Convergence report for *Plasmon dispersion in Graphite: A comparison of current ab initio methods*

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In this report, we present a convergence study for the q-dependent EEL spectra of graphite. The matter of convergence is an important one, since it is required if we wish to accurately present these calculations. In particular, we are interested in presenting the most accurate peak positions of the π plasmon (0–10 eV energy range); namely Figs. 4, 5, and 7 of the main manuscript. We will therefore restrict the energy range of the present convergence study between 0–10 eV. The range of frequencies where the $\pi + \sigma$ plasmon occur, instead, is more delicate and while the RPA and TDDFT calculations well converged with the parameters presented below, the full BSE CP is not in this range. These results have been moved to the new Supplemental Material and serve as qualitative benchmarks and trends.

Table I presents the relevant parameters for the calculations featured in this work. The only exception, which is explicitely mentioned in the main manuscript, is for the Bethe-Salpeter calculation including the coupling terms in the excitonic Hamiltonian (BSE CP); for this method, we only use a total of 20 bands instead of 80. However, as we demonstrate below, 20 total bands is enough to accurately represent the 0–10 eV energy range of the π plasmon. Our convergence study for three select points along the $\Gamma \rightarrow \mathrm{M}_4$ path as follows; Fig. 1 is for $q = 0.00$ (at Γ), Fig. 2 is for $q = 1.48\,\text{Å}^{-1}$ (at M), and Fig. 3 is for $q = 2.96\,\text{Å}^{-1}$ (at M in the fourth Brillouin zone). The final parameters that were used throughout this work (listed in Table I) are labeled on each figure. We have used a Guassian broadening of 0.25 eV for every result presented below, in order to have a clear picture of the convergence behavior.

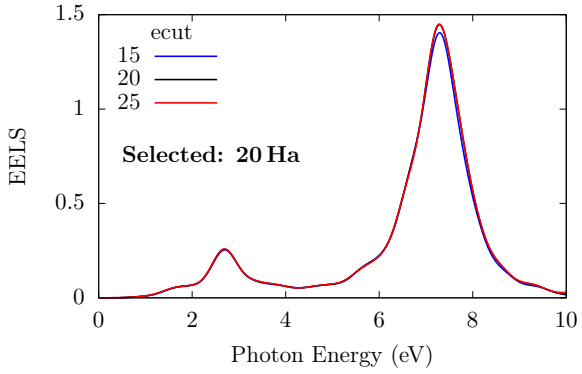
For $q = 0.00$ (Fig. 1), we see that convergence is readily reached for almost every parameter. Peak position differs by around ~ 0.1 eV for the **k**-points (Fig. 1b); the **k**-point grid also determines what values of q can be probed, so we must compromise between the total number of **k**-points and the specific grid being used. For $q = 1.48\,\text{Å}^{-1}$ (Fig. 2), the peak positions for the various **k**-point grids remain almost unchanged (Fig. 2b), with very slight variation in peak intensity. For the total number of bands (Fig. 2c), the selected 80 total bands far exceeds the necessary number for convergence. We noted above that we used 20 total bands for the BSE CP calculation; at least for RPA, the intensity may be slightly overestimated but the peak position remains virtually unchanged.

The situation is quite similar for $q = 2.96\,\text{Å}^{-1}$ (Fig. 3); however, it becomes clear that the spectra are unconverged with respect to the number of **k**-points (Fig. 3b). These curves indicate that convergence may require several thousand **k**-points, which is well beyond our current computational capacity for calculating the BSE CP spectra. That being said, it is very important to note that Figs. 4, 5, and 7 of the main manuscript do not feature points beyond the first Brillouin zone; thus, these results do not enter into that analysis. Furthermore, the intensity is 1–2 orders of magnitude lower when compared to the smaller values of q, so these results will not significantly impact the heatmap plots presented in the main manuscript and supplemental material. The same is true for the experimental counterpart: the intensity of the electron energy loss signal decay as $\frac{1}{q^2}$ with increasing **q**.

