

REPLY TO REFEREE 1

We thank the Referee for the thorough report and useful comments. Below we provide a point-by-point reply

Referee *I am not really convinced that the definition of the exciton-phonon coupling provided in previous works such as in Ref. [73,75] of the present manuscript is affected by overscreening. From basic equations of many body Green's function theory, the Bethe-Salpeter equation (BSE) in presence of electron-phonon interaction can be obtained once an approximation for the electron self-energy in terms of the electron-phonon coupling is given. In particular, the functional derivative of the electron self-energy respect to the electron Green's function gives the kernel of the BSE from which we can extract an effective exciton self-energy that provides also the definition of the exciton-phonon coupling as discussed in Ref. [50] of the present manuscript.*

Authors Before delving into the technicalities of this point we consider it essential to point out that that we did not claim that the exciton-phonon coupling \mathcal{G} is affected by overscreening. Our statement is slightly more complex. We are claiming that 1) the use of \mathcal{G} in the *electronic self-energy* of Fig. 1a gives rise to an overscreening

- The equation of motion for the polarization are calculated directly from Σ , so no functional derivative is needed here. As the correct Σ is the one in Fig. 1b, the occurrence of the asymmetric $\tilde{\mathcal{G}}$ is unavoidable.

2) the use of \mathcal{G} in the *diagrams for L* of Fig. 2 gives rise to an overscreening

- This point is intimately related to the next, and deserves a careful discussion. In fact, the derivation in Section 2.3 is, to the best of our knowledge, original. Starting from the first-principles electron-phonon Hamiltonian, one finds that the Dyson equation for L is [see Eq. (25)]

$$L = \tilde{L} - i\tilde{L}(v + gD_0g)L,$$

where \tilde{L} satisfies the BSE with kernel $K_{xc} = \delta\Sigma_{xc}/\delta G$. As shown in Eq. (28), a more convenient (since the dressed electron-phonon coupling appears) way of writing the above equation is

$$L = L^{(v)} - i\tilde{L}g^s D g^s \tilde{L}$$

where $L^{(v)}$ satisfies the BSE with kernel $K_{Hxc} = \delta\Sigma_{Hxc}/\delta G$. The diagrams in Fig. 2 represent the second term in this equation. Again, the occurrence of the asymmetric $\tilde{\mathcal{G}}$ is unavoidable.

3) the use of \mathcal{G} in the *kernel for $L^{(v)}$* of Fig. 3 *does not* give rise to an overscreening.

- We here fully agree with the Referee, and our results are perfectly in line with Ref. [73,75]. According to Eq. (67) [now Eq. (69)], we have

$$L^{(v)} = L^{\text{HSEX}} + iL^{\text{HSEX}}K^c L^{(v)} = \ell + \ell K_{Hxc} L^{(v)}$$

In other words, *in electron-phonon systems the full L does not satisfy a BSE with the kernel $K_{Hxc} = \delta\Sigma_{Hxc}/\delta G$. Instead, it is $L^{(v)}$ that satisfies it. One of the key messages of this work is that the (so far ignored) second term of the full L – that is $-i\tilde{L}g^s D g^s \tilde{L}$ – is the one responsible for converting coherent excitons into incoherent excitons (and is expressed in terms of the asymmetric $\tilde{\mathcal{G}}$) whereas the term containing the kernel K^c is the one responsible for the inelastic exciton-phonon scattering studied also in Ref. [73,75] (and is expressed in terms of the symmetric \mathcal{G}).*

We would like to point out that the above statements do not imply the absence of a BSE for the full L . Adding the Ehrenfest self-energy $\Sigma_{\text{Eh}} = gU$ [with $U = -iD_0gG$ the coherent lattice displacement, see Eqs. (93) and (121a) in PHYS. REV. X 13, 031026 (2023)] to the Hartree+exchance+correlation self-energy one finds the BSE

$$L = \ell + \ell K_{\text{Eh}+\text{Hxc}} L,$$

where $K_{\text{Eh}+\text{Hxc}} = \delta(\Sigma_{\text{Eh}} + \Sigma_{\text{Hxc}})/\delta G$. Notice that $\delta(\Sigma_{\text{H}} + \Sigma_{\text{Eh}})/\delta G = v + gD_0g$ is precisely the kernel of the Dyson equation above [which is Eq. (25) in the manuscript].

