Response to referee reports
AP11756/Montanari

April 21, 2020

1 Reply to report of the First Referee

1. Since only protons are considered as projectiles, the title needs to be modified accordingly.

The title has been modified following the referee's recommendation to "The stopping power of hydrogen in hafnium and the importance of relativistic $4f$ electrons".

2. It appears that calculations assume bare protons. According to CasP, neutrals play a considerable role in charge equilibrium around and below the Bragg peak. Some explanation is needed here.

The referee is correct; our calculations assume bare protons. We considered that there is no bound electron (or insignificant probability of there being any bound electron) because the free electrons in the metal screen the hydrogen, and, at low energies, this screening is sufficient as to have no bound electron. CasP includes an excellent fitting of experimental charge states and a robust scaling rule about them. However, it is based on measurements of charge states outside the metal. For multi-charged ions, almost no differences are expected, and the CasP charge state works very well. For H and He ions, differences are significant. We incorporated a new paragraph (lines 263-273) to explain why we are considering just proton impact, the reference to CasP, and the paper of charge states by Schwietz and Grande.

3. Thickness measurements by Rutherford backscattering rely 'heavily' on the scattering cross section, while energy loss is a minor correction depending on foil thickness (p.1, 2nd paragraph).

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4. In order to get a more precise thickness value of the Hf foil, the authors use the energy loss of 5.486 MeV alphas as a standard, with SRIM as a reference. SRIM is based on empirical data, and for alpha particles in Hf, the IAEA database lists one single data point for He in Hf. Considering the spread in published stopping cross sections for e.g. He in Au, listed in the IAEA database, some explanation is needed to justify an error estimate of only 5% (1st paragraph in section IIB).

The referee is correct; we have used the stopping of 5.486 MeV alphas and the SRIM software package as a reference to get the thickness. Although SRIM fits the experimental data available, it is not just a fitting; the software implements a mix of modeling and fitting (semiempirical). At high impact energies, where the stopping is well known, SRIM is quite reliable. Figure 1 included in this reply can clarify these assertions. a) In this figure, we plotted H and He in Hf, both divided by Z^2. Above 1 MeV/amu, SRIM and our theoretical results agree within 2%. The vertical pink line indicates the impact energy used as reference. In the region, the SRIM predictions are reliable. b) By comparing the SRIM results for hydrogen and helium in the same target, one can see that SRIM for H ions rapidly changes its concavity to fit Sirotonin data. Furthermore, SRIM for He ion overestimates the scaled-with-Z^2 cross-section at 500 keV/amu in order to fit the single measurement by Chu, Ziegler, and collaborators. We say the stopping is overestimated because the stopping of He ions divided Z^2 can only be equal or below the stopping of H ions.

5. In connection with the discussion of relativity and outer-shell electrons (p.3) it might be instructive to mention that this is the reason for the existence of relativistic quantum chemistry programs. Since the authors find it surprising that the effect increases in magnitude from inner to outer shells, the reader needs an explanation. I should think the effect of deviations in the screening add up shell by shell, but I may be wrong. Moreover, the sign of the discrepancy in figure 2a deserves attention, which seems to change from positive up to 4p- to negative from 5p+.

The referee is correct. We included two paragraphs in Section III (lines 211-230) to refer to her/his comments.

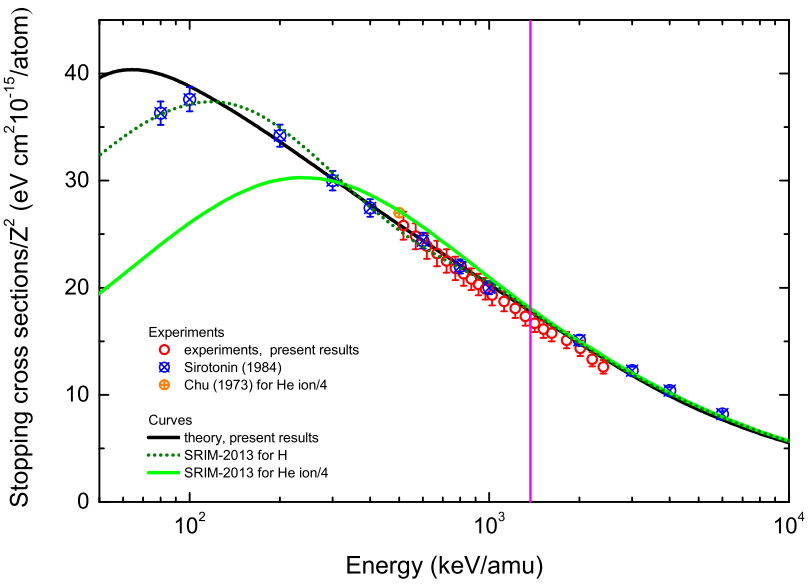

Figure 1: Stopping cross section of H and He in hafnium at high impact energies.