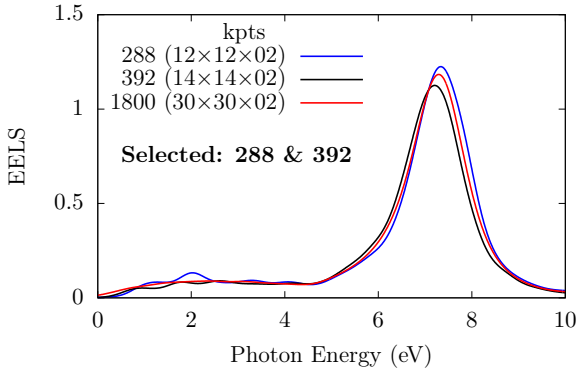
In conclusion, we consider that the calculations presented in this work are more than adequately converged. We would like to point out that, even though the convergence study has been carried out in RPA (and ALDA), the very same holds true for BSE. BSE calculations, in fact, converge at the same pace of RPA, sometimes even faster (e.g. with respect to the number of bands).

TABLE I. Calculation parameters used throughout this work.

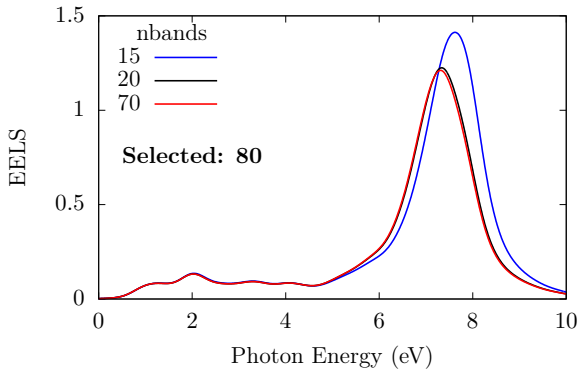
Parameter	Variable	Value
Cutoff energy (Ha)	ecut	20
k-points	kpts	288 (12×12×02), 392 (14×14×02)
Total number of bands	nbands	80 (20)
G-vector shells	matsh	12
Wavefunction shells	wfnsh	20