Referee *Still in that work the authors have shown that a suitable approximation for the electron self-energy is that reported in Fig. 1 (b) of the present manuscript. Indeed in this expression, as mentioned by the authors, the electron-phonon coupling is not overscreened in contrast with the expression reported in Fig.1 (a) where the overscreening is clear. Thus, I totally agree*

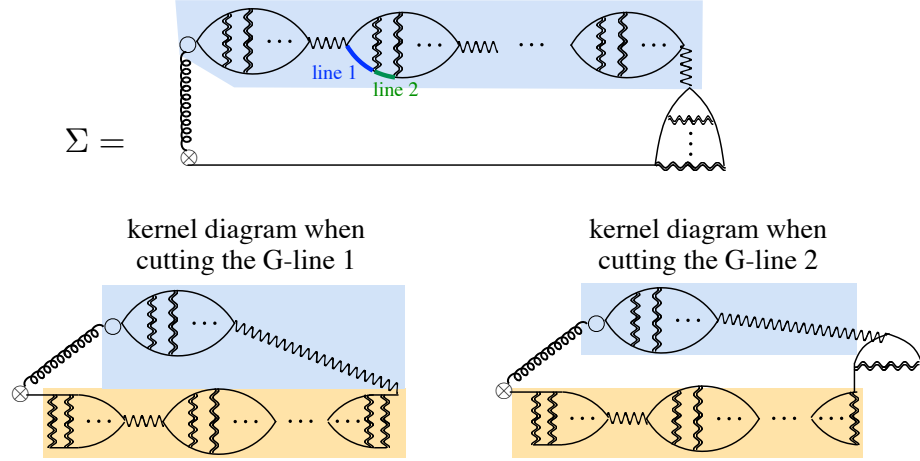


FIG. R1. Top: Self-energy diagram where the screened g^s is expanded (see faint blue area). Bottom: kernel diagrams resulting from the cut of line 1 (left) and 2 (right).

with authors that the correct expression of the electron self-energy is that reported in Fig. 1 (b). At this point, it is important to note that the structure of the exciton self-energy (and hence the exciton-phonon coupling) depends from the way in which the functional derivative of the electron self-energy is performed. In Ref. [50] the functional derivative is done neglecting the explicit dependence from the electron Green's function of $K^{(r),SEX}$ and the electron-phonon matrix elements g^s . This leads to an expression of the exciton self-energy in terms of the proper part of the two-particle correlation function \tilde{L}^{SEX} instead of the full L^{HSEX} as in Ref. [73,75]. This is the origin of the asymmetric structure of the exciton-phonon coupling $\tilde{\mathcal{G}}$ in Eq.(52).

Authors In the light of the clarifications given in the previous points, we hope that the Referee now appreciates that this is not the reason of the origin $\tilde{\mathcal{G}}$ in Eq. (52) [now Eq. (54)]. In Eq. (52) we have simply evaluated the scattering term ΣG with the self-energy of Fig. 1b – no functional derivative is involved.

A comment about Ref. [50]. As we wrote in the manuscript, looking at Fig. 5 of Ref. [50] we can infer that the authors of Ref. [50] have considered a scattering channel different from the one of Refs. [73,75], and hence the one of Fig. 3 of the present manuscript. In fact, their Eq. (45) contains a kernel depending on \tilde{L} whereas our Eq. (72) [now Eq. (74)] contains a kernel depending on L , in agreement with Refs. [73,75].

Referee However, in principle there is no reason to neglect the functional derivative of g^s which depends from the electron Green's function through the screening. This leads to the appearance of additional diagrams in the exciton self-energy. In particular, I suspect that, when the screening is evaluated using L^{HSEX} (i.e. consistently with our treatment of vertex corrections), the inclusion of the terms arising from $\delta g^s / \delta G$ would lead to the natural appearance of L^{HSEX} in the exciton self-energy and thus to a symmetric exciton-phonon coupling \mathcal{G} as in Eq. (44).

