Comment on "Estimating Excitonic Effects in the Absorption Spectra of Solids: Problems and Insight from a Guided Iteration Scheme"

In a recent Letter [1], Rigamonti *et al.* claim that the bootstrap kernel (BSK) [2] of time dependent density functional theory does not yield reliable absorption spectra and that their kernel, to which they refer as the revised bootstrap (RBO) kernel, leads to significantly improved spectra. In this Comment we demonstrate that these claims are overstated and that these authors were unfortunately misled by focusing on only three materials: Si, Ar, and LiF. We also demonstrate that the RBO kernel significantly worsens the macroscopic dielectric constant ϵ_{M}.

In Figs. 1 and 2(a) we present the results for 15 small to medium and six large band gap insulators. Direct comparison with the experimental data reveals that for the former class of materials the RBO kernel yields no improvement over the BSK, while for the latter, the peak positions of the RBO spectra agree with experiment for Ar and LiF only. Indeed, on average, the percentage deviations of the BSK and RBO binding energies from experiments are almost the same (62% for the RBO kernel and 42% for the BSK), with the BSK slightly better: while the RBO kernel works well for Ar and LiF, (two of the three materials studied in Ref. [1]), the situation is reversed for NaH, PPV, and Ne [see Fig. 2(b)]. It should be noted that, while the RBO kernel performs comparably for excitonic peak positions, it overestimates the spectral weight even more than does the BSK.

As we now show, this purported improvement peak position accuracy of the RBO kernel is achieved at the cost of significantly worsening other key properties of interest. Straightforward algebra shows that $\epsilon_{\mathrm{M}}^{\mathrm{RBO}} = \epsilon_{\mathrm{M}}^{\mathrm{RPA}} + 1$. As $\epsilon_{\mathrm{M}}^{\mathrm{RPA}}$ is usually in good agreement with experiments, the accuracy of this quantity is significantly degraded by RBO—a fact that is evident from Fig. 2(c). The BSK by very construction allows for local field effects (LFE), while RBO does not as in Eq. 10 f_{xc} is not a matrix. In order to make a fair comparison between the two kernels we therefore switched off LFE in Fig. 1 and 2(a) (LFE enters only via head of the RPA matrix). All calculations are fully converged, as they were in Ref. [2]: 8000 k points and 80 bands above the Fermi level were used.

We close this Comment with a rebuttal of the claim of an improved computation time for the RBO kernel. The computational bottleneck for both kernels is the calculation of $\chi_0(\omega)$, so choosing the single shot RBO kernel over the iterative BSK has no noticeable impact on the computation time [3].

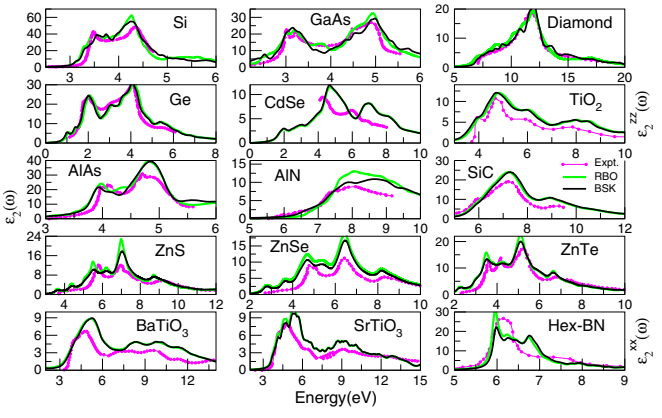

FIG. 1. Imaginary part of the dielectric function. Results obtained using the BSK are shown in black and those obtained using the RBO kernel are shown in green. Experimental curves are in pink.

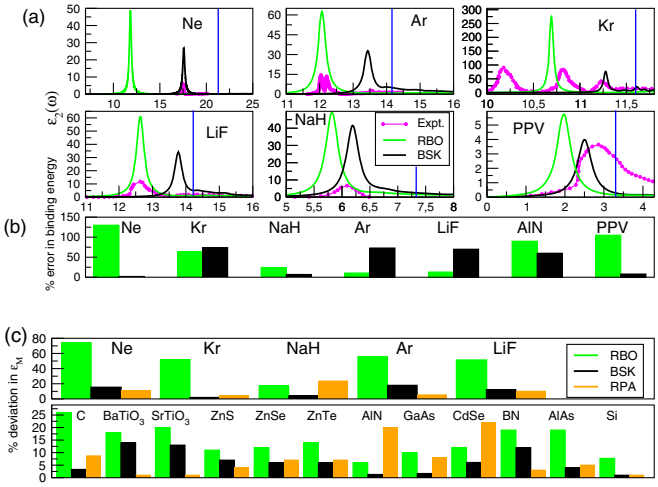

FIG. 2. (a) Imaginary part of the dielectric tensor as a function of energy (in eV). (b) Percentage deviation of the binding energy from experiments and (c) percentage deviation from experiment of ϵ_{M}. Results obtained using the BSK are shown in black and those obtained using the RBO kernel are shown in green. Experimental curves are in pink. The fundamental gap is indicated by the vertical blue line.

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Received 23 June 2015; published 7 October 2016
DOI: 10.1103/PhysRevLett.117.159701

[1] S. Rigamonti, S. Botti, V. Veniard, C. Draxl, L. Reining, and F. Sottile, Phys. Rev. Lett. **114**, 146402 (2015).
[2] S. Sharma, J. K. Dewhurst, A. Sanna, and E. K. U. Gross, Phys. Rev. Lett. **107**, 186401 (2011).
[3] S. Sharma, J. K. Dewhurst, S. Shallcross, G. K. Madjarova, and E. K. U. Gross, J. Chem. Theory Comput. **11**, 1710 (2015).

