Dr. Jason T. Haraldsen
Assistant Editor
Physical Review B

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Dear Dr. Haraldsen,

Attached is the revised version of our paper entitled *Plasmon dispersion in graphite: A comparison of current ab initio methods*, manuscript BZ13264/Anderson. We thank the referees for their useful comments and suggestions, as they have helped us to significantly improve the quality of our work.

In the following, we answer all the points raised by the referees and list all the changes made to the paper. We have marked changes in red for easy reference in the revised PDF version of the manuscript. Our responses to the reviewer comments are enclosed in blue boxes below.

We are confident that all suggestions have been met and hope that our manuscript is now acceptable for publication in Physical Review B.

Best regards,

Dr. Sean M. Anderson
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I. REPORT OF THE FIRST REFEREE – BZ13264/ANDERSON

Anderson and colleagues present a theoretical study of the momentum dependent EELS on graphite, comparing their results with published experimental data. The work compares three methods, BSE, ALDA, and RPA, assuming the same starting band structure, and investigates also the effect of the neglect of coupling between positive and negative energy e-h pairs (Tamm-Dancoff approximation). The main conclusions are that in graphite BSE gives the best results and the coupling term is important. The paper is clearly written, although somewhat repetitive in parts and somewhat long considering many of the points mentioned have been discussed in previous works and several similar calculations have been reported elsewhere (the references given appear adequate).

Thank you for your assessment.

In order to minimize some of the repetitive discussion, we have shortened the length of the manuscript by 3 pages by moving Section IV B (regarding the $\pi + \sigma$ plasmon) and Appendix A (computational benchmarks) to the new Supplemental Material, and by removing Fig. 8 which added very little to the overall message of the article.

As the authors note, the work is a "systematic study" on a "benchmark material". However, the conclusions drawn about coupling may be relevant only for a semi-metal like graphite, a material which is of limited interest nowadays in comparison to its 2D counterpart (the TDA appears to work well in other materials like BN, for instance). It is also disappointing that the authors do not discuss the different plasmon dispersions, in particular, their BSE-CP data appears linear (Fig. 4) instead of the measured parabolic behavior in q, while other approximations appear to yield the correct dispersion.

Graphite was selected as our material of study due to the relatively large quantity of available experimental data that is quite consistent (almost 5 decades worth). It also happens to be a plasmonic material where the TDA does not yield spectra that closely match experimental measurements. Graphene is also a semi-metal, so even if these results are indeed limited to only semi-metals, they would still be applicable.

However, 2D systems (such as graphene) often pose significant computational challenges, such as the application of the Coulomb cutoff to the electronic screening, and the large supercell volumes required to eliminate the spurious interlayer interactions. We have experience with GW calculations for a variety of bulk and 2D materials, such as graphane/graphone, MoS_2 and In_2Se_3; these calculations are often very difficult (or impossible) to converge. Again, we consider bulk graphite to be a good platform with which to consistently test these theoretical methods.

The apparent linear behavior of the q dispersion was caused by an error on our part, which is explained in detail in point 2 below. Now that we have corrected that error, we obtain the correct quadratic dispersion relation. We have added a curve to Fig. 5 in the main manuscript to demonstrate this behavior.

We have also toned down the language in the article in order to more accurately convey the results of the work.

Other specific points:

1. Both Ref 65 [Marinopoulos 2004, Fig 10] and Ref 51 [Liou, Fig 5c,d] report EELS calculations on graphite within RPA and ALDA. The agreement with experiment in those works is quite perfect. Instead, the present work, with the same approximations, yields worse agreement.

   In our opinion, there are two potential explanations for this disagreement: convergence and eigen-energies.

