimensional layers (THT = 2,3,6,7,10,11-triphenylene hexathiol). The calculated electronic band structure and density of states indicated a semiconductor character with a band gap of ~ 350 meV (~ 250 meV from IR measurements). Quantum chemical calculations established the stacking mode of 2D layers of K_3Fe_2[(phthalocyanine)Fe-O_8], which showed p-type semiconductor behavior with high charge carrier mobility and superparamagnetic nature up to 350 K.

- Data from DFT molecular modeling and structural experiments (ACHRTEM, GIWAXS) have been successfully combined to determine the molecular structure of a quasi-two-dimensional polyaniline film. Models of quasi-two-dimensional polyaniline were constructed, geometric optimization was performed and the molecular structure was proved by comparison with the experiment.

2. *Modeling the interaction of drug molecules with mesoporous materials and biopolymers.*

- Through DFT modeling of structural models of adsorbed on different carriers, *quercetin, curcumin, verapamil* (DFT/M06–2X/6–311++G**/PCM), *miltefosine* (DFT/PBE and PAW potentials with plane wave basis in VASP software package) and *doxorubicin* (classical MD

simulations), the type, stability and (local) structure of the corresponding adsorption complexes have been established. The specific interactions between the drug molecules and the functionalized carriers were estimated by the calculated adsorption energies.

3. Quantum chemical modeling of spectral characteristics of molecules or clusters in different environments.

- DFT calculations combined with femtosecond IR spectroscopy were applied to study the vibrational dynamics of O-H bonds in $Ba(ClO_4)_2x3H_2O$. For two trimers located in two adjacent parallel planes, calculations have shown that pairs of water molecules placed on opposite sides of the barium cation vibrated either in phase or in antiphase, indicating a strong interaction between adjacent trimers in the crystal lattice.

- The effect of 6-Cl and 6-Br substituents in 3-diethylphosphonocoumarin on photophysical molecular properties was studied by DFT(CAM-B3LYP/6-311+G(d,p)/PCM) and TDDFT calculations as well as by femtosecond transient absorption spectroscopy. The results of the combined study showed that upon excitation, an intramolecular charge transfer and a significant change in the molecular dipole moment take place. The results on the dynamics of excited singlet and triplet states, together with the "heavy atom effect", are important for the control of the singlet lifetime and the singlet-triplet quantum yield in these compounds.

- Theoretical considerations (DFT and BOMD) and cryogenic ion vibrational spectroscopy were used to study the structure and internal fluxionality of a B_{13}^+ cluster with a planar double-ring structure. BOMD simulations have shown that B_{13}^+ exhibits internal quasi-rotation of the rings already at 100 K. The vibrational spectra obtained from these simulations allowed extracting spectroscopic evidence for the exceptional fluxionality of B_{13}^+ from photo-dissociation spectrum in the infrared region (IRPD).

- Using combined periodic DFT and FTIR studies of nitrates formed during the co-adsorption of NO + O_2 on a surface of cerium dioxide, an extended classification of surface nitrates has been proposed, which allowed the nitrate type to be assigned to a specific set of bands in the IR spectrum. It includes the three main types of nitrates (mono-, bi- and tridentate), but also takes into account the number of metal cations to which each nitrate oxygen atom is attached.

4. Study of ions dynamics with ab-initio molecular dynamics.

- Review article on the topic exhaustively presented many studies on the position and manner of binding of alkaline and alkaline earth ions, compensating the charge of ionized groups in RNA. Crystallographic and spectroscopic (vibrational) studies, as well as simulations with *ab initio* molecular dynamics in the Born-Oppenheimer approximation are presented and analyzed. The candidate's contributions are in the conducted MD simulations, from which new data were obtained on the coordination of Na^+ and Mg^{2+} ions to phosphate groups in RNA.

- *Ab initio* calculations combined with the method of meta-dynamics have shown that protium (H) particles, but not protons (H^+), are transported through the van der Waals gaps in hexagonal boron nitride (h-BN) and molybdenum disulfide (MoS_2) crystals. These results are important for the comprehensive interpretation of experimental results on the transport of hydrogen isotopes through Van der Waals gaps and can help identify other materials for hydrogen isotope separation applications.

- Another study evaluated the ecological nature of 18 heterogeneous catalyst systems containing transition metals (Pd, Pt, V, Co, Ni, Mo, Ru, Mn, Au, Cu, Cd, Zr, Fe, Rh, Ir, Sn, Zn, Ag), which are classified according to various relevant criteria, such as toxicity of pure metals and their salts to fish, plants, rats, carcinogenicity, etc (multicriteria decision analysis approach). The assessment showed ruthenium, iron and molybdenum as the most favorable alternatives in contrast to nickel, cobalt and rhodium.

Conclusion. In the competition for the academic position "Professor", Assoc. Prof. Dr. Petko Petkov has presented a sufficient number of scientific papers published after the "Doctor" degree and the occupation of the academic position "Associate Professor". They have been published in reputable international Q1 journals with a high impact factor and have been cited very well, which is a proof of their high quality and international recognition. The candidate's research has original scientific contributions and valuable data. As a result of very intensive research work, for a relatively short period of time after the habilitation, Dr. Petkov has accumulated a lot of data, extensive experience and specific qualifications in the field of theoretical modeling of structure and properties of different coordination and organic polymers, (bio)molecules, complexes and clusters, spectral characteristics. Based on all his scientific achievements and my personal impressions, I am confidently voting "yes" for Assoc. Prof. Dr. Petko Petkov to take the academic position of "Professor" in professional field 4.2. "Chemical Sciences" (Theoretical Chemistry) at Faculty of Chemistry and Pharmacy, Sofia University.

Reviewer:

Sofia, April 04, 2021 (Natasha Trendafilova, Prof. Dr., IGIC-BAS)