REVIEW

of a dissertation for the acquisition of the educational and scientific degree "doctor"

in a professional area 4.1. Physical Sciences (Atomic and Molecular Physics)

by defense procedure at the Faculty of Physics

of Sofia University "St. Kliment Ohridski" (SU)

The review was prepared by: Prof. DSc. Elena Stoykova, Institute of Optical Materials and Technologies - Bulgarian Academy of Sciences, in her capacity as a member of the scientific jury according to Order No. RD 38-469/23.07.2024 of the Rector of Sofia University.

Title of the dissertation: " Extrapolation properties of the Morse-Long Range potential at large internuclear distances”

Author of the dissertation: Alketa Ali Sinanaj

I. GENERAL DESCRIPTION OF THE PRESENTED MATERIALS

1. **Description of the submitted documents**

The applicant, Alketa Sinanaj, has submitted a dissertation and an author's abstract, in English and Bulgarian as well as the mandatory tables for Physical Science from the Regulations for the Terms and Conditions for Acquiring Scientific Degrees and Holding Academic Positions at SU "St. Kliment Ohridski". A total of 9 other documents are also presented (higher education degree diplomas, curriculum vitae according to the European model, enrollment order and PhD training period extension order, application for preliminary defense, declaration of authorship, 3 publications on the dissertation topic) supporting the applicant's achievements. The similarity check of the dissertation shows very low values which are much lower than the accepted critical values. Alketa Sinanaj has passed all the required exams within the educational program. The documents submitted by the applicant for the defense correspond to the requirements of the Law on the development of the academic staff in the Republic of Bulgaria and its Regulations and the Regulations for the terms and conditions for acquiring scientific degrees and holding academic positions at SU "St. Kliment Ohridski".

2. Applicant’s data

The applicant Alketa Sinanaj has solid professional experience in the field of physics. After graduating in 2014 from the Department of Mathematics and Physics at University ”Aleksander Xhuvani” of Elbasan, Faculty of Natural Science, and in 2016 from Department of Physics at

University of Tirana ", Faculty of Natural Science, she became a PhD student in 2019 in the Department of Optics and Spectroscopy of the Faculty of Physics at SU "St. Kliment Ohridski". Since her graduation, she has been involved as a teacher in High school education and as an assistant lecturer at University "Aleksander Xhuvani" of Elbasan, Faculty of Natural Science, where she organizes seminars and laboratory exercises on general physics, theoretical mechanics, astronomy, experimental physics, non-destructive testing for structural integrity, materials technology and materials science, equipment and environmental monitoring. She is the author of several publications, has good software skills and has more than 10 certificates for participation in international conferences.

3. General characteristics of the applicant's scientific achievements

The dissertation under review addresses a highly significant task in the field of molecular spectroscopy which is analysis of the potential energy curves used for interpretation of the spectroscopic data. The analysis is based on the Morse long-range potential curve, a mathematical model used to approximate the potential energy of a diatomic molecule as a function of interatomic distance. The Morse long-range potential is especially valuable for studying molecular vibrations and bond dissociation, providing a more realistic description than the simple harmonic oscillator model, as it accounts for bond anharmonicity and finite dissociation energy. The mathematical expressions for the used potential energy curves must lead to flexible solutions and allow long-range approximations, as well as to ensure smooth and differentiable curves. The long-range part of the potential energy curves is of vital importance for the field of atoms cooling and trapping. The primary goal of the dissertation analysis is to develop a methodology for estimating the uncertainties of the dissociation energy and the leading dispersion coefficient - the main fitted parameters of the long-range potential - based on the uncertainties in the experimental data and theoretical predictions. To achieve this goal, the applicant has conducted an in-depth study of the theory behind potential energy curves, incorporating this knowledge into the dissertation. Along with the significance of the presented review and analysis in the dissertation, it contains specific scientific results as follows:

1) Critical review is performed of analytical potential functions for modeling high resolution experimental data in diatomic molecules in order to select a function/functions with good extrapolation properties at large interatomic distances. The Morse long range model and the Chebishev-polynomial-expansion are chosen as suitable.
2) The extrapolation properties of the Morse long-range potential are analyzed for the first time, demonstrating that accurate dissociation energy values can be obtained even when the last 10-12 energy levels are absent from the input data.

