

26 March 2023

The referee report for the PhD thesis by Anna V. Zaharova “Influence of vibrations and rotations on effects of parity and time reversal violations on multi-atomic molecules”.

The thesis consists of 5 chapters. Chapters 1 and 2 present a general introduction in the field, Chapter 1 describes methods of calculation of electron structure, and Chapter 2 presents a short review of parity and time-reversal violation effects in molecules.

The original research results of the candidate are presented in Chapters 3, 4, 5.

Chapter 3 addresses the tri-atomic molecule RaOH.

Chapter 4 addresses the tri-atomic molecule YbOH.

Chapter 5 addresses the hexa-atomic molecule RaOCH₃.

The central aim of this research is the application of sophisticated numerical methods to calculations of parity and time-reversal violation effects in multi-atomic molecules.

I’ve read the thesis with great interest. I have no doubts that the candidate deserves awarding the PhD degree. Nevertheless, my responsibility as a referee is to make comments. I do so below.

1) Page 19. If Eq.(1.13) is a consequence of Eq.(1.12), then it also must contain long derivatives that include the scalar and the vector potentials.

2) Page 21, Eq.(1.25). The standard definition of energy corresponds to the opposite sign in the exponent.

3) Page 21, Eq.(1.27). What is v in the vI_4 term?

4) The Hartree-Fock (HF) method is discussed on pp.26-27. It is well known that the method has an essential ambiguity. For example unrestricted HF can generate a non-spherical atom which is a non-physical effect, a byproduct of the method. The same method can generate non-spherical nuclei, which is a physical effect. In infinite condensed matter electron gas HF can generate charge density wave and/or spin density wave. Dependent on situation these waves can be physical or nonphysical.

We know how this issue is resolved in atoms. To the best of my knowledge there is no general way to resolve the issue in nuclear and condensed matter physics. In context of this work it would be appropriate to comment on status of this issue in molecules.

5) Page 46. It would be appropriate to define CKM and PMNS matrices.

6) Page 48. Eq.(2.108) presents an estimate of d_e . Then the sentence after Eq.(1.109) claims that “account of hadronic processes” enhances the estimate by 11 orders of magnitude!? A factor 2 or even an order of magnitude would be OK. However, 11 orders of magnitude is an enormous effect and it must be explained. What is the physics behind this enhancement?

7) Page 52. The redefinition of the EDM operator in Eqs.(2.121),(2.122) must be explained. I am

not sure that the sentence just before these Eqs. is quite correct.

8) Page 53. It seems that the definition of E_{eff} in Eq.(2.128) is given in the proper (co-rotating) reference frame of the molecule, E_{eff} is directed along the axis of the molecule. It is OK, but one must also define the positive direction along the axis. I cannot find a definition of the positive direction. I suspect that this is the root of inconsistency in signs that I will point out later (comment **11**).

9) Page 57. Again, I do not understand the reference frame. Now it is probably the laboratory frame because the l-doubling makes sense only in the lab frame. By the way, it would be useful to explain the mechanism of the l-doubling. What is d_z ? Is this the usual chemical EDM of the molecule, $d_z \sim e \times 1\text{\AA}$? Probably it is. If so all Eqs. on this page must contain coefficients related to the rotational D-functions. The coefficients depend on l and on the total angular momentum J .

10) Page 58. Eqs.(2.141). This equation is written in the laboratory reference frame, no doubts. Hence, the coefficient P depends on J , l and, most importantly, on the ratio $\Delta E/(\mathcal{E}d_z)$. In a sufficiently strong electric field, $\Delta E/(\mathcal{E}d_z) \ll 1$, the coefficient must be equal to unity, $P = 1$. This is independent of chemistry and number of atoms in the molecule. So, I cannot agree with the statement in the paragraph after Eq.(2.141).

11) Page 60. Tables 2.2; 2.3. I want to compare results for RaOH and YbOH presented in these tables with those from Table 2.1 for RaF and YbF. Of course these are not results of the present work, but the comparison is relevant to the definition of the direction pointed out in my comment **8**. With respect to E_{eff} the molecule RaOH is very similar to RaF, and YbOH is similar to RbF, both OH and F attract one electron from the heavy atom. Therefore, E_{eff} must be approximately the same in RaOH and RaF, and also, approximately the same in YbOH and YbF. Looking at the above Tables we see that this is true for YbOH and YbF. However, for RaF and YbOH the signs are different. I am practically confident that this is not a physical difference, the effect is approximately the same. The difference is a byproduct of different definitions of the positive directions accepted in calculations for these molecules, see my comment **8**.

12) Page 68. I guess that the vibrational frequencies in the 1st paragraph of Section 3.3 are given in cm^{-1} . I more or less understand how they have been obtained, it is a quantum chemistry in the co-rotating reference frame.

What is J that appears in the 2nd paragraph of Section 3.3? I guess that this is the angular momentum in the laboratory reference frame. How the value of the l-doubling has been obtained and why it is proportional to $J(J + 1)$?

13) Page 70, Table 3.4. The same comment as **11** that was relevant to Ref[28]. Now the comment is relevant to the present work. Why the sign of E_{eff} is negative while it is positive for RaF? I am practically confident that it is due to the different definitions implicitly accepted for these molecules. If not, the difference in sign must be explained qualitatively without a calculation.

14) Page 79, Table 4.8. The results for YbOH presented in the table make sense to me. They are close to that for YbF and very weakly depend on the vibrational state.

15) Page 89, the last paragraph on the page. I cannot agree with the statement that P cannot reach 100%. I reiterate my comment **10**: P is related to the rotational physics and unrelated to quantum chemistry, $P=1$ in the limit $\Delta E/(\mathcal{E}d_z) \ll 1$.

16) Page 111, Table 5.12. The results for RaOCH₃ make sense to me. The group OCH₃ effectively

works as F atom. Therefore results for RaOCH_3 and RaF are close.

To summarise. This work of Anna V. Zaharova demonstrates a sufficient degree of technical capacity. The thesis is a contribution to the field of violations of fundamental symmetries at low energies. As always there are questions and comments, but this is normal and hopefully this will stimulate further developments. I recommend awarding Anna V. Zaharova the PhD degree.

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A handwritten signature in black ink, appearing to read 'O Sushkov', written in a cursive style.