   Concerning convergence: attached to this document, we supply a convergence report for the TDDFT RPA calculation, for three distinct values of transferred momentum q. We find that our results are well converged for almost all parameters, with the exception of **k**-points for q values that are far beyond the first Brillouin zone. However, these large values of q do not even factor into our plasmon dispersion analysis of Figs. 4, 5, and 7, so the lack of convergence in such cases does not change our final results. Additionally, the **k**-point grids have a serious impact on every result presented, as they not only determine convergence but also the available values of q that can be probed; the selected 12×12×02 and 14×14×02 grids offer a good compromise between convergence and available q values. Liou et al., for instance, use a very fine **k**-point grid of 40×40×14, but with a cutoff energy of less than 8 Ha, as opposed to the 20 Ha we use here.

   Concerning eigen-energies: Fig. 3 of our manuscript clearly demonstrates that the application of a correction to the DFT eigen-energies can have a significant impact on the peak position and intensity. Liou et al. make no specific mention of any type of correction being applied to their calculated eigen-energies; thus, we cannot readily assume that they have carried out some type of quasiparticle correction to their base eigen-energies. On the other hand, Marinopoulos et al. mention that the valence bandwidth from photoemission data is stretch by 11 % with respect to the DFT results, and that GW calculations bring the DFT band structure into much better alignment with the experimental results. As these corrections are indeed necessary to accurately describe the observed spectra, we have applied stretching values obtained from GW calculations to our eigen-energies. It is also worth noting that our stretching values were calculated by one of the authors of that article.

   Therefore, we are confident that the results presented in this work are thoroughly converged, and that the stretched eigen-energies do play a significant role in providing accurate peak positions across all methods.

2. The author's data at $q \to 0$ seems out of step with the $q > 0$ data, clearly shown in Fig. 6, and in Fig. 4. This makes it harder to judge the dispersion. Is there a problem of convergence, or of methodology? Are the EELS peak positions determined from the eigenvalues or from the broadened curves?

   This discrepancy is due to an error on our part, and we thank the reviewer for pointing this out (we should have not made this mistake): we selected the wrong column when extracting the peak positions for the spectra at $q = 0.00$ for all methods.

   In all $\mathbf{q} \neq 0$, our files contain two columns: the energy loss and the EELS signal $\epsilon_M^{-1}(\omega)$. Only the $\mathbf{q} = 0$ case contains nine columns: the energy loss and the value of $\epsilon_M^{-1}(\mathbf{q}, \omega)$ for different directions of $\mathbf{q} \to 0$: along the x, y, z Cartesian coordinates, along $\mathbf{b}_1, \mathbf{b}_2, \mathbf{b}_3$ reciprocal lattice primitive vectors, and the averages.

   Fig. 1a depicts the results for the different available columns; r and c are reciprocal and Cartesian averages. The out-of-plane response corresponds to the $b_3 = z$ direction, and does not play any part in this study, where we are probing along in-plane paths. The previous wrong result, taking the default second column corresponding to the average along the reciprocal directions, was strongly biased in both intensity and peak position by the influence of the out-of-plane component (in a cubic material this would have not biased the result at all). By selecting the spectra for the $\mathbf{b}_1$ direction (correspondent to the $\Gamma \to$ M direction), we restore the correct result for the $\mathbf{q} = 0$ case.

In Fig. 1b, we present the EEL spectra for values of q along the $\Gamma \rightarrow$ M path. We have selected small values of q, calculated with a fine $40\times40\times02$ **k**-point grid. Comparing the $q = 0.00$ curve plotted from column 2 (averaged) and column 4 (along the $\mathbf{b}_1$ direction, which corresponds to the $\Gamma \rightarrow$ M direction), we see that the latter is much more representative of the q dispersion behavior. As mentioned above, this does not affect any of the calculations for $q > 0$.

After choosing the appropriate column for the spectra at $q = 0.00$, we see that the plasmon dispersion does indeed have quadratic behavior. We have corrected every figure in the main manuscript involving these results.

