

Dr. Athanasios Chantis
Assistant Editor
Physical Review B

May 4, 2016

Dear Dr. Athanasios Chantis,

Please find here enclosed the revised version of the manuscript BP12969/Anderson.

We thank the referees for their positive and useful comments and suggestions of our manuscript and we believe that it helped us to improve the quality of our work.

In the following, we answer all the points raised by the referees and we also list all the changes made in the paper. In the pdf version we have put in red the changes for easy reference. Below, our responses are enclosed in blue boxes.

We are confident that all suggestions have been met, and hope that our manuscript can now be published in Physical Review B.

1 Report of the First Referee – BP12969/Anderson

Anderson and colleagues present a follow up to their PRB 2015 paper [Ref. 19] which described a theoretical framework that allows quantitative calculation of surface second harmonic generation at the independent particle level. The main concepts treated in that work - scissors shift, nonlocal terms in the matrix elements, and a slab cut function, within a single formulation - are demonstrated here by means of ab initio calculations on Si(111)-(1x1):H and compared with various experimental data. In addition, the authors report on other technical aspects such as three vs two layer models and sensitivity to atomic geometry. The text is very well written and easy to read. The theory section repeats only the essential formulae of Ref 19, but otherwise reports no new theoretical development beyond what is reported in e.g. Refs 19 and 24-27. The calculations and conclusions deserve publication in some form, since practical SSHG calculations beyond the IP level remain out of reach for most systems and researchers in the near future, but I consider it a borderline work for PRB. In the following, I raise some issues that should nonetheless be addressed.

1. One interesting demonstration in Ref. 19 was the sensitivity of computed spectra (both lineshape and energy) to the chosen value of the scissors shift. There, the authors used 0.5 and 0.63 eV for clean Si(100)-(2x1), but here they use 0.7 eV for Si(111)-(1x1):H as taken from a published GW calculation. Since the authors neglect temperature, local field, and excitonic effects, this choice is somewhat arbitrary. However, they cannot claim such good agreement with experiment unless they show such a comparison again here (at least for one dataset). The authors should also comment on why GW eigenvalues/transition energies are appropriate here, when in linear optics the GW+BSE transition energies are needed.

The value of the scissors shift comes from GW calculations and depends on the surface of the material (see Refs 65, 66, and 67 from our previous work for the clean Si(100)(2x1) surface). It turns out that the scissors value for the clean Si(100)(2x1) surface is smaller, due to the

presence of the surface states. For linear optics and SHG, GW transition energies are needed. Doing a Bethe-Salpeter calculation for SSHG will improve the position and the amplitude of the peaks, but is far beyond the present possibilities. Therefore, we did not adjust the value of the scissors shift as we want to keep our calculation at the ab initio level.

We have added a discussion on the scissors shift and the GW and the GW+BSE transition energies in the paragraph just before the Conclusions, and Ref. 53 in connection to this.

2. Related to this, I find that the authors overinterpret their results and frequently overstate the agreement with experiment. For instance:

- Page 5: “relaxed coordinates have an improved peak position”. Can the authors really claim that agreement is improved, in light of the IP approximation used?

The results presented in Fig. 2 are compared to low-temperature measurements and correspond to an in-plane susceptibility for which the local-field effects are expected to be small (see point 8 below for more details). However, we have changed the sentence to “...relaxed coordinates have a peak position...”

- The authors on Page 6 refer to Ref. 46, Dadap PRB 1996 for “It is well known that temperature causes shifting in the peak position of SHG spectra”. That work does not discuss temperature. I believe the authors intended to refer to Dadap PRB 56 13367 (1997), which shows several spectra redshifting with higher T. Hence “Low temperature measurements for the SHG yield will lead to more closely matched results” does not seem to be correct - quite the opposite.

Indeed, we cited the wrong article; it is now correctly cited. It is worth noting that the correct article, PRB 56, 13367 (1997), concerns \mathcal{R}_{pP} from a different surface altogether. \mathcal{R}_{pS} from the Si(111)(1×1):H surface may not behave in the same way.

We have modified the text accordingly in the fourth paragraph in Sec. V B, page 6. We have also added some discussion along the same lines for \mathcal{R}_{pP} in first paragraph of Sec. V D, page 8.

- Page 6: “the three layer model best reproduces both the lineshape and intensity” is again somewhat generous, since the bulk/2L spectra have near identical lineshapes (“mostly consistent”, as written on page 7). Such a conclusion might be valid after Fig. 7.

We have changed “Ultimately, the three layer model best reproduces both the lineshape and intensity...” to “Ultimately, the intensity of the three layer model is the closest to the experiment.”

Also, we have modified the text towards the end of the first paragraph of Sec. V D, page 8.

- Page 7: “inclusion of .. nonlocal part .. gives much better comparison”. Again, the evidence for this is tiny. I do not doubt that the inclusion is formally correct, and perhaps for some other material/pseudopotential essential, but the results presented here do not justify such a strong conclusion. Furthermore, this point was already well demonstrated in Ref. 19.

We have changed this concluding remark to how it now appears at the end of Sec. V B, page 7.

- The few speculative remarks on temperature and oxidation effects on experimental SSHG spectra does not justify “Our comparisons also indicate the effects of temperature and surface adsorption” in the abstract, although they are acceptable in the text.

We have removed the specified sentence from the abstract.

Besides above points, we have toned down the overstatements regarding the agreement with experiment.

3. In all cases shown, the bulk model yields near identical lineshapes and seems just as good as the 3L model except for a constant underscaling of about 5. I suspect this is because the authors chose a passivated surface with no surface states, so that all features appear around E1 and E2. If the authors repeated such a comparison using the Si(100)-(2x1) surface (used in Ref 19) they might demonstrate a clearer difference between 3L and bulk. I think such a comparison is most important here, even in the absence of experimental data. Secondly: do the authors’ calculations on Si(111)-(1x1):H demonstrate that surface SHG, for a system without surface states, can be well modeled simply from a bulk calculation (plus scaling of about 5) and use of the appropriate formulae? This seems to be a useful result in itself.

We regret that this might be a misunderstanding due to our naming convention for the radiation models of \mathcal{R}_{IF} . What we called the *Bulk* model is actually the case for which $\chi(-2\omega; \omega, \omega)$ radiates from the bulk layer, but $\chi(-2\omega; \omega, \omega)$ itself is the *surface* nonlinear susceptibility, as it is defined and calculated in the manuscript. If we were to do a bulk calculation of $\chi(-2\omega; \omega, \omega)$, we would get zero as Si is centrosymmetric. We cannot use a bulk calculation of $\chi(-2\omega; \omega, \omega)$ to model a surface, with or without surface states.

To correct this possible misunderstanding, we have renamed the three models as: the 3-layer, the 2-layer-vacuum, and the 2-layer-bulk models; the “3” or “2” refers to the number of layers, and “vacuum” or “bulk” refers to the place from which $\mathcal{P}(2\omega)$ radiates. We stress the fact that we always take the surface into account to obtain the susceptibility $\chi(-2\omega; \omega, \omega)$, otherwise for a bulk system it is zero.

We have followed the recommendation of the referee, and have analyzed the effect of the 3 models on the Si(100)(2x1) surface. We agree that, while the 3-layer and the 2-layer-

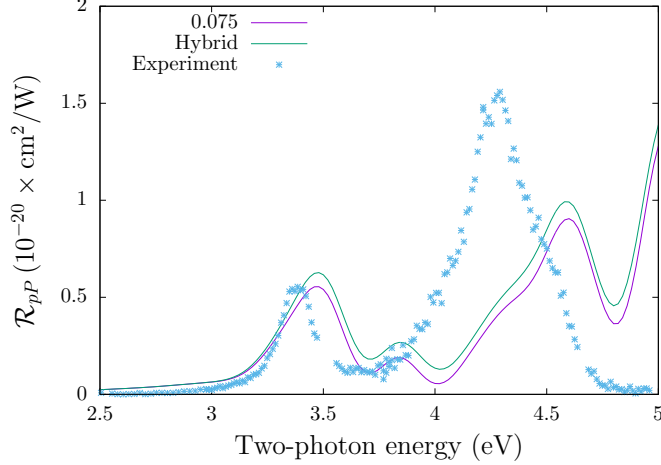


Figure 1: (Color online) Comparison between theoretical results for $\sigma = 0.075$ eV for both $\chi^{\text{abc}}(-2\omega; \omega, \omega)$ and \mathcal{R}_{pP} , and the “hybrid” case where $\sigma = 0.05$ eV for $\chi^{\text{abc}}(-2\omega; \omega, \omega)$ and $\sigma = 0.1$ eV for \mathcal{R}_{pP} . We show the experiment for \mathcal{R}_{pP} , for $\theta = 65^\circ$.

bulk are similar for the Si(111)(1×1):H surface, they do not coincide for the Si(100)(2×1) surface. Since the Si(100)(2×1) surface is another case entirely with limited experimental data available (without absolute units or covering a wide range of energy), we consider that including results for this surface it is outside of the scope of this manuscript.

4. Two broadenings are chosen. These also affect the intensities, of course. The authors should justify their usage and value (a priori?)

The original idea behind the two different broadenings was that for the comparison of $\chi_{\text{||||}}(-2\omega; \omega, \omega)$ with the experiment (Fig. 2), $\sigma = 0.05$ eV gives a reasonable result; so we fixed $\sigma = 0.05$ eV for $\chi^{\text{abc}}(-2\omega; \omega, \omega)$. Then, for \mathcal{R}_{IF} we used $\sigma = 0.1$ eV so that the SSHG yield has a broadening similar to the experimental spectra.

Of course, at this level of approximation there is no a priori value for σ other than trying to find a value that fits well to the experimental results. We do agree that using two values for σ is confusing, so we have changed all the plots for a unique value of $\sigma = 0.075$ eV, where we achieve an adequate compromise that is just as good as what we had with the two different values. For the sake of proving this point, in this reply we show in Fig. 1 the comparison between theoretical results for $\sigma = 0.075$ eV for both $\chi^{\text{abc}}(-2\omega; \omega, \omega)$ and \mathcal{R}_{pP} , along with the “hybrid” case where $\sigma = 0.05$ eV for $\chi^{\text{abc}}(-2\omega; \omega, \omega)$ and $\sigma = 0.1$ eV for \mathcal{R}_{pP} . We see that qualitatively both approaches give very similar results. We have added a few sentences about our choice of σ in the text at the end of the Sec. IV, page 5.

5. The authors renormalize the surface dielectric function to the volume of the slab, not the supercell. On page three, they describe the slab as containing “front, back, subsurface re-

gions...and between these, a bulk region". Would it not be more precise, therefore, to renormalize to the volume of the surface region? Or the half slab? This point is not clear.

The sentence containing "front, back, subsurface regions...and between these, a bulk region" is indeed confusing, so we have removed it.

The super-cell is composed of two regions, a material slab and a vacuum part. The surface dielectric function is normalized only to the volume of matter and not to the super-cell. However, we could have calculated the response of the half slab only (using the cut-function). It has been checked that the response of a slab is equal to the average of the two half slabs (see also Refs. 36, 37, and 38). We have added a remark concerning this at the end of Sec. III, page 4.

The situation is different for the second-order susceptibility. As it is mandatory to use the cut-function, the susceptibility is normalized to the half-slab. But the quantities used in Sec. V are surface susceptibilities, normalized to the surface plane. They are then independent of the height of the material slab. Therefore, the $\chi^{\text{abc}}(-2\omega; \omega, \omega)$ entering in \mathcal{R}_{iF} are always surface susceptibilities. We have added some remarks at the end of the left column on page 4.

6. Page 8, "but with four times less intensity" should read "but with eight times less intensity."

We have corrected the text, changing "four" to "eight."

7. The temperature used in the experiments should be noted in each figure caption (or on the figure), and not only in the text.

The temperature at which the experiment was taken is added at the end of each figure caption.

8. On page 8, local fields are mentioned as possibly being important for the out of plane components. A sentence expanding on this (what local fields are and why they are more important perpendicular to the surface) would help a non expert.

Local fields reveal the inhomogeneities in the material, which are by far more important perpendicular to the surface than in the plane. This can be evidenced for Silicon, as Reflectance Anisotropy measurements are well described by ab initio calculations neglecting local field Effects (see for example, Refs. 51 and 52). It is therefore expected that the component in the plane ($\chi_{\parallel\parallel\parallel\parallel}(-2\omega; \omega, \omega)$) will be less sensitive to the inclusion of local-fields, while it might be important for the others. Note however that this conclusion may be material-dependent.

We have added a few comments about these effects in the second paragraph of Sec. V D, page 8.

2 Report of the Second Referee – BP12969/Anderson

In this paper an ab initio calculation of surface second-harmonic generation of Si(111)(1x1):H surface has been carried out using the ABINIT pseudopotential code for the ground state calculation and the DP code for the calculation of the nonlinear part of the pseudopotential to the nonlinear susceptibility. Like in their previous paper (see Ref. 19), they used the independent particle approximation to include the scissors correction, the contribution of the nonlocal part of the pseudopotentials, and a cut function to extract the surface response to the calculation of the nonlinear susceptibility tensor and the surface second-harmonic generation (SSHG) yield. This work is therefore a continuation of their previous work published in Phys. Rev. B 91, 075302. In this work they used their previous results of the nonlinear susceptibility to calculate the SSHG yield of Si(111)(1x1):H surface and compare the results with various experiments. The scissors operator used seems to make their calculation in fair agreement with experiments. However, it is unfortunate that the details of their derivations of the SSHG yield are put in a paper (Ref. 34), which is submitted, but the information about the journal is missing. I suppose this is a mistake. I advise the authors either to put this paper in arXiv.org or to put the derivation in an appendix or supplementary information. This will be helpful to the specialized reader. He (she) will be able to fully derive their formulas, especially when their previous publication of the SSHG yield (PRB 66, 195329) seems to be incorrect due to errors in their previous formulas.

We have written the full derivation of the three layer model for the SSHG yield in a e-print manuscript at the [arXiv.org](https://arxiv.org). The derivation is 9 pages long, and thus not suitable for an appendix. We have added this as Ref. 25 in the resubmitted manuscript.

The authors should also cite properly the work of Z.H. Levine, published in PRB, who was among the first to include the scissors correction and the contribution of the nonlocal part of the pseudopotentials to the calculation of the nonlinear susceptibility.

The reference has been added.

In conclusion, this is an interesting work, which gives a full calculation of the SSHG yield within the independent particle approximation. Unfortunately in its present state the paper is not ready for publication in PRB (see above).

2.1 Minor points:

- The authors should not repeat formulas which were already published in their previous paper (Ref. 19), like equations 6a-d and many others. Instead they should give more details about the derivation of Eq. 2 and cite their previous paper whenever needed.

Since we have put the full derivation of the three layer model in the [arXiv](https://arxiv.org) (Ref. 25), and Referee 1 states that we have included all the “essential formulae” from our previous article,

we have decided to keep them so the article is self contained.

- At the end of page 2, it is written that $T_i^{a,b} = t_i^{a,b}$. Is this a mistake?

It is not a mistake; however, the original notation was confusing. We have changed the notation to make it clearer. See the new notation for Γ_{iF} and the text in the second paragraph of Sec. II, page 2.

- Change all dk^3 to d^3k .

We have changed Eqs. (6a-6d), replacing dk^3 with d^3k .