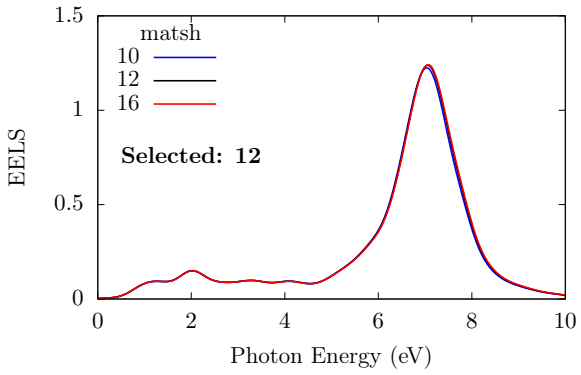
(a) Cutoff energy



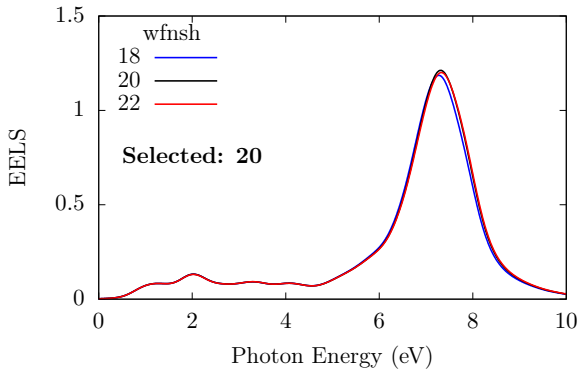
(b) **k**-points



(c) Total number of bands

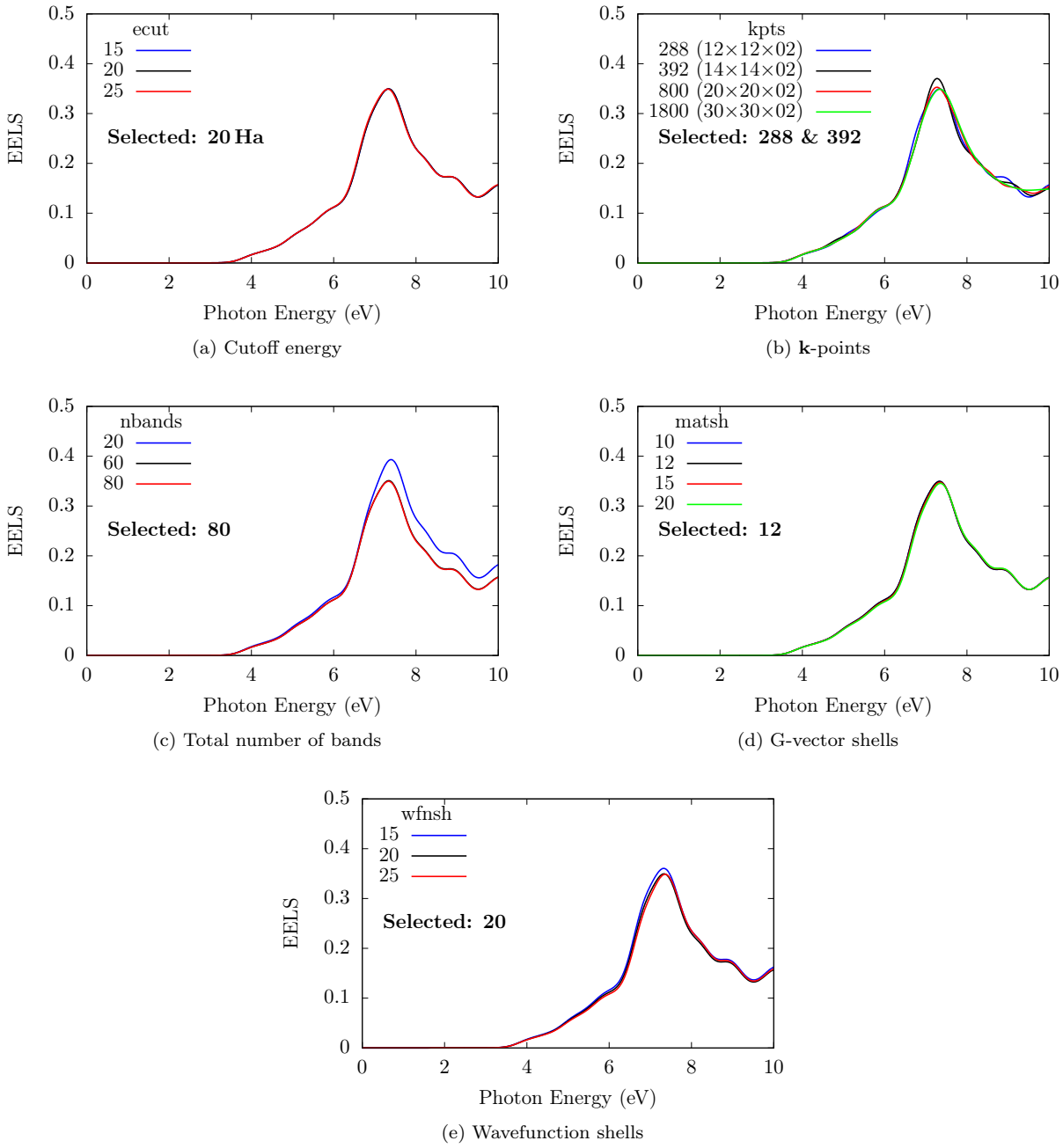


(d) G-vector shells



(e) Wavefunction shells

FIG. 1. Convergence for $q = 0.00\ \left(0\ \ 0\ \ 0\right)$.



