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Report on the PhD thesis submitted by
Ms. Sangami Ganesan-Santhi
entitled
Interactions and cold collisions involving AlF molecules

The PhD thesis by Ms. Sangami Ganesan-Santhi was prepared at the Faculty of Physics, University of Warsaw, Poland under the supervision of Prof. Michał Tomza and Dr. Marcin Gronowski. The scope of this doctoral dissertation includes theoretical studies of a cold aluminium monofluoride (AlF) molecule, using *ab initio* methods, as a potential candidate for cooling to ultralow temperatures under various direct cooling techniques in the view of obtaining a stable quantum degenerate gas. The interactions of AlF molecules with helium atoms, other AlF molecules, and rubidium atoms are investigated in the context of understanding the mechanisms underlying cooling methods such as buffer-gas cooling, evaporative cooling, and sympathetic cooling. It should be emphasized that ultracold molecules enable precise control over quantum states, making them perfect for testing fundamental physical constants. Moreover, they play a key role in developing quantum technologies such as molecular clocks and quantum simulators, which could surpass current atomic-based systems in accuracy and versatility. They also open the door to discovering the truly quantum nature of matter. Therefore, the results presented in this thesis are of great importance, especially for the ongoing AlF experiments in Berlin and London.

The dissertation was written in English in a traditional format. Its layout is clear and allows easy navigation between sections. It consists of an abstract, an acknowledgment, a table of contents, eight chapters including an introduction and a summary, and an appendix (all together 116 pages long). The results presented in chapter 5 are based on the original paper: Sangami Ganesan-Santhi, Matthew D. Frye, Marcin Gronowski, and Michał Tomza, *Interactions and cold collisions of AlF in the ground and excited electronic states with He*, J. Phys. Chem. A 129 (2025) 8239-8250. The extensive bibliography includes 265 entries and contains all the most important papers related to the subject of the thesis.

In the first chapter, the Author presents the behavior of atomic and molecular systems at extremely low temperatures and emphasizes that in such a regime various quantum effects are crucial. The discussion then smoothly shifts to cold molecules and their formation. Currently, there are two main methods for creating (ultra)cold molecules: indirect and direct. The first involves combining previously prepared cold atoms by applying a magnetic field (using Feshbach resonances) or a laser light tuned to an atomic resonance frequency. Thus, molecules can be formed via magnetoassociation or photoassociation. In turn, the second method is the direct cooling of already existing molecules. Direct techniques include, among others, buffer-gas cooling, sympathetic cooling, evaporative cooling, Stark and Zeeman deceleration, laser cooling, and Sisyphus cooling. I noticed that the Author occasionally uses a lowercase letter for "Sisyphus". Let me remind that, in Greek mythology, Sisyphus was a mortal who was punished for angering the gods. Next, the Author describes applications of ultracold molecules to cold and controlled chemistry, precision measurements, and many-body physics. At the end of the chapter, an attempt is made to convince the reader that *ab initio* quantum chemistry methods are an excellent tool for studying the electronic structure and various properties of ultracold molecules. I have a stylistic comment here: in the literature, the term "ab initio" is often written in italics. In this doctoral thesis, however, three different forms appear ("*ab initio*", "ab initio", and "*ab* initio"), even close together (see pages 16-17). The Author should select one style and apply it consistently throughout the work.

The second chapter is short. It presents the research motivation and the main objective of the thesis, which is to examine, under *ab initio* quantum chemistry methods, the feasibility of cooling of the aluminium monofluoride molecule through direct techniques described in chapter 1. The studies focus primarily on determining the potential energy surfaces for the isolated AlF molecule, its interactions with a helium atom, another AlF molecule, and a rubidium atom, as well as on performing some scattering calculations. They are intended to help assess whether a given cooling method (buffer-gas cooling, evaporative cooling, sympathetic cooling) has the prospect of being applied to the system under consideration.

