Author Response to Reviews of

Lattice dielectric properties of rutile TiO_2: First-principles anharmonic self-consistent phonon study

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RC: ***Reviewer Comment***, AR: *Author Response*, ☐ Manuscript text

1. the First Referee

1.1. General comment

RC: ***This work studies the anharmonic lattice dynamics of rutile TiO_2 using the newly developed selfconsistent phonon + bubble (SCPH+B) theory. The SCPH+B incorporates the third-order anharmonic bubble self-energy into the original SCPH theory. The anharmonic phonon frequencies and linewidths of the Gamma point optical phonons produced by the SCPH+B are improved significantly with respect to those by harmonic calculations or conventional perturbative approach. Now the theoretical optical properties are in much better agreement with reported experimental measurements. Results obtained by two different functionals, LDA and r2SCAN, are compared and discussed. Experimentally observed but unidentified peaks of the dielectric function are attributed to the two-phonon emission process, which is included by the frequency-dependent bubble term. This work is novel and comprehensive. Therefore, I recommend that it should be published in Physical Review B once the authors address the following minor points.***

AR: We sincerely appreciate the referees supportive and insightful comments on our manuscript. We believe that this manuscript will be of interest to many researchers as it discusses the dielectric properties of rutile TiO_2 with a detailed analysis of its anharmonic phonons. Following the suggestions of the referee, we have amended the manuscript appropriately. The point-by-point responses to the referees comments/questions are provided below:

1.2. #1

RC: ***I understand the current method improves the phonon frequencies and linewidths significantly. How about the renormalization effect on eigenvectors? Take the phonon modes shown in Fig. 1 for example. How different are the eigenvectors obtained by harmonic calculations, SCPH, and SCPH+B, respectively?***

AR: FIN We thank the reviewer for pointing out the renormalization effect of phonon eigenvectors. First, in the current calculation, SCPH+B does not cause changes in eigenvectors because we do not include off-diagonal components of bubble self-energies. In the SCPH calculation, three E_u modes differ slightly from harmonic approximation in relative magnitude of Ti and O displacement, but at an almost negligible level.

As can be seen from Eq. (3), eigenvectors are needed to calculate the dielectric function, so the eigenvectors also need to be calculated accurately as well as the eigenvalues, but in this example the difference between the eigenvectors of the harmonic approximation and SCPH+B makes almost no difference to the dielectric function either. Renormalization of phonon eigenvectors is important when an imaginary phonon exists, but the influence is limited because rutile TiO_2 has no imaginary phonon.

Since the renormalization effect of phonon eigenvectors was not mentioned in the original submitted version of the manuscript, we have added the following sentense in the dielectric function section:

> On the other hand, in the E_{u}^2 and E_{u}^3 phonons, the two Ti atoms move in opposite directions, so the mode oscillator strength is much smaller. The renormalization of phonon eigenvectors by SCPH is negligible, and it is the phonon frequencies and self-energies that affect the calculation results of dielectric properties. The SCPH+B calculations agree remarkably...

1.3. #2

RC: ***In Table III, the harmonic B_{1u}^1 frequency by r^2SCAN agrees with the experiment much better than the anharmonic frequencies, no matter which method is used. This is also seen in the same optical branch along Gamma-M and Gamma-X in Fig. 3(a). Any idea why anharmonic frequencies agree with experiments worse than harmonic ones?***

AR: FIN We sincerely appreciate the referees insightful remarks about the discrepancy between our SCPH+B calculation and the experiment regarding the phonon bands. There seem to be different factors for this discrepancy between LDA and R2SCAN.

As for LDA, Because the Gruneisen parameter of this mode is positive, underestimating the lattice parameter leads to an overestimation of the frequency. From this point of view, it is natural that SCPH+B overestimates the frequency in the LDA. When calculated using the experimental lattice constant, the SCPH+B calculation gives a frequency of $121\,\mathrm{cm}^{-1}$, which is in better agreement with the experiment.

In the R2SCAN functional, however, the Gruneisen constant cannot explain the overestimation of the frequencies because the lattice constant is larger than the experimental value. We believe that the inability to accurately describe the B1u branch is due to the R2SCAN functional itself rather than to our anharmonic phonon calculations, because the potential energy surface of B_{1u}^1 phonon is better described by the anharmonic calculation than the harmonic approximation, as in Fig A1.