Authors This is an extremely interesting point. As already pointed out, the contribution stemming from the kernel in Fig. 3 is already written in terms of the symmetric \mathcal{G} [see Eqs. (86), now Eqs. (88)], since $K^c[L]$ is a functional of the full L . However, the way we have deduced such functional dependence was simply through the observation reported in the manuscript below Eq. (70) [now Eq. (72)], i.e., “We emphasize that no overscreening issue arises if we use the screened e-ph coupling in K^c . In fact, the Green's functions entering an e-ph vertex come from different xc functions, ensuring that screening is counted only once”. The Referee is suggesting that the same kernel can be derived by taking the functional derivative of the self-energy in Fig. 1b where the $\delta g^s / \delta G$ is not discarded. This suggestion certainly deserves to be further investigated. We are inclined to agree with the Referee provided that g^s is screened with the full \tilde{L} (not just the bare ℓ leading to an RPA screening) and that only specific contributions to $\delta g^s / \delta G$ are retained. Let us motivate this answer.

In Fig. R1(top) we show one of the self-energy diagrams of Fig. 1b in the main text. The screened electron-phonon coupling on the right is expanded as $g^s = g + g\tilde{L}v + g\tilde{L}v\tilde{L}v + \dots$ where \tilde{L} is calculated in the SEX approximation. The faint blue area surrounds the piece of the diagram corresponding to g^s . Let us now consider two Green's function lines: line 1 which is directly connected to a bare v , and line 2 which is an internal line of the polarization diagrams. Cutting line 1 we obtain the kernel in the bottom-left of Fig. R1. We recognize the diagrammatic structure belonging to g^s (faint blue area) and the diagrammatic structure belonging to L^{HSEX} (faint orange area). These diagrams belong to the kernel in Fig. 3 of the main text. However, if we now cut line 2 we find the kernel in the bottom-right of Fig. R1. These type of kernel diagrams are not included in Fig. 3 of the main text

(their inclusion would not allow to close the equations). To conclude, it seems reasonable to state that the kernel in Fig. 3 of the main text results from taking the functional derivative of the self-energy in Fig. 1 of the main text, but contributions to $\delta g^s/\delta G$ where G is an internal line of \tilde{L} have to be discarded.

Referee *In the present manuscript, an expression of the exciton-phonon matrix element formally equivalent to that of Ref. [50] has been obtained evaluating the collision integral in Eq. (43) using the ansatz in Eq. (46) and taking only terms linear in the off-diagonal part of G . However in doing this, the authors consider only off-diagonal G appearing in the external lines. But what about the linear terms where the off-diagonal G appear inside g^s ? I suspect that neglecting these terms is in some way equivalent to neglect $\delta g^s/\delta G$ in the derivation of Ref. [50].*

I suggest to think about this point before resubmitting the manuscript.

Authors In the light of the clarifications given in the first point, we hope that the Referee now appreciates that the occurrence of \tilde{G} is not related to the neglect of the off-diagonal part of G inside g^s . We also point out that in Appendix A we have discussed the contributions arising from off-diagonal internal Green's function lines. The conclusion is that these contributions are of higher order in the excitation density, and can therefore be discarded for the typical excitation densities attained in experiments.

Referee *The eigen-value problem in Eq. (2) describes excitons in absence of population. Thus it can be used only for optical absorption. In the present case the authors are treating excitons out-of-equilibrium. What about the Pauli blocking factors. Is there a reason to neglect them in Eq. (2)? Is this related to some assumption concerning the laser pulse (frequency of the laser pulse close to the exciton energy, small population etc)?*

The author should clarify this point in the manuscript.

Authors The Referee is correct. Our theory is applicable only for small excitation densities, and contains contributions up to second order in the excitation density. However, this does not mean that our theory contains *all* second order contributions. In particular, the renormalization of the excitonic wavefunctions due to Pauli blocking factors is neglected. Thus, we are implicitly assuming that the change of the exciton wavefunctions and exciton energies affect only slightly the rates governing the XBE dynamics. Let us observe that the inclusion of these effects would be numerically unaffordable. Indeed, one should solve the finite-momentum BSE with updated Pauli blocking factors for all momenta *at every time-step*. To the best of our knowledge, the impact of the Pauli blocking factors in the exciton dynamics has not been explored by anyone so far.

In the revised version we comment on this limitation of the theory at the end of Section 2.

Referee *The Bloch equations obtained in this work should describe how photoexcited coherent excitons are converted into incoherent excitons and how the latter propagate and eventually thermalize. Thus when the quasi-equilibrium is reached, these equations predict a photoexcited system consisting of a thermalized incoherent exciton gas. However, in general we expect a configuration in which incoherent excitons coexist with an electron-hole plasma [see for example: phys. stat. sol. (b) 131, 151 (1985)]. What about the electron-hole plasma? What is the regime in which the theory developed by the authors is applicable?*

I think the author should discuss these aspects in the article.

Authors The applicability of the XBE is only limited by the excitation density. As we write in the manuscript below Eq.(3): "Henceforth we use the word excitons for all solutions (bound and unbound) of Eq. (2)". Therefore, excitons and particle-hole pairs (plasma) are treated on equal footing. We clarify this point at the end of the introduction and below Eq. (3).

Of course, that for high excitation densities the screening of the Coulomb interaction differs from its equilibrium value and must be updated. The update of the screening is not accounted for in the current version of the theory. In the revised version we comment on this limitation of the theory at the end of Section 2.

Referee *In Eq. (2) I do not see any index associated to the spin degrees of freedom. Thus, I suppose that spin variables have been summed up in some way. This requires the introduction of two decoupled BSEs. One for the singlet channel and one for the triplet channel [see: RIVISTA DEL NUOVO CIMENTO VOL. 11, N. 12]. If this is the case Eq. (2) refer to the singlet channel [see Phys. Rev. B 62, 4927 (2000)]. As a consequence, the matrix elements of the bar Coulomb potential in Eq. (3) should be multiplied for a factor 2.*

Authors The band indices μ, ν etc are spin-orbital indices. In fact, the theory can equally be applied to systems with spin-orbit interactions. For systems described by a Hamiltonian that is invariant under spin rotations then $\mu = m, \sigma, \nu = n, \sigma$ etc can be written as a pair of indices, the first describing the orbital part and the second describing the spin-projection onto, say, the z axis. In the revised manuscript we clarify this point at the beginning of Section 2.1.

Referee *In the manuscript the author call v "direct electron-hole interaction" and W "exchange electron-hole interaction". In the literature, on the contrary, direct and exchange are usually used to indicate W and v , respectively.*

Author We are aware of this different terminology. However, it's important to note that the BSE kernel W arises from the derivative of the (screened) exchange self-energy whereas v stems from the derivative of the (Hartree) direct self-energy. In diagrammatic treatments of L , the terms “direct” and “exchange” are often interchanged: the functional derivative of the “exchange” self-energy is referred to as the “direct” kernel W . We find this terminology somewhat counterintuitive.

REPLY TO REFEREE 2

We thank the Referee for the thorough report and useful comments. Below we provide a point-by-point reply

Referee *The BSE has a spin structure exhibiting different channels: excitons (singlet and triplet) plus magnons. In the case of collinear spin polarization, singlet and triplet excitons are mixed. In the case of spin-orbit interaction, excitons and magnons are mixed. [See Bechstedt, Many-Body Approach to Electronic Excitations, Chapter 18.2] The theory presented here is most likely applicable to the exciton channel (singlet+triplet) for all kinds of spin polarizations and including spin-orbit coupling, while neglecting the magnon channel. The authors could explicitly remark on this.*

Author In the revised version, see beginning of Section 2.1, we clarify that the band indices μ, ν etc include both spin and orbital degrees of freedom - they are spin-orbital indices. We agