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

In a recent Letter, Choi *et al.* 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 quasiparticle band gap E_g [1]. The authors further suggested 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 band gap 2D materials.

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 band gap. 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 band gap* 2D semiconductors. The computational details can be found in the Supplemental Material [2]. Specifically, we stretch the zero band gap graphene with tensile strains to open small band gaps, and compress the 2D phosphorene to reduce its band gap; 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 band gaps ($E_g < 2$ eV), the linear scaling relation is clearly violated, and E_b decays much faster than the linear scaling prediction. Second, we confirm that the linear scaling remains valid for 2D semiconductors whose band gap 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 ϵ 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, ϵ should depend on the electronic structure and particularly the band gap of the 2D materials [11]. The details of our model can be found in the Supplemental Material [2].

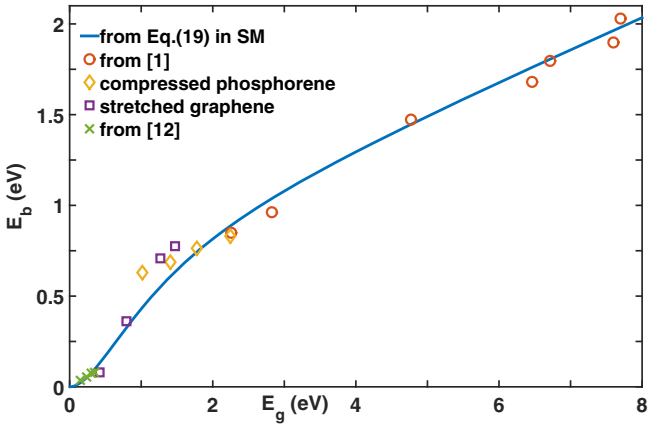

FIG. 1. E_b vs E_g relation determined from first-principles *GW*-BSE method (symbols). The solid curve is a fit based on the analytical expression.

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 band gaps (>2 eV), and (ii) a deviation from the linear scaling relation happens for smaller band gaps. *GW*-BSE calculations were recently performed on gated bilayer graphene where small band gaps were opened [12]. These results are included in Fig. 1; they clearly deviate from the linear relation but agree very well with 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 [13]. As shown in Fig. 2 of Ref. [13], the results also appear to agree with our finding, i.e., a deviation from the linear scaling is apparent for small band gaps. 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 band gaps close to zero. The asymptotic behavior of E_b as E_g approaches zero remains an open question.

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[2] See Supplemental Material at http://link.aps.org/supplemental/10.1103/PhysRevLett.118.209701, which includes Refs. [3–10], for analytical model of Eb vs. Eg and computational parameters of GW-BSE calculations.

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