6. The importance of 4f-5p screening is documented clearly (p.3), but the reader will ask why this does not affect other shells. I assume that the effect is important when two or more subshells have similar energies and, hence, overlap in real and velocity space. If so, I suggest to mention this. If not, another explanation is needed.

The mixing criterion is explained on page 3; we considered the quantum uncertainty in energy so that bound electrons with similar energy values and mean radio $\langle r \rangle$ response as a single density of electrons, including screening among them. We acknowledge that a more detailed study is required. We are currently working on developing a systematic approach for different targets involving 4f electrons. So far, we have corroborated the importance of the contribution of the 4f shell to the total stopping in Hf. We have also determined that the 5p-4f mixing influences the total cross section mainly because they are the second most significant contribution after the FEG. Other shells may be mixed, and we have computed them, but the total stopping varies very little. Reference to this analysis is given in lines 258-262.

7. In view of the large contribution of the outermost shell, I suggest to include the core contribution in figure 3.

We thank the referee for her/his suggestion. At first, we thought of showing all contributions separately but opted for a simpler version. Upon recommendation, we have included in Fig. 3 of the manuscript the FEG and bound electron contribution curves.

8. In addition to comparisons with experiments and empirical models, it would be instructive to see comparisons with theoretical models like CasP and DPASS in figure 4.

We compared our results with Casp5.2 and DPASS before submission, but we were discouraged to include them by the number of curves in the figure. However, we have now managed to include CasP5.2 and DPASS to figure 4. We comment about these changes in the Introduction (lines 71-72), and in Section IV (lines 308-311).

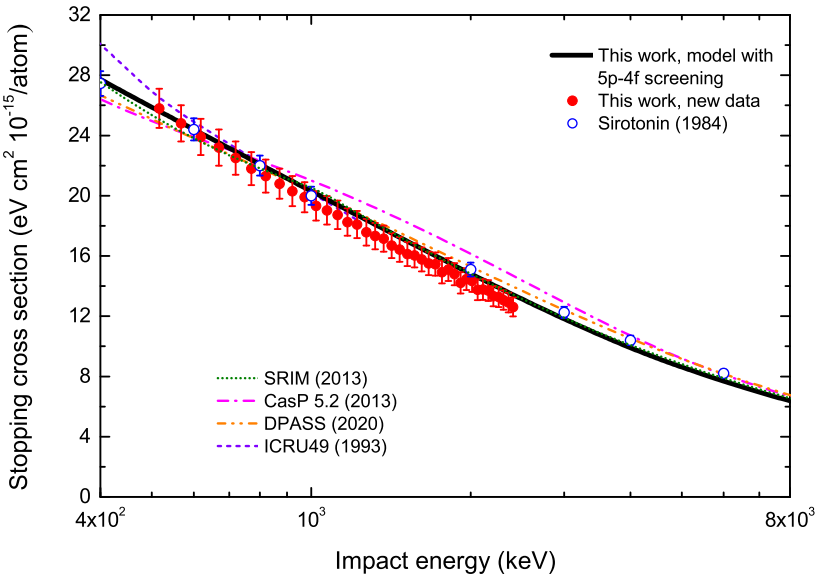

Figure 2: Stopping at high impact energies. Theoretical curves and symbols for data are explained inside the figure.

2 Reply to report of the Second Referee

1. Can the authors discuss how possible impurities in the sample and -especially- on both sides of the target would affect the final stopping data? The authors must discuss it in the manuscript.

Pedro Miranda.....

2. In the same context, the authors have to clarify whether potential surface roughness and/or target non-uniformity might affect the final results obtained in transmission method.

Pedro Miranda.....

3. What is accuracy of the primary beam energy of the accelerator? Moreover: when the target is placed and removed from the front of the detector, does the detector itself need to unbiased and the chamber opened? If so, might there be any offset (∼keV) in the detection system that would affect the energy distribution peaks, hence the Gaussian position from the fits (Fig. 1)?

Pedro Miranda.....

4. The experimental data above ∼1.5 MeV is systematically below the data from Ref. [7], hence SRIM semi-empirical approach, and also below the authors' theory output. At these energies (and higher), the agreement between experiment and theory is expected to be better than a few percent (that is why you used stopping power for 5.486 MeV alpha on Hf to obtain the target thickness). Can the authors explain why there is such systematic difference for the present measurements using protons?

There is a small systematic difference between our experiments and theory for impact energies above 1.5 MeV, but it is within the experimental error. Figure 2 of this reply amplifies the results shown in the manuscript by focusing on the high energy region. Note that we included our theoretical results, SRIM, Casp5.2, and DPASS in the figure. The difference is small, being less than 3% for the two values above 2 MeV. We included comments regarding this subject in the manuscript.