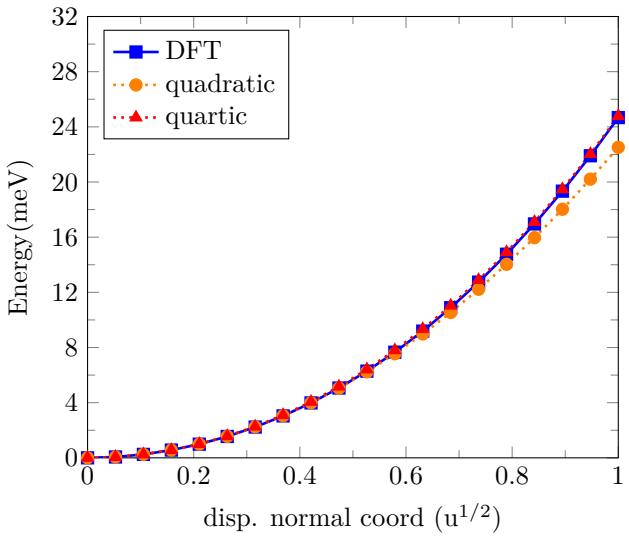

Figure A1: Frozen phonon potential (blue) of $B_{1\mathrm{u}}$ mode with x axis being the normal coordinate of $B_{1\mathrm{u}}$ phonon.

To discuss the dependence on the functional, we also performed SCPH+B calculations using the PBESOL functional. table 1 shows the optimized lattice parameters and Fig. A2 shows the band diagram with

Table 1: calculated lattice constants with LDA, r^{2}SCAN and PBESOL.

	a (Å)	c (Å)	u	c/a	v_0 (Å^3)
LDA	4.552	2.922	0.3038	0.642	60.55
r^{2}SCAN	4.602	2.961	0.3046	0.643	62.71
PBESOL	4.595	2.942	0.3044	0.640	62.12

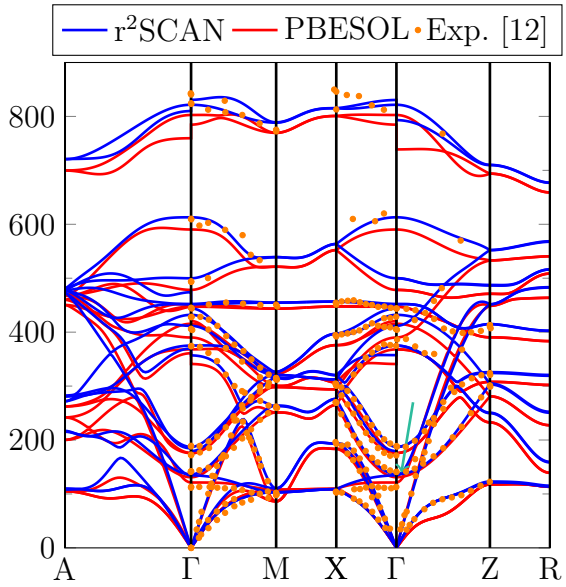

Figure A2: TEMPORAL

SCPH+B. As can be seen here, despite the fact that PBESOL has a smaller lattice constant than R2SCAN, the frequency of the B1u mode is 121 cm^{-1}, which is smaller than that of R2SCAN and reproduces the experimental value well.

For rutile TiO_2, several previous studies reported the differences in the results originating from functionals and pseudopotentials. The choice of the correct functionals and pseudopotentials is still an open question. In the present study, we have focused on the lattice dielectric properties, and have used the R2SCAN functional for the good description on the lattice constant and IR-active phonon modes. The lack of agreement in the B1u phonon branch is a drawback of R2SCAN. To make this point clearer, we have revised the manuscript as follows.

> The combination of the r^{2}SCAN functional and the SCPH+B calculation agrees well with the experimental data except for the lowest optical phonon mode (B_{1u}), which is mainly due to the functional itself rather than the anharmonic calculation.

1.4. #3

RC: ***In Fig. 3(b) and the first paragraph of Page 7, the authors indicated a generally good agreement between LDA and r^{2}SCAN phonon dispersions and LDAs overestimation of A_{2u} frequency due to its underestimation of volume (optimized at static zero pressure). I think it may be a better idea to compare***

LDA and r^{2}SCAN phonon dispersions at the same volume, say the experimental value, disregarding the calculated pressure. If that is the case, is LDA still good to use for vibrational properties calculations of TiO_2 and related materials?

AR: FIN We thank the referee for the insightful suggestion. To confirm this point, SCPH+B calculations with LDA were carried out using the lattice constants obtained experimentally and with R2SCAN. When we use the lattice constant of R2SCAN, which is greater than the experimental value, A2u becomes an imaginary mode phonon. If we use the experimental lattice constant, the frequency of the A_{2u} phonon is $146\,\mathrm{cm}^{-1}$, which is 15% smaller than the experimental value.