3. I am skeptical about the authors claims regarding the peak intensity (IV A) comparison with experiment since their broadening is very large (0.6eV); again, previous works found more reasonable intensities within RPA and ALDA. These three points in fact suggest a lack of convergence in the authors' calculations. While I appreciate that BSE-CP is a very tough calculation, it is unfortunately a serious point in a work whose main message requires a careful comparison of different approaches.

Concerning broadening and previous works,

- Marinopoulos et al. uses a broadening of 0.5 eV (see caption of Fig. 6).
- Liou et al. does not explicitly mention any particular broadening value but the curves look just as broadened as, or even more than, Marinopoulos et al.
- Trevisanutto et al. (Ref. 49) present several results for Im $\epsilon(\omega)$ for graphite; the in plane absorption spectra featured in Fig. 1 use a relative Gaussian broadening of $\sigma = 0.075\omega$, which puts the broadening at very comparable values in the π plasmon energy range of $\sim$6–10 eV.

We do not think that our value of 0.6 eV is particularly large in light of these previous works. In the attached convergence report, we have used a smaller broadening of 0.25 eV. Comparing the spectra intensity between the two broadenings, we obtain average percent differences below 20 % for every point.

Therefore, any differences between the results presented in this work, and those previously reported in the literature are more likely due to convergence discrepancies or from the eigen-values used, as mentioned in the points above. We agree with the reviewer when saying that the intensity clearly depends on the broadening, but our claim about the importance of including coupling effects for a better description of the intensity of the peaks still holds; it is valid not only for the BSE, but also for RPA or ALDA.

In summary, although the paper has appeal as a reference work, I have some doubts about the numerical convergence of some of the data, much of the physics "message" has been published elsewhere, the novel features are quite limited in scope being related mostly to methodology.

Thank you for your shrewd observations and very useful comments. We strove for this work to be a relatively complete, self-contained reference on the application of these theoretical frameworks on a well-characterized material. Specifically, we have

- Shortened the length of the main manuscript by 3 pages,
- Demonstrated that our calculations are adequately converged (see attached convergence report),
- Cited most of the relevant literature, both for theoretical developments and experimental measurements,
- Toned down the language to better convey the results and conclusions, and finally
- Expanded our Theory section in order to present a more complete reference for the reader.

With these changes, we hope that this paper can serve as an important reference material for researchers working in related fields.

II. REPORT OF THE SECOND REFEREE – BZ13264/ANDERSON

The paper "Plasmon dispersion in graphite: A comparison of current ab initio methods" by Sean M. Anderson, Bernardo S. Mendoza, Giorgia Fugallo, and Francesco Sottile presents a comparison of different numerical methods to determine the dielectric function and EELS spectrum of a solid. The techniques are applied to the calculation of the plasmon spectrum of graphite and compared to experimental results obtained over the past several decades to serve as a benchmark for the use of these methods for future systems. The methods include TDDFT, adiabatic LDA (ALDA), RPA and the solution of the Bethe-Salpeter equation (BSE). They also compare the full method including interactions between excitons with the Tamm-Dancoff approximation.
The article is a careful study of involved methods applied to a well-known system. As such, it is worth publishing as it may serve as a reference for calculations made on new materials. Overall the article is well written, but a few revisions are needed before the article can be accepted for publication in Physical Review B.

Thank you for your assessment and helpful suggestions. We have integrated these suggestions into the manuscript as follows below.

1. The second half of the abstract should be more explicit about the results of the article (TD is not good, BSE good but time-consuming, etc.) Also, the abstract has the statements "We accurately discern" and "We accurately compare". What does "accurately" mean in this context? What does "discern" mean in this context?

   We have expanded on the abstract to include a more explicit description of the results and improved some of the phrasing therein.

2. The introduction describes the methods and difficulties related to the calculation of optical spectra in solids. The paper then states that it compares these methods as they apply to graphite. There is not much new physics but the paper focuses on a comparison of methods. What is unclear in the introduction is if the authors were motivated to do their study by a present-day physical problem or system. Was the main interest only to compare different numerical methods? Or was it to study the plasmon spectrum of graphite? In short, the introduction should be more explicit about the underlying motivation. It would also have been desirable to apply the methods to a novel material that is presently under investigation.