(a) Cutoff energy

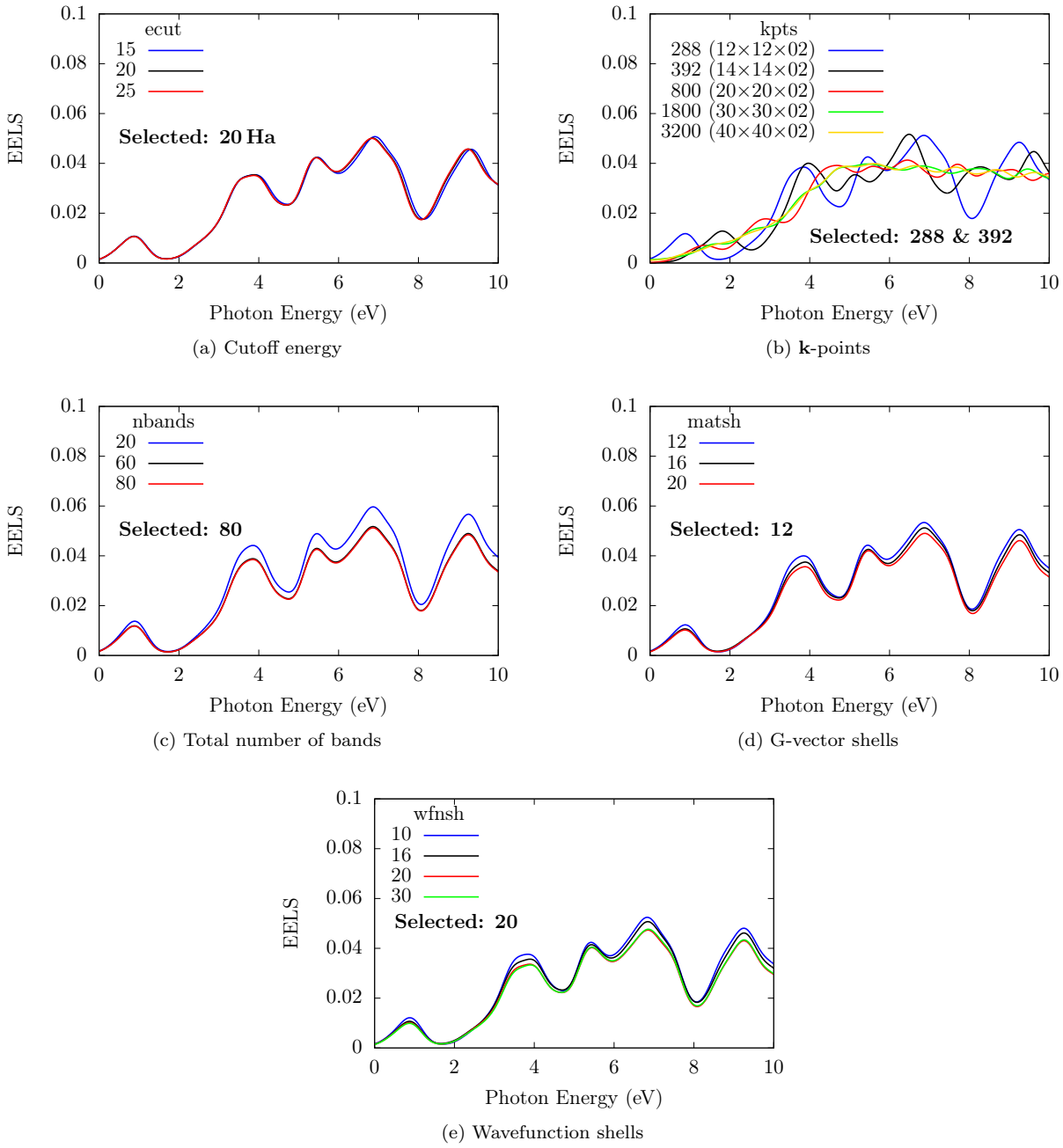
(b) **k**-points

(c) Total number of bands

(d) G-vector shells

(e) Wavefunction shells

FIG. 2. Convergence for $q = 1.48\,\text{Å}^{-1}$ $\left(\frac{1}{2}\ 0\ 0\right)$.



(a) Cutoff energy

(b) **k**-points

(c) Total number of bands

(d) G-vector shells

(e) Wavefunction shells

FIG. 3. Convergence for $q = 2.96\,\text{Å}^{-1}$ $\begin{pmatrix}1 & 0 & 0\end{pmatrix}$.