5. The authors claim an overall uncertainty of 5%, but it is not clear how they obtained this value, or whether only statistical contributions were taken into account. Nevertheless, uncertainties of measurements have to be treated following the Guide to the Expression of Uncertainty in Measurement, International Organization for Standardization, Geneva Switzerland, 1995. Especially for stopping power measurements in transmission approach, there are other sources of uncertainties that might potentially affect the final results systematically (see comments 1, 2 and 3), and they must be discussed in more details.

Pedro Miranda.....

6. Can the present theory in the manuscript be compared to other models (e.g., CasP and DPASS), especially towards low energies? Aiming thus a constructive discussion on the overall-agreement among different models to predict SCS of "challenge" materials, as transition metals (f-subshell)?

We thank the referee for her/his suggestion. We have included the CasP5.2 and DPASS curves in Fig. 4 of the manuscript. We made the corresponding modification in the Introduction (lines 71-72), and Section IV (lines 308-311).

7. In the last sentence of Sec. IV, the authors point out for a need of more experimental data below 100 keV H+ but, in my opinion, more data are needed even at higher energies, e.g., nearby (and slightly above) the Bragg peak... Please enhance discussions about it.

We agree with the referee's comment. In an ion-target system with only two sets of measurements, more data is needed. In the energy region 80-500 keV, only the data by Sirotinin et al. is available and cannot be compared with others. SRIM is not a test for this data since it adjusts these measurements itself (a more detailed discussion about the matter can be found in reply 4 of the first referee report). We changed our manuscript accordingly in Section IV (lines 331-339) and Section V (lines 374-377).

3 Reply to report of the Third Referee

1. Regarding the theoretical model that describes the contribution to the stopping power of the bound electrons, the authors emphasize the importance of including relativistic effects in the description of the binding energies and densities of the Hf 1s-4f states. However, it is not clear if the calculations performed by the authors are done for gas phase Hf atoms or for the solid Hf as in the experiments of Ref. [38]. In case of being for the former, the slightly worse agreement found for the 4f states as compared to the experimental values could be related to this point.

The referee is correct; our calculations are performed for gas- phase Hf atoms. We have now explicitly clarified the difference between the experimental and theoretical binding energies in the manuscript (lines 215-219).

2. The results from the three different theoretical calculations shown in Fig. 3 are not completely clear. The authors emphasize the importance of considering both screening effects and relativistic effects for the 4f and 5p electrons, but it is not clear if later in the text the authors use indistinctly the terminology "relativistic" and "screening" to refer to the same issue. For instance, are the ML results shown in Fig. 3 calculated with the relativistic binding energies and densities, but with and without including screening corrections, or do the two ML curves differ in whether the relativistic corrections are or not included? It is neither clear what description of the bound electrons is used in the curve labeled as "SPCC(FEG)+SLPA(bound)".

We thank the referee for her/his comment since it will help us clarify this point. Our SLPA calculations use relativistic wave functions and binding energies for the bound electron contribution to the stopping power. In this sense, the three curves in figure 3 and the solid curve in Fig. 4 are called relativistic. We have added explicit mention of the use of relativistic wave functions and binding energies on page 4 lines 244-246 and lines 283-286.

3. If all the results of Fig. 3 were calculated for the relativistic description, it would be also interesting to show the results obtained with the non-relativistic description in order to demonstrate the importance of this correction.

The SLPA calculations for the bound electrons uses the Hartree- Fock wave functions and binding energies, which are available in the tables by Clementi-Roetti or by Bunge for elements up to Xe (Z=54). The errors in the non-relativistic calculations worsen for higher Z atoms, and this is the reason why these tables do not extend any further than Z=54. The fail of the non-relativistic description of the binding energies is shown in Fig. 2. We have added a comment on this on page 3, lines 220-230. When dealing with stopping in targets with Z¿54, we need to compute the wave functions and binding energies ourselves. And we do it within the relativistic approximation to the best of our possibilities. However, one can wonder if such a discrepancy in the non- relativistic results affects the stopping power. First, it will only affect the bound electron contribution to the total stopping. Second, at high energies (i.e., 1 MeV), the results converge to the Bethe limit for any density of electrons as far as the correct number of target electrons is included. Having clarified this, we added in figure 3 of this reply, the total stopping using the non-relativistic values we calculated using the AutoStructure code. As can be noted, at sufficiently high energy values, the results agree, but they start to differ around the stopping and at lower impact energies. We have included in this figure, and in Fig. 4 of the manuscript, the DPASS results by Sigmund.

4. Furthermore, it would also be meaningful to show the results from the ML(FEG) calculation alone in order to identify better the contribution of the bound electrons to the SP.

Thank you for this suggestion. We have added the curves for FEG and bound electrons to Fig. 3 of the manuscript, and the corresponding comments in the text and figure caption.

5. When comparing the new and existing experimental data, clarify what experimental technique was used in Ref. 7 to measure the stopping power.