   We have added a sentence to the second-to-last paragraph of the Introduction (page 2) with a clear statement of our motivation.

3. There is a typo on the left hand side of Eq. (8).

   In the new revision of the manuscript, Eq. (8) is now Eq. (3); we have corrected the left hand side, changing $\epsilon_{\mathrm{M}}(\mathbf{q},\omega)$ to $\epsilon_{\mathrm{M}}^{-1}(\mathbf{q},\omega)$.

4. When describing the results of Fig. 3, the authors state "however, the nature of the stretching causes a redistribution of the band energies, which causes changes in both the peak position and intensities." The statement should be qualified: is the redistribution improving or worsening the description of the EEL spectrum?

   The stretched band energies definitely improve the agreement between the theoretical and experimental peak positions. The reason is that the stretching simulates the correct band structure, as it would be experimentally given by photo-emission spectroscopy. We have added a sentence at the end of the paragraph (second-to-last paragraph of page 6) that clarifies this.

5. In the description of Fig. 5 the authors compare their results with the "Zeppendfeld" and "Liou" data and state that they are closer to the former. What conclusion can be drawn from that observation?

After reviewing both references, we were not able to find any relation between the two experiments and this observation. As it does not contribute anything to the discussion, we have removed the phrase entirely.

6. The figure captions should be more elaborate and self-explanatory. When reading them, one should be guided to the important features of the figure. For Figs. 6, 8, 9, 10 it would be useful to have a column label (either above or below the column) that specifies "with coupling" and "without coupling" (the authors will likely have a better keyword).

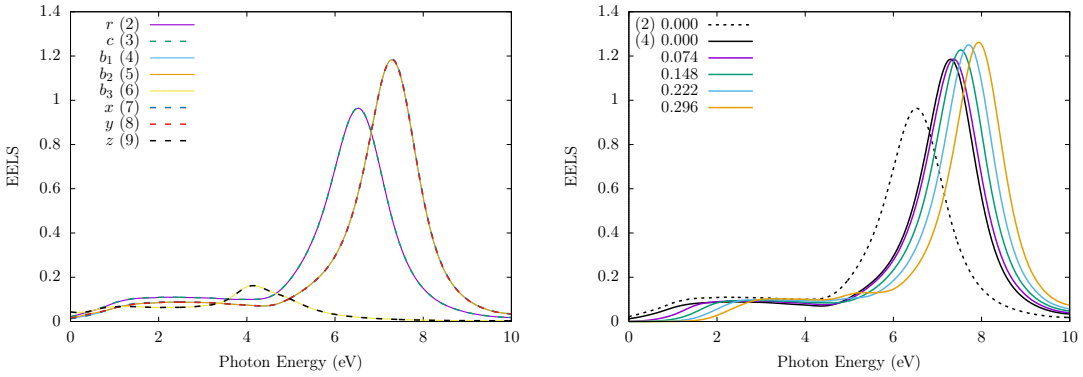
We have revised and expanded the captions of 9 figures to improve their comprehension.

Once the above points have been addressed, the paper can be recommended for publication.

Again, thank you for the very useful feedback. Besides the corrections and additions made above, we have also included a slightly expanded Theory section to make the entire work more self-enclosed. We also reduced the length of the paper by moving some content to a new Supplemental Material.

With these changes, we hope that this paper can serve as an important reference material for researchers working in related fields.

FIGURES



(a) The different directions, both in the reciprocal lattice and Cartesian spaces.

(b) EEL spectra for small values of q; $q = 0.00$ is plotted from an average across all directions (column 2) and along the $\mathbf{b}_1$ in-plane direction (column 4).

FIG. 1.