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## Comment on “Linear Scaling of the Exciton Binding Energy versus the Band Gap of Two-Dimensional Materials”

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## Comment on “Linear Scaling of the Exciton Binding Energy versus the Band Gap of Two-Dimensional Materials”

In a recent Letter, Choi *et al.* have performed first-principles GW-Bethe-Salpeter equation (GW-BSE) calculations for a number of two-dimensional (2D) semiconductors and discovered a linear scaling relation between exciton binding energy  $E_b$  and quasi-particle bandgap  $E_g$  [1]. The authors further suggest that the linear scaling is expected to be applicable to essentially all existing and future 2D materials. In this Comment, we show that this linear scaling relation does not apply to all 2D materials, and a deviation from the linear scaling is predicted for small bandgap 2D materials.

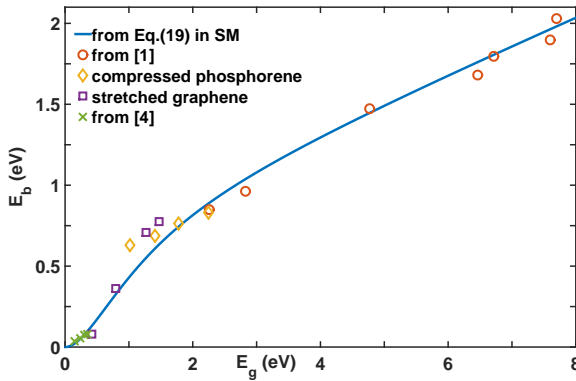


FIG. 1.  $E_b$  vs.  $E_g$  relation determined from first-principles GW-BSE method (symbols). The solid curve is a fit based on the analytical expression.

We first note that the linear relation revealed in Fig. 4 of Choi’s work cannot extend to a vanishing  $E_g$ , because it would imply a negative optical bandgap. We have carried out the first-principles GW-BSE calculations with essentially the same computational parameters as Choi *et al.* for a number of *small bandgap* 2D semiconductors. The computational details can be found in Supporting Material. Specifically, we stretch the zero bandgap graphene with tensile strains to open small bandgaps, and compress the 2D phosphorene to reduce its bandgap; all of them are energetically stable. The results are summarized in Fig. 1 along with the original data points from Choi’s paper. First of all, we reveal that for small bandgaps ( $E_g < 2$  eV), the linear scaling relation is clearly violated, and  $E_b$  decays much faster than the linear scaling prediction. Secondly, we confirm that the linear scaling remains valid for 2D semiconductors whose bandgap is greater than 2 eV. In fact, our data point of the largest  $E_g$  coincides with that of Choi of the smallest  $E_g$ .

We have derived an analytic expression correlating  $E_g$  and  $E_b$ , based on the similar hydrogenic model as used in [1]. In Choi’s Letter, the static dielectric constant  $\epsilon$

was taken to be the vacuum value ( $\epsilon = 1$ ), which is not justified in our opinion. Although there is no screening outside the atomic plane of the 2D material, the screening nonetheless exists within the plane and cannot be ignored. Thus,  $\epsilon$  should depend on the electronic structure and particularly the bandgap of the 2D materials [2]. The details of our model can be found in Supporting Material [5].

In Fig.1, we fit the analytic expression to the GW-BSE results, yielding a reasonable agreement between the two. The analytic model predicts that (i) the linear scaling relation applies to larger bandgaps ( $> 2$  eV); (ii) a deviation from the linear scaling relation happens for smaller bandgaps. GW-BSE calculations were recently performed on gated bilayer graphene where small bandgaps were opened [4]. These results are included in Fig. 1; they clearly deviate from the linear relation, but agree very well to our analytical expression without additional fitting. Moreover, an effective 2D dielectric constant has been recently proposed by averaging electronic screening over the extent of the exciton, based on which the correlation between  $E_b$  vs.  $E_g$  was examined for 51 transition metal dichalcogenides [3]. As shown in Fig. 2 of Ref. [3], the results also appear to agree with our finding, i.e., a deviation from the linear scaling is apparent for small bandgaps. Although the hydrogenic model reproduces the qualitative trend of the GW-BSE calculations, it cannot predict the exact correlation between  $E_b$  and  $E_g$ , particularly for bandgaps close to zero. The asymptotic behavior of  $E_b$  as  $E_g$  approaches zero remains an open question.

We thank the anonymous referee for her/his suggestion to include the results from Ref. [4] in Fig. 1.

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