Good suggestion, thank you. Sirotinin et al. used the backscattering method for these measurements. We have made reference to the method implemented in the Introduction (line 70) and in Section IV (line 305).

6. The data by Sirotonin et al. plotted in Fig. 4 seem to suggest that the stopping power maximum would be around 100-200 keV, while the maximum predicted in the present work by the theoretical calculations is located at slightly smaller energies. Please comment on this point and discuss possible reasons for this discrepancy: What are the main limitations in the theoretical model that can be causing this energy shift?

The stopping maximum is very sensitive to the theoretical model and to the experimental method. Sirotinin paper mention "possible reasons for the disagreement of the measurement results near the E(E) curve maximum". For targets with many different sets of data (i.e. H in Ag, Al, Au, Fe, Cu, Si, and others) it is usual

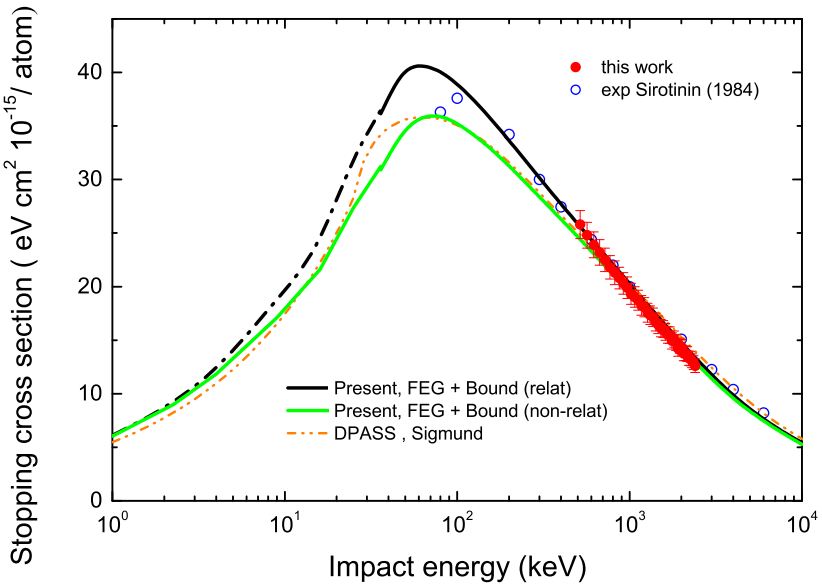

Figure 3: Total stopping cross section. Present results using relativistic and non-relativistic solutions for hafnium atom. Curves and symbols explained inside the figure.

to note great dispersion of values around the maximum. In the case of Hf, only one set of data is available and it is perfectly matched by SRIM semi-empirical curve. SRIM clearly includes these values in the adjust of the code, so it does not represent a test for this data. One of the goals of this work is to call the attention on possible differences between theory and the existing values, and to remark the necessity of more experimental data in certain energy regions, mainly, the stopping maximum and below. We have changed the comments in page 6 lines 328-336 and lines 364-366 as follows:

"Future experiments would be important to complete this study on the stopping of Hf for protons. In the energy region $80-500$ keV only the measurements by Sirotinin group in 1984 are available. SRIM clearly includes these values in the adjust of the code, so it does not represent a test for this data. Undoubtedly, new measurements are needed in three specific energy regions: below 500 keV, around the stopping maximum (i.e. $50-200$ keV) and at low impact energies"

"Future experiments for impact energies around the stopping maximum and in the low energy region would be important to complete this study."

In relation with the referee comment about the maximum of the stopping, in Fig. 4 we have added the comparison with other two theoretical results: CASP and PASS. The following comment has been included in page 6, lines 315-322:

"The stopping maximum is a very sensitive region for any full theoretical description, with no parameters at all, and this is quite visible in a linear-scale plot like Fig. [4]. However, the impact energy for the maximum seem to agree between our curve and DPASS, although DPASS is 10% below ours. Instead, CasP predicts a stopping maximum 10% above our value and a completely different shape at lower energies."

7. When reviewing on the experimental work performed on Hf oxides in the introduction, note that there is a quite recent work by Roth and co-workers published in Phys. Rev. Lett. 119, 163401 (2017), in which the SP of protons is precisely measured in this target.

We thank the referee for suggesting this missing reference. We have included it in the revised manuscript.

Finally, there are few misprints in the generated pdf file:

- Y-axis labels in Figs. 3 an 4 are unreadable

We have changed to larger prints and have written explicitly "stopping cross section" -Y- and "Impact energy" -X- instead of S(E) and E.

- Page 3,2nd column, 2nd full paragraph: "Too assess"

Corrected.

- Caption of Fig.2: "hollow circles" -> "open circles" or "unfilled circles"

Corrected.

We have also made some improvements in the English redaction of the manuscript.