3) Determination of the leading dispersion coefficient is less reliable compared to the dissociation energy, and usage of the theoretical values for this coefficient is recommended at large extrapolations It has been estimated that even a 5% uncertainty in this coefficient has strong negative impact on the uncertainty in the dissociation energy.
4) The dissertation addresses, for the first time, a gap in understanding how the chosen model of the potential energy curve affects uncertainties in its fitted parameters. A methodology is suggested for assessment of these model-based uncertainties of the fitted parameters.

Three publications are included in the dissertation, of which two publications are from Group II (Q3 and Q4), and one publication is from Group III (SJR). Alketa Sinanai is first author in all three publications – two with impact factor and one with the SJR. Three posters were presented at international conferences in Albania, Serbia and France. The scientific publications included in the dissertation meet the minimum national requirements (according to Art. 2b, paragraphs 2 and 3 of the Law on the development of the academic staff in the Republic of Bulgaria and its Regulations) and, accordingly, the additional requirements of the SU "St. Kliment Ohridski" for the acquisition of the educational and scientific degree "doctor" in the scientific field 4. Natural sciences and professional area 4.1. Physical sciences. There is no proven plagiarism in the submitted dissertation and abstract.

4. Characteristics and assessment of the applicant's teaching activity

Applicant Alketa Sinanai has been active in training students in the Universities of Albania. As far as I know, she has no teaching activity at SU "St. Kliment Ohridski".

5. Content analysis of the applicant's scientific and applied achievements contained in the dissertation

The dissertation submitted for review contains 137 pages, 1 table, 66 figures and 79 cited sources. The dissertation consists of 8 chapters, of which Chapter 1 presents a brief survey of the methodological issues associated with solving the inverse problem of determination of potential function parameters from the spectroscopic data. The main purpose of this survey is to formulate the goals of the dissertation. The author has provided a comprehensive introduction to the theory of potential energy curves for diatomic molecules, addressing various challenges that arise when approximating the long-range portion of these curves using experimental data sets. This specific goal is implemented by including extensive review parts in Chapters 2-4 that are combined with critical analysis. This approach to presenting the dissertation results justifies the need of a more general study of the Morse long-range extrapolation properties. It helps for a deeper understanding of the methodology proposed and developed by the author for determining the model and parameters of the potential function. The main contribution of the dissertation is described in Chapter 5 and Chapter 6. Chapters 7 and 8 present some conclusions and the author contributions.

I assess the presented dissertation as a definitive scientific and practical achievement. The contributions of the dissertation can be characterized as novel approaches to improving the accuracy of spectroscopic parameters determination in diatomic molecules, an enrichment of existing knowledge in diatomic molecular spectroscopy, and the application of scientific advancements in spectroscopic practice. The dissertation results have been published in 3 publications, two of which have an impact factor and one has SJR, respectively. Dissemination of results also includes 3 poster presentations at international conferences. So far, no citations have been noticed. The main achievement of the dissertation are given below.

Chapter 2 "Energy levels of diatomic molecules" presents important and very comprehensive theoretical background as a base of the methodology proposed in the thesis. The length of this chapter is over 50 pages. It starts with very simplified models of the general form of any interatomic potential for diatomic molecules and continues with rigorous methods for determination of the energy levels of these molecules. The simplified model considers the diatomic molecule as a vibrator and a rotor and introduces molecular constants and Dunham coefficients. Vibrational and rotational spectroscopy are also analyzed. Rigorous analysis includes the Hamiltonian of a diatomic molecule and the Born-Oppenheimer approximation. Chapter 2 introduces the potential energy curve and focuses on its long-range part with an option for analytical description. Numerical solutions of one-dimensional radial Schrödinger equation are also discussed.

In Chapter 3, "Experimental determination of PECs" various analytical potentials are analyzed and compared. The potential energy curve is given as a function of the inter-nuclear distance and some model parameters, which must be adjusted accordingly to ensure correct reproduction of the experimental data within their uncertainty. As the parameters and the experimental data are related through the radial Schrödinger equations, the fitting is not linear and becomes a non-trivial task. The analyzed potentials are Morse potential, Lennard-Jones potential, expanded Morse oscillator model with its long-range properties, Morse-Lennard-Jones analytical model, model based on Chebyshev polynomials and Tiemann polynomial model. For the experimental study of the double minimum states, spline forms are discussed. The emphasis of the analysis is set on the Morse long-range potential.