The third 24-page chapter introduces methods of electronic structure theory employed by the Author in *ab initio* calculations. The description starts from the Born-Oppenheimer approximation and the Hartree-Fock (HF) method, which is the fundamental variational method of quantum chemistry. In this framework, the variational function takes the form of a single Slater determinant built of orthonormal molecular spinorbitals. The chapter also addresses basis sets, including the complete basis set limit and the problem of basis set superposition error. More advanced methods, which include electron correlation, are then presented, such as the configuration interaction (CI) method, the multireference CI method, the coupled cluster (CC) method, the equation of motion CC method, and the R12 method. Moreover, the Author describes the Douglas-Kroll-Hess (DKH) and exact two-component (X2C) approaches that allow the inclusion of relativistic effects. The treatment of long-range interactions using multipole expansion is discussed, with explicit expressions for isotropic and anisotropic dispersion and induction coefficients. The second part of the chapter introduces the fundamentals of scattering theory and the concept of coupled-channels calculations. Overall, the essence of each method, approach, and

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issue is effectively captured with an appropriate level of detail and length. However, the chapter contains numerous editorial and stylistic errors, particularly related to the equations and their derivations. I have listed them below:

1) Page 26: "It can also be written in an integral form like this, When summed over $b \neq a$, we obtain ..." - It seems that a certain equation is missing. Moreover, what do the symbols a and b represent?
2) Page 26: "... orbitals ($\delta\Phi$)" → "... spinorbitals ($\delta\Phi$)"
3) Eqs. (3.14)-(3.16) are inconsistent with the remaining equations presented in the section on the Hartree-Fock method, particularly eq. (3.23). The derivation of the HF method in this section is given within the general framework using spinorbitals. However, eqs. (3.14)-(3.16), due to the factor of 2, suggest a derivation of the restricted Hartree-Fock (RHF) method for closed-shell systems, which assumes double orbital occupancy.
4) The integral symbol is repeatedly used incorrectly. The Author sometimes uses the single integral symbol for two-electron integrals, eqs. (3.19)-(3.22), as well as the double integral symbol for one-electron integrals, eq. (3.29).
5) Eq. (3.24): $\varepsilon_{ji} \rightarrow \varepsilon_{ij}$
6) Eq. (3.28): **Fc** = Sce → **Fc** = **Sc**$\boldsymbol{\epsilon}$ (**S**, **c**, $\boldsymbol{\epsilon}$ are matrices)
7) Page 28: It is written: "The single Slater determinant formed from the eigenfunctions χ_k is an eigenfunction of the Hartree-Fock Hamiltonian ..." - The functions χ_k are not the eigenfunctions; they serve as expansion functions. In practice, atomic orbitals are often used as χ_k.
8) Page 28: The upper limit of summation in $\sum_{k=1}^{1} f(k)$ is incorrect. Moreover, f is the Fock operator, hence, it should be written as $\hat{f}$.
9) In Section 3.1.6, the Author writes: "The correlation energy is defined as the difference between the Hartree-Fock energy and the exact (non-relativistic) energy, $E_{\mathrm{corr}} = \varepsilon_{\mathrm{exact}} - E_{\mathrm{HF}}$ (3.38)". To avoid ambiguity, it should be written as: "The correlation energy is defined as the difference between the exact (non-relativistic) energy and the Hartree-Fock energy, $E_{\mathrm{corr}} = \varepsilon_{\mathrm{exact}} - E_{\mathrm{HF}}$ (3.38)". The Author then adds: "According to the variational theorem, the Hartree-Fock energy is an upper bound to the exact energy. Hence, the correlation energy, E_{corr}, will always be negative". After this, the result of a correlation energy calculation, obtained within the CCSD(T)/aug-cc-pVTZ method, is given as 12214.2 cm^{-1}. Surprisingly, this result is positive. The author explains: "It is to be noted that the correlation energy reported at 12214.2 cm^{-1} is positive because it is not the total correlation energy but the contribution of correlation to the interaction energy between Al and F". In my view, the result is positive because, as can be seen in fig. 3.1 (bottom right corner), the correlation energy was calculated in the opposite manner to that defined in eq. (3.38), that is, by subtracting the energy obtained using the coupled-cluster method from the Hartree-Fock energy ($E_{\mathrm{HF}} - E_{\mathrm{CCSD(T)}}$).
10) The statement (page 32) "Pauli's principle allows the presence of at most 2 electrons in the same point in space ..." is imprecise. The Pauli principle admits a maximum of a double orbital occupation by electrons, provided they have opposite spins. Electrons with the same spin coordinate cannot reside in the same place.
11) Page 36: "... multiplying equation 3.51 from left by $\hat{U}_k$ and subtracting equation 3.51 from equation 3.50, ..." → "... multiplying equation 3.52 from left by $\hat{U}_k$ and subtracting equation 3.52 from equation 3.51, ..."
12) Page 36: "... a scalar product of equation 3.52 with ..." → "... a scalar product of equation 3.53 with ..."
13) Page 36: "We aim to solve equation 3.53 to obtain" → "We aim to solve equation 3.54 to obtain"
14) Page 36: The vertical bar "|"at the beginning of eq. (3.54) is an error as well as "$a_{ab\ldots}^{mn\ldots}$" in the bra component, $a_{ab\ldots}^{mn\ldots} \rightarrow {}_{ab\ldots}^{mn\ldots}$.
15) In the Dirac Hamiltonian, eq. (3.55), a factor of 4 appears. Where does this come from? Shouldn't the electron (rest) mass be there instead? Furthermore, the quantity $\boldsymbol{\beta}$ is incorrectly defined in the Dirac Hamiltonian.