Our additional calculations confirm that the behaviour of the lattice constant-sensitive A2u modes, which is noted in previous studies with the harmonic approximation, is also seen at the level of anharmonic phonon calculations. Even if experimental lattice constants were used, the LDA would not correctly reproduce the frequencies of the A2u modes, demonstrating the usefulness of R2SCAN.

To better clarify the sensitivity of the A2u mode to lattice constants, we added the following sentense to the manuscript:

> The underestimation of the lattice constants of LDA may cause the overestimation of the A_{2u} phonon, as the A_{2u} phonon is sensitive to lattice constants. To clarify this point, we have performed the SCPH+B calculation with LDA using the experimental lattice constants. The resultant frequency of the A_{2u} phonon was $146\,\mathrm{cm}^{-1}$, which underestimatesthe experimental value by 15%. This result shows that the A_{2u} mode is sensitive to the lattice constant even at the level of anharmonic phonon calculations. For the LO phonons, the LDA results overestimate the ...

1.5. #4

RC: ***In Table IV, except for the TO E_u^1 mode, the 4ph contribution to the rest of the phonon modes linewidth by the SCPH+B is not as significant as the bubble contribution, yet non-negligible. Whereas in the abstract, it is stated, We show that the four-phonon scattering process contributes as much as the third-order anharmonic term to phonon linewidths. Perhaps this statement can be improved.***

AR: FIN WeOB thank the referee for pointing this out. We agree that the 4-ph contribution is as large as the bubble contribution only in TO E_u^1 and A_{2u} phonons, and that the original manuscript was incorrect. We have amended the manuscript as follows:

> We show that the four-phonon scattering process contributes as much as the third-order anharmonic term to phonon linewidths in some phonon modes.

2. The Second Referee

2.1. General Comment

RC: ***In this paper, the authors calculated the lattice dielectric function of TiO_2 by the anharmonic self-consistent phonon approach. The SCPH+ bubble (SCPH+B) theory proposed by [T. Tadano et al. Phys. Rev. Lett. 129, 185901 (2022)] is used, which includes the bubble phonon scattering. The importance of phonon anharmonic effect in the calculation of dielectric function is illustrated by comparing with experimental results. For typical phonon modes, the contribution of four-phonon scattering process to the phonon linewidth is not negligible. Anharmonic phonon properties and related issues, such as dielectric function are meaningful topics. The novelty of this paper mainly lies in the study and discussion of the necessity of phonon anharmonic correction of dielectric function. Before considering publication in PRB, the authors need to consider the following comments.***

AR: We sincerely appreciate the referees insightful comments on our manuscript. We believe that this manuscript will be of interest to many researchers as it discusses the dielectric properties of rutile TiO_2 with a detailed analysis of its anharmonic phonons. Following the suggestions of the referee, we have amended the manuscript appropriately. The point-by-point responses to the referees comments/questions are provided below:

2.2. #1

RC: ***The temperature-dependent static dielectric constant in the x direction obtained by the SCPH+B method is in good agreement with the experimental data, while the difference in the z direction is very large (Fig. 5), which obviously should not be attributed to the bubble scattering. The authors need to discuss this issue.***

AR: waiting for PBESOL calculations

2.3. #2

RC: ***Although the SCPH+B is significant to correct the phonon frequency and phonon width for specific phonon modes, some typical modes, such as E_{3u} ($26.5\,\mathrm{cm}^{-1}$) and A_{2u} ($16.2\,\mathrm{cm}^{-1}$) listed in Table IV, have a larger deviation from experimental results ($43.9\,\mathrm{cm}^{-1}$ and $46.4\,\mathrm{cm}^{-1}$) compared with non-SC results ($41.4\,\mathrm{cm}^{-1}$ and $30.4\,\mathrm{cm}^{-1}$). Do phonon scattering processes beyond the bubble scattering play a major role?***

AR: FIN We sincerely appreciate the referees insightful question on the discrepancy in linewidths in the LO phonons. We agree that the agreement between SCPH+B and the experiment is not good for E3u and A2u. The E3u and A2u modes have high frequencies at about $800\,\mathrm{cm}^{-1}$ and the number of phonons contributing to these self-energies is not large. It is therefore natural that the bubble diagram are smaller for these LO modes than TO modes.

Generally speaking, higher-order contribution is more important in the high frequency region such as LO E_{3u} and A_{2u} phonons. We could get better results by including higher-order diagrams, but higher-order calculations are difficult at this stage due to computational costs. However, the evaluation of higher-order diagrams is currently difficult from a computational point of view.

It should also be mentioned again that the values given in Table IV are the result of fitting with the FPSQ model: the non-SC results for E3u and A2u are in good agreement with the model, but the reflectivity (Figure 6) significantly underestimates the experimental values. We consider that the non-SC results do not correctly describe reality, as the reflectivity is usually smaller in theoretical calculations, where there are no impurities or other problems that can occur in experiments.

The following additions about the role of higher-order diagrams were made to the linewidth section.

> It indicates that the calculation of linewidth requires accurate determination of phonon frequencies, including anharmonicity, as pointed out by Fu et al. Discrepancies are observed in the E_u^1 and A_{2u} TO modes with relatively high frequencies, which could be improved by incorporating higher-order diagrams. We also found that self-energies ...

2.4. #3

RC: ***The contribution of the four-phonon scattering process to phonon linewidth is only significant for Eu1 and A2u modes. For other modes, however, the contribution of four-phonon scattering is much lower than the three-phonon scattering. Therefore, the statement of "We show that the four-phonon scattering process contributes as much as the third-order anharmonic term to phonon linewidths" in the abstract should be rewritten.***

AR: FIN We thank the referee for pointing this out. We agree that the 4-ph contribution is as large as the bubble contribution only in TO E_u^1 and A_{2u} phonons, and that the original manuscript was incorrect. We have amended the manuscript as follows:

> We show that the four-phonon scattering process contributes as much as the third-order anharmonic term to phonon linewidths in some phonon modes.

2.5. #4

RC: ***Figure 3b demonstrates a good agreement between between LDA and r^{2}SCAN throughout the Brillouin zone.The word "between" is repeated.***

AR: FIN We thank the referee for pointing out the error. We have fixed it.

3. The Third Referee

3.1. General Comment

RC: ***Amano and co-workers report a first principles study of the dielectric properties of TiO_2 using an anharmonic description of the lattice dynamics. Specifically, they use a self-consistent phonon theory including third and fourth-order terms. With this, they discuss temperature-dependent phonon frequencies, linewidths, and derived quantities, which are in general in good agreement with experiment. They are also able to assign a number of previously unidentified peaks of the dielectric function to two-phonon processes. Rutile TiO_2 is a scientifically and technologically interesting material, and the authors use state-of-the-art methods to describe its dielectric behavior. They clearly show that anharmonic lattice dynamics is essential for an accurate description of this compound. I would like the authors to consider:***

AR: We sincerely appreciate the referees supportive and insightful comments on our manuscript. We believe that this manuscript will be of interest to many researchers as it discusses the dielectric properties of rutile TiO_2 with a detailed analysis of its anharmonic phonons. Following the suggestions of the referee, we have amended the manuscript appropriately. The point-by-point responses to the referees comments/questions are provided below:

3.2. #1

RC: ***In Fig. 3(a), it looks like the harmonic (red) curve agrees better with experiment (orange dots). This is particularly clear with the lowest energy optical mode at the Gamma point. The authors instead write in the text: "The combination of the r^2SCAN functional and the SCPH+B calculation agrees well with the experimental data", seemingly ignoring the better agreement with harmonic calculations for some modes? Along the same lines, from Table III a mixed picture emerges, where agreement with experiment is best for different combinations of theory depending on the mode. Can the authors comment on these points?***

AR: The same as response to 1-st reviewer's question 2.

3.3. #2

RC: ***Can the authors speculate as to why the temperature dependence of ϵ_z is not well-reproduced in Fig. 5?***

AR: waiting for PBESOL calculation

3.4. #3

RC: ***More generally, the authors show that four-phonon processes are important, sometimes comparable to three-phonon process. Based on this, could the authors justify stopping at four-phonon processes? What role could higher-order processes play?***

AR: FIN We thank the reviewer for pointing out the role of higher-order diagrams. First, as regards the justification for stopping the expansion at 4ph diagram, it should be noted that the 4ph diagram is sometimes comparable to the bubble diagram for the line widths shown in Fig. 4, but the bubble diagram is still larger in the whole frequency domain. Also, higher-order diagrams are not calculated in previous studies pointing out the importance of the four-phonon diagram mainly due to computational costs.

Secondly, as regards the role played by higher-order diagrams, higher-order contribution is more important in high frequency region as in LO E_{3u} and A_{2u} in general. This is because higher-order diagrams involve more phonons, so contributions are more likely to appear at higher frequencies. We guess that including higher-order correction can improve the results for lifetime of these two modes in Table IV. But again, the

calculation is difficult due to computational costs.

The following additions about the role of higher-order diagrams were made to the linewidth section.

> It indicates that the calculation of linewidth requires accurate determination of phonon frequencies, including anharmonicity, as pointed out by Fu et al. Discrepancies are observed in the E_u^1 and A_{2u} TO modes with relatively high frequencies, which could be improved by incorporating higher-order diagrams. We also found that self-energies ...