Chapter 4 "Determination of the long-range part of PEC" reviews a variety of different approaches, proposed in recent experimental studies focused on determination of the long-range part of the potential from experimental data. More specifically, potential models for the ground state of Rb dimer, the ground state of Ca dimer, ground electronic states of the hydrogen halide and the ground state of NaRb are critically analyzed.

Chapter 5 “Extrapolation properties of the MLR potential” is dedicated to extrapolation properties of Morse long-range potential and the studies conducted in this Chapter are crucial for the dissertation. The main task solved in this Chapter is evaluation of reliability of estimation of the depth of the potential well and the leading long-range term. The potential curve for the ground state of calcium dimer is used as the most appropriate for testing. Evaluation is conducted with different subsets of experimental data at gradually reducing the highest vibrational number. It should be noted that a special fitting routine with a modified software is developed by the applicant. It makes possible fitting of Morse long-range and other popular potentials. The solver for the radial Schrodinger equation is built in the main program. The modified software includes singular value decomposition (SVD) approach. The applicant proves that this decomposition is very suitable for fits which weakly depend on the fitting parameters. A conclusion is made that the SVD excludes from the fit linear combinations of parameters, which weakly improve the fit quality. The parameter uncertainties for every fitted potential energy curve are estimated using the matrix of variances and covariances. Block-diagram of the fitting procedure is included with detailed description of all blocks. The IO (input-output) operations are performed in Python environment.

Chapter 6 “Results” gives the results of the performed fits for Ca dimer choosing potentials leading to dimensionless standard deviations of the calculated energies from the experimental data less than 0.64. The computations are made at different values of the maximum vibrational quantum number and for a set of parameters of the Morse long-range potential. The results are plotted as points with the dissociation energy and the leading dispersion coefficient as coordinates and the uncertainties of both parameters are also depicted on the plot. The obtained graphical representations characterize the model-dependent uncertainty of the dissociation energy and the leading dispersion coefficient. The results prove applicability of the Morse long-range potential and the possibility to obtain good extrapolation results at missing last 10-12 energy levels.

6. Critical notes and recommendations

The dissertation is a step forward in the field of high resolution spectroscopy of diatomic molecules. It offers valuable methodological solutions and provides a base for more accurate extrapolation of potential energy curves and determination of their parameters from the experimental data. The methodological level is high and the provided analyses are of useful not only for the beginners but also for the experienced researchers in the field. The dissertation is structured and written largely as a monograph. I have the following critical remarks and questions:

1.) To correspond to a monographic style, the notations should be consistent throughout the text. For example, the vibrational quantum number is not represented in the same way in the different parts of the dissertation, e.g. in formulas (2.74) – (2.78). (2.81) – (2.83), (3.6), the table on page 110 etc. Notations as ν, υ or v are introduced. The same can be said about the notation of the inter-nuclear distance. The main inconsistencies are in Chapter 6 “Results”, where notation $\nu''_{\max}$ is used to characterize the results of the simulation without being defined in the text.
2.) The author’s contributions are more concise and clear in the Abstract of the dissertation.
3.) Some important statements are not explained in details as e.g. the choice of the acceptable dimensionless standard deviations of the calculated energies from the experimental data.
4.) The dissertation will gain in quality if a more detailed description of the used experimental data is provided.
5.) Why is the Monte Carlo simulation of synthetic experimental data ineffective in solving the problem with the model dependences of the estimated uncertainties?
6.) Is it feasible to develop a deep learning training procedure to perform high quality approximations?

7. Personal impressions of the applicant

I do not know the applicant personally.

8. Conclusion

After having considered the presented dissertation work, Abstract and other materials, and based on the analysis of their significance and the scientific and applied contributions contained, I confirm that the scientific achievements meet the requirements of the Law on the development of the academic staff in the Republic of Bulgaria and its Regulations and the Regulations for the terms and conditions for acquiring scientific degrees and occupying academic positions at SU "St. Kliment Ohridski" and the Regulations for its application and the relevant Regulations of the SU "St. Kliment Ohridski" for the acquisition of the educational and scientific degree "Doctor". In particular, the applicant satisfies the minimum national requirements in the professional field and no plagiarism has been found in the dissertation, abstract and scientific works submitted for the defense.

I give my positive assessment of the dissertation work.

II. GENERAL CONCLUSION

Based on the above, I recommend to the Scientific Jury to award the educational and scientific degree "doctor" in professional area 4.1- Physical sciences to Alketa Ali Sinanai.

06.11.2024 **Signiture:**