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It must take the form $\boldsymbol{\beta} = \begin{pmatrix} \boldsymbol{I}_2 & 0 \\ 0 & -\boldsymbol{I}_2 \end{pmatrix}$ for the Dirac equation to be correct.

16) In eqs. (3.63) and (3.64), the parentheses are unbalanced. There are extra closing parentheses. Moreover, eq. (3.64) contains a double plus sign.
17) In eqs. (3.73)-(3.75), the prime symbol is misplaced. It should appear next to the summation symbol rather than as its upper limit.
18) Page 43: "... the equation 3.77..." → "... equation 3.82 ..."
19) Page 44: The Author writes: "Comparing the equation 3.93 to equation 3.72, ...". Both references are incorrect. They point to equations located in different sections.
20) Eqs. (3.89) and (3.90) for the total cross sections contain errors. Instead of $\sin(\delta_l(k))^2$, it should be $\sin^2(\delta_l(k))$. Since $\sin^2(\delta_l(k)) = \frac{1}{4}|1 - S_l|^2$, eq. (3.90) should not include the factor of 4.

The fourth chapter contains the original results obtained by Author for the pure AlF molecule. The coupled cluster method with singles, doubles, and perturbative triples (CCSD(T)) was employed to determine the potential energy curves for the ground ($X^1\Sigma^+$) and excited ($a^3\Pi$) electronic states, using the supermolecular approach with the counterpoise correction to account for basis set superposition error. Calculations were performed in various Dunning basis sets to examine the convergence of interaction energies with respect to the basis set cardinal number. Then, midbond functions and relativistic effects were introduced to further refine the potential energy curves. It turned out that the addition of the midbond functions to the aug-cc-pCV5Z basis set increased the well depth of the $X^1\Sigma^+$ state by approximately 50 cm^{-1}, whereas relativistic effects reduced it by about 100 cm^{-1}. It is worth noting that the Author also evaluated the contribution of core-electron correlation. The obtained results for the dipole moment and dipole polarizability components are reported later in the chapter. Table 4.2 compares the experimental dipole moment findings for the AlF molecule with the corresponding theoretical values calculated for the equilibrium bond length. Here, I am curious to know the dipole moment values for the vibrationally averaged bond length, which is slightly larger than r_e. I expect that these values will more closely match the experimental data for both the ground state $X^1\Sigma^+$ and the excited state $a^3\Pi$. Another issue concerns the depth of the potential given on pages 51 and 56 for CCSD(T)/aug-cc-pCV5Z+MB. The reported value is 57152.2 cm^{-1}, whereas in table 4.1 it is greater by 10 cm^{-1}. Which value is correct?

The fifth chapter provides the accurate potential energy surfaces for the ground (X^1A') and four excited (a^3A'', b^3A', A^1A', B^1A'') electronic states of the AlF+He system. These surfaces were obtained within the rigid-rotor approximation utilizing the explicitly correlated coupled cluster method (CCSD(T)-F12) augmented by the CCSDT correction and the multireference configuration interaction method (MRCI) for the higher excited states. As in previous chapter, the Author examined the convergence of the interaction energy with respect to both the basis set size and the level of theory. Since the interaction potential depends on R and θ, the two-dimensional maps of the potential energy surfaces were constructed, clearly revealing the anisotropy of the interaction. The deepest potential well is found to be 54.1 cm^{-1} for the a^3A'' state, while the global minima of the other states are between 24.0 and 27.5 cm^{-1}. Interestingly, the optimal geometry of the complex in the ground state is linear, with He closer

