REFEREE REPORT

on the PhD thesis

for the acquisition of the scientific degree "doctor"

in the professional research field 4.1. Physical sciences (Physics of atoms and molecules)

in defense procedure at the Faculty of Physics

at Sofia University “St. Kliment Ohridski”

The referee report was prepared by Assoc. Prof. Tsvetelina Paunska, Faculty of Physics at Sofia University "St. Kliment Ohridski," as a member of the scientific jury, according to document № РД 38-469/23.07.2024 г. of the Rector of Sofia University.

Dissertation topic: “Extrapolation properties of the Morse-Long Range potential at large internuclear distances”

Author of the thesis: Alketa Sinanaj

General description of the presented materials

1. Submitted documents

The candidate, Mrs. Alketa Sinanaj, has submitted a PhD thesis in English and an Abstract in English and Bulgarian, as well as the mandatory tables for the Faculty of Physics (FP) from the Regulations on the terms and conditions for the acquisition of scientific degrees and employment in academic positions at SU "St. Kliment Ohridski." She has submitted eleven other documents: the curriculum vitae, bachelor's and master's diploma, a declaration of admission to pre-defense, a declaration of authorship of the dissertation, a plagiarism protocol (Appendix 1), a statement on plagiarism (Appendix 2), a plagiarism report, scientific publications included in the dissertation (3), an order to extend the period of doctoral studies and a certificate of passing mandatory examinations for doctoral studies. The submitted documents are to the requirements of the Faculty of Physics at SU "St. Kliment Ohridski."

The documents presented for the defense by the candidate fulfill the requirements of the Development of Academic Staff in the Republic of Bulgaria Act, the Regulations for its application, and the Rules of Procedure and the Regulations on the Terms and Conditions for Acquisition of Scientific Degrees and Academic Positions at Sofia University “St. Kliment Ohridski.”

2. Data for applicant

The candidate, Alketa Sinanaj, started as a full-time doctoral student at the Department of Optics and Spectroscopy at the Faculty of Physics of the Sofia University "St. Kliment Ohridski" on January 7, 2019. After an interruption due to maternity leave, Ms. Sinanaj continued work on her doctoral thesis, and she finished her PhD study with the right of defense on June 24, 2024. The candidate's bachelor's degree was obtained from Alexander Juvani University in Elbasan, Albania (2011) in the Department of Mathematics and Physics. Alketa Sinanaj has a Master of Physics from the University of Tirana since 2016. The candidate's professional experience is in the field of education and science. She worked as a primary and secondary school teacher and an assistant at Alexander Juvani University. Alketa participated in numerous national and international scientific forums, internships, and training (16 in total) in Physics and Mathematics.

3. General description of the candidate's scientific achievements

The candidate's thesis is 137 pages long and consists of an Introduction, five chapters, and a bibliography including 79 cited sources. For better reading and orientation, lists of figures, tables, and abbreviations used in the text of the dissertation are also presented.

The dissertation's topic is molecular physics and, more specifically, the modeling of potential energy curves (PEC). The reconstruction of sufficiently accurate potential curves is significant in molecular spectroscopy, as it enables precise calculation of the levels' energies and the spectral lines' intensities. Ms. Sinanaj's work is focused on modeling molecular spectra, primarily the asymptotic part of the potential at large internuclear distances. The ground electronic state of the calcium dimer (Ca_2) studied in previous works was used. The results in the dissertation show that the Morse Long Range (MLR) potential model has good extrapolation properties and gives realistic values of the dissociation energy of the molecule D_e. In terms of dispersion coefficients, the determination of the leading coefficient C_6 is not as reliable, but introducing a bounded uncertainty in C_6 *significantly* reduces the uncertainty on the determination of D_e. Developing a methodology for obtaining the uncertainties of the PEC parameters resulting from the election of the model is a valuable result of the work.

There are three candidates' scientific papers, and they are described in the thesis. Two of them are in journals with an impact factor, quartiles Q3 (*Journal of Molecular Spectroscopy*) and Q4 (*Acta Phys. Polonica*), and fall into group II of the additional requirements of the Faculty of Physics. The third publication (conference report) is also indexed in the SCOPUS platform and has SJR (0.115). Alketa Sinanaj is the first author to contribute to all three scientific publications in the thesis. The candidate has participated in three scientific conferences. She was presented with two oral and one poster report. It should be noted that the candidate is the only co-author of their supervisor on all publications.

The scientific publications included in the dissertation fully cover the minimum national requirements and, accordingly, the additional requirements of SU "St. Kliment Ohridski" for acquiring the educational and scientific degree "doctor" in the relevant scientific field and professional direction. Based on the provided documents, the Author's report on the contribution nature of the works (comparison tables for the national requirements and those of the Faculty of Physics), plagiarism protocol (Appendix 1), statement on plagiarism (Appendix 2), and Application for authorship with full conviction can it was stated that: The scientific publications included in the dissertation **do not repeat** those from previous procedures for acquiring a scientific title and academic position.

The submitted dissertation and Abstract do not contain proven plagiarism. The Abstract accurately reflects the content of the dissertation.

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

In the Regulation of the SU "St. Kl. Ohridski" and Alketa Sinanaj's individual plan, there is no requirement to carry out teaching activities. The candidate's career is entirely in the field of education. However, I can conclude from Ms. Sinanaj's resume that she has extensive teaching experience. However, during her PhD studies, she did not lead exercises or seminars in the Faculty of Physics.

5. Analysis of the candidate's basic and applied scientific achievements as evident from the documents for participation in the procedure.

Although the candidate was not directly involved in experimental measurements, her work involved processing and analyzing a large amount of experimental data. That complex study requires excellent theoretical training and experience with various software products. The dissertation has formulated the goals presented in the introduction: 1) Create a methodology for assessing uncertainty in determining the parameters of the potential curve of molecules, the dissociation energy, D_e, and the main dispersion coefficient C_6. This uncertainty should depend only on the selection of the experimental data and not on the choice of model to fit the data. 2) Find a way to compare the uncertainties of D_e and C_6 from the matrix of variances and covariances with the true uncertainties. 3) To answer the question with what accuracy D_e and C_6 are determined with a limited set of experimental data. 4) Choosing a number of the coefficients in an asymptotic model, i.e., theoretical predictions, affects the accuracy with which D_e and C_6 are determined.

In **Chapter 2**, the author introduces the basics of the theory of energy levels of diatomic molecules. First, a more intuitive quantum-mechanical approach is presented, introducing the basic motions in the molecule, resulting in electronic, vibrational, and rotational energy states. Then, the author introduces the strictly theoretical description of the potential curves $U(R)$ as solutions of the radial Schrödinger equation (RSE). A basic quantum mechanical perturbation method – the inverse perturbation approach (IPA), is described, by which a PEC that matches the experimental data within its uncertainty can be recovered. This method is fundamental for obtaining accurate potential curves with available experimental data. A fitting function must be found to recover the long-range region of the potential curve (asymptotically large interatomic distance) and some parameters. Extrapolation is done through it, so it is essential to meet strict requirements.

Chapter 3 of the dissertation is dedicated to critically analyzing different types of potentials. The following potentials are considered: Morse Potential, Lennard-Jones Potential, Extended Morse Oscillator (EMO), Morse-Lennard-Jones Potential, Morse-Long-Range (MLR) Potential, Chebyshev Polynomials, Hanover Polynomials, and Spline Form. In this chapter, simulation tests were made with the most promising potential functions, fitting experimental data for the Ca2 molecule. Through Monte Carlo simulations, synthetic noise was introduced to the experimental data with standard deviation $\sigma = 0.1\ cm^{-1}$, and the generated data were fitted by changing the parametric coefficients of the potential functions. The results show that the EMO gives a reasonable value for D_e but is strongly influenced by the choice of the value of the reference radius R_{eff}. At the MLR potential, the simulations show a strong correlation between the coefficients. The choice of several parameters of the fit function is also critical. Chebyshev polynomials are also tested as a possibility to model the potential extrapolation at large internuclear distances. Like most polynomial functions, they provide easy fitting of coefficients, but correlations between parameters are significant, and spatial attention is needed when choosing an optimal set of parameters. This model can be applied with experimental data for larger internuclear distances. From the analysis and comparison of different models (functions), the author concludes that the Morse-Long-Range potential is the most suitable for the requirements set in the research.

In **Chapter 4**, the region of the potential curve at long distances is defined, and experimental data from the literature on the ground states of Rb_2, Ca_2, NaRb, and hydrogen halide molecules are analyzed. These electronic ground states have only been obtained experimentally and are cases beyond the Born-Oppenheimer approximation.

Chapter 5 of the dissertation contains the main contribution of the candidate to the research. It is dedicated to a description of the developed methodology for studying the extrapolation properties of the Morse-Long-Range potential. Experimental data on the ground state of the calcium dimer were again used for the research. (β_i, D_e, C_m, r_e) are fitted for a wide range of fixed parameters. If the obtained results for D_e and C_6 are not too scattered regardless of the choice of the fixed parameters, then the extrapolation properties of the potential are considered good. In the dissertation, the fitting procedure, which uses two programs, Betafit and IPA8, is presented in detail. The Betafit code generates MLR potential curves from a measured point potential at appropriately chosen fixed parameters. The IPA8 program actually serves to precisely refine these MLR potential curves by fitting the parameters (β_i, D_e, C_m, r_e) until differences between calculated and experimental energies with minimal uncertainty are obtained. A Python script was written to control and manage the procedure. Uncertainties are estimated using the variance and covariance matrix.

Chapter 6 graphically summarizes the results of the fitting procedure with the MLR potential. It has been proven how important the model choice is to obtain a correct value of the dissociation energy and the C_6 dispersion coefficient. This election affects the uncertainties with which the coefficients are determined. A specific result of the processing is that when two parameters, C_8 and C_{10}, are fixed, significantly lower values for the uncertainties of D_e and C_6 are obtained. The obtained results are analyzed in the context of similar studies by other authors.

This chapter investigates the influence of a limited data set on the energies of the vibrational levels for the region describing the upper regions of the potential curve. The fitting methodology with the MLR potential is applied for the hypothetical cases with known energies up to v''= 38, 35, 30, and 25. The MLR potential behavior shows unexpectedly good behavior. Even extrapolating data taking into account relatively low v'' values, the results are close to the best estimate for the dissociation energy D_e.

The main result is that, in terms of dispersion coefficients, the determination of the leading coefficient C_6 is not so reliable, but introducing a bounded uncertainty in C_6 significantly reduces the uncertainty bounds on the dissociation energy D_e.

6. Critical remarks

I have some remarks about the writing of the thesis, which are primarily concerned with the typing of the formulas and the definition of quantities. In the text, some quantities are written as "Italic" and as "Justify," which makes it difficult to read and is not correct. Formulas 2.1 (p. 17) and 2.2 (p. 19) are the same formula for the Coulomb interaction force between nuclei, i.e., the same thing is defined twice. Some formulas are missing summation subscripts (for example, formula (5.16), p. 104). In the same formula, "m" is not defined. Often in the text "σ” is written as “s”. On page 91, the ground electronic state of Ca_2 is labeled in the caption of the figure as $X^1\Sigma_g^+$, and in the main text, it is $X^1S_g^+$. These inaccuracies are common in the text, so I recommend reading the thesis carefully and improving the text! The quality of the figures in Chapter 3 could be improved!

Despite the mentioned remarks, the work has research value.

I have the following questions for the candidate:

1. Can you conclude from the research that the developed methodology can be applied to the determination of dissociation energy D_e at other molecules with electronic states similar to Ca_2?
2. The dissertation uses experimental data for the calcium dimer mainly from the article: O. Allard, C. Samuelis, A. Pashov, H. Knöckel, and E. Tiemann, "Experimental study of the Ca2 1S+1S asymptote.," Eur. Phys. J.D., vol. 26, pp. 155-164, 2003. It is clear from the presentation and from the publications made that the goal is not the processing of data from various spectral measurements, but rather the extrapolation qualities of the MLR potential. However, have you planned to apply the fitting procedure with other experimental data if suitable ones are available in the literature?

7. Personal impressions of the candidate

I have not known the candidate personally.

8. Conclusion

After reviewing the presented dissertation work, Abstract, and other materials, and based on the analysis of their significance and the scientific and scientific-applied contributions contained in them, **I confirm** that the scientific achievements meet the requirements of Development of Academic Staff in the Republic of Bulgaria Act and the Rules for its application and the relevant Regulations of the SU "St. Kliment Ohridski" for acquiring the educational and scientific degree "doctor." In particular, the candidate **satisfies** the minimum national requirements in the professional direction, as well as the minimum requirements of the Faculty of Physics, and no plagiarism has been found in the dissertation, Abstract, and scientific works submitted for the competition. I give my **positive** assessment of the dissertation work.

II. OVERALL CONCLUSION

Based on the above, I recommend that the scientific jury **award** Alketa Sinanaj the educational and scientific degree "Doctor" in professional direction 4.1 Physical Sciences after a successful defense presentation.

Tsvetelina Paunska

Digitally signed by Tsvetelina Paunska
Date: 2024.10.25 14:34:40 +03'00'

October 25, 2024 г. Reviewer Signature: ....

(Assoc. Prof. Dr. Tsvetelina Paunska)