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to F, whereas in the a^3A'' state, the complex adopts an almost T-shaped configuration. All electronic states are well characterized, illustrated, and discussed. This chapter also reports elastic and inelastic cross sections for low-energy collisions of AlF with He, obtained through coupled-channel calculations. The results indicate that the ratio of elastic to inelastic collisions may be sufficient for buffer-gas cooling of AlF molecules. One noteworthy observation concerns the sensitivity of the scattering results: "For the j = 0 rotational state of AlF, the first few shape resonances are more sensitive to the scaling of potential, but their relative sensitivity decreases for higher energies." (page 73). At first glance, fig. 5.9(b) might give that impression. However, note that the x-axis is plotted on a logarithmic scale. Did the Author compare the shifts in the positions of the resonances in the elastic cross sections using a linear scale rather than a logarithmic one to be certain? The results presented in this chapter have already been published in J. Phys. Chem. A 129 (2025) 8239-8250 by S. Ganesan-Santhi, M. D. Frye, M. Gronowski, M. Tomza. Strangely, this is not explicitly mentioned. The introduction to chapter 5 only states that "the chapter is based on the published article ??". Probably, this refers to the above-mentioned article authored by the PhD Candidate, which, moreover, is not even listed in the bibliography.

The sixth chapter presents the accurate potential energy surfaces for the ground (X^1A') and about thirteen excited electronic states of the AlF+AlF dimer. The four-dimensional computations with fixed intramolecular separation were performed at the CCSD(T)-X2C/CBS level of theory for the lowest state, while the MRCI and EOM-CCSD methods were applied for the excited states. The presentation and discussion of such an extensive set of results for this system was a considerable challenge, which the PhD Candidate managed well. The figures are very clear. The molecular geometries shown in panels (a) of figs. 6.13-6.19 make the discussion easier to follow. The chapter also includes two-dimensional cuts through the potential energy surface for the ground state. Notably, five-dimensional optimization, where the dihedral angle was set to 180°, revealed that nonrigidity effects play a significant role. Does the Author consider taking into account the nonrigidity effects in future studies? Furthermore, could the Author comment on the shape of the blue solid curve (representing the d^3A' state) in fig. 6.18(b)?

In the seventh chapter, the Author focuses on the interaction between the AlF molecule and the rubidium atom. The determined potential energy surfaces are presented for the ground (X^2A') and four excited (B^2A', A^2A'', $^4A'$, $^4A''$) electronic states. The CCSD(T)-X2C/aug-cc-pwCVQZ-X2C method was applied to the ground and excited quartet states, whereas the MRCI/aug-cc-pwCVQZ-PP method was used for the first two excited doublet states. Since the AlF+Rb system possess a large number of electrons, pseudopotentials were utilized to effectively reduce its computational complexity. The discussion and presentation of the results follow a similar structure to that of the previous chapters. In the paragraph devoted to the discussion of the $^4A'$ state of the AlF+Rb system, one can read: "Another interesting thing to note is that the interaction landscape of AlF molecule ($a^3\Pi$) with rubidium atom is very similar in pattern to the interaction of AlF with He molecule b^3A'. The global minima of both the interactions lie near the linear configuration where the atom approaches the AlF molecule from the side of aluminium." (page 93). Is that really the case? The global minimum occurs at $R = 7$ bohr and $\theta = 0°$, which, according to fig. 7.1, means that the rubidium atom is closer to fluorine (not to aluminium). Moreover, table 5.2

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indicates that the global minimum for the AlF+He system in the b^3A' state lies at $R = 7.17$ bohr and $\theta' = 141.4°$, where $\theta' = 180° - \theta$ (since the angle θ for AlF+He is defined differently than for AlF+Rb). This clearly corresponds to a nonlinear configuration. Nevertheless, a local (not global) minimum is observed at $\theta' = 180°$, whose depth is only 0.3 cm^{-1} less than that of the global minimum. In this case as well, the helium atom is located on the fluorine side. I would like the PhD Candidate to comment on this matter during the public defense.

In terms of content, the dissertation is very interesting. Unfortunately, this positive impression is undermined by a large number of various editorial and linguistic errors. First, I would like to point out that the opening sentence of the abstract (p. 3) contains an error in the name of the system under study. It is written: "Aluminum monoflouride is a great candidate...". The correct name for AlF is "aluminum monofluoride". This misspelling appears on pages 3, 19, 31, 47, 53, 75, 91, 97, and 98. A similar issue occurs with the chemical element fluorine, which is repeatedly written as "flourine" (pp. 47, 80, 84, 92, and 93). In addition, the thesis frequently contains figures without references in the text (e.g., 1.1, 1.2, 1.3, 2.1, 3.5, 3.6, 3.7, 4.1, 6.1), references to nonexistent tables (e.g., Table 4.2.1 (p. 49), Table 5.1.1 (p. 57), Table 5.2.1 (pp. 61, 67, 69, and 70), Table 6 (p. 76)), references marked with "??" (e.g., pp. 41, 57, and 80), incorrect references (e.g., "In Fig. 5.8 (b) we show ..." (p. 73) , "... is seen in Fig. 6.10 with ..." (p. 80)), unnecessary indents (e.g., below eqs. (3.7), (3.13), (3.54), (3.63), (3.68), (3.88), (4.3), (5.2), (5.3), (5.5), (5.6), (6.1), (6.2), (6.3), (7.1)), sentences ending with a comma instead of a period, especially after equations (e.g., after eqs. (3.3), (3.10), (3.12), (3.34), (3.45), (3.50), (3.51), (3.52), (3.59), (3.60), (3.85), (3.87)), operators written without a hat (e.g., $h(i)$ in eqs. (3.7) and (3.23), $h(i)$ between eqs. (3.7) and (3.8), the Fock operator in eqs. (3.24), (3.25), and (3.27), the Dirac Hamiltonian in eq. (3.55)), no space between the numerical value and the unit symbol (e.g., pp. 11, 12, 13, 59, 70, 72, 75, 85, 92, 93, 96), errors in surnames (e.g., "van der Waal" (p. 17), "Schrodinger" (pp. 23-24), "gaussian" (pp. 29 and 35)), the word "minima" incorrectly used as singular (e.g., pp. 31, 49, 51, 53, 62, 74, 78, 80, 81, 84, 85, 90, 92, 93, 96, and 97), chemical element names incorrectly capitalized (e.g., "... Rubidium" on pp. 3 and 92), inconsistent application of the *r* and *R* symbols (e.g., fig. 4.6 on p. 52, pp. 92 and 97), incorrect use of the hydrogen bond symbol ("..." instead of "⋯" (p. 17)), repetitions (e.g., "Buffer gas cooling Buffer gas cooling" (p. 10), two "A. Appendix A" sections (p. 98)), and other typographical and linguistic mistakes (e.g., "nano kelvin" (pp. 11 and 15), "nuclear coordinated" (p. 24), "... function is be written ..." (p. 44), "aug-cc-[empty citation]pV5Z basis set" (p. 59), "dipoledipole" (p. 75), "highand" (p. 75), "$d^3 3'$" (table 6.2, p. 77), "flourine molecules" (p. 84), "anti parallel" (p. 86), "non linear" (pp. 93 and 96), "AlF+He*" (p. 98)). In the table of contents (p. 8), the item "List of Figures" suggests that it should appear after chapter 8. However, it is missing from the thesis. In turn, two other items are absent in the table of contents: the appendix and the bibliography. Finally, it is unclear why chapter 7 does not consist of three sections, like chapters 4, 5 and 6, but of three subsection labeled 7.0.1, 7.0.2, and 7.0.3.

The imperfections I mentioned above do not affect my overall assessment of the PhD thesis, which remains **positive**. Undoubtedly, the PhD Candidate has demonstrated broad theoretical knowledge in the fields of theoretical chemistry and molecular physics, as well as strong proficiency in applying advanced

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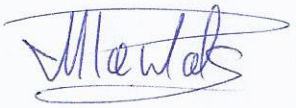
ab initio computational methods of quantum chemistry. The Candidate determined the highly accurate potential energy surfaces for the AlF, AlF+He, AlF+AlF, and AlF+Rb systems, not only for the ground state but also for the excited electronic states. Moreover, the Candidate carried out a detailed and substantial analysis of the obtained results. I appreciate both their quality and the evident amount of work required to obtain them. It is worth emphasizing that the findings are not only of theoretical importance but also provide a valuable source of information for experimentalists working with cold aluminum monofluoride molecules. In conclusion, the PhD thesis submitted by Ms. Sangami Ganesan-Santhi contains original, valuable, and scientifically significant results. A portion of these findings has been recently published in The Journal of Physical Chemistry A, a highly regarded American journal, with the PhD Candidate as the first author. The thesis constitutes a substantial contribution to the fields of theoretical chemistry, molecular physics, chemical physics, and computational chemistry. In my opinion, the thesis meets all the standard criteria and formal requirements for doctoral dissertations. I therefore recommend the admission of the PhD Candidate to the subsequent stages of the procedure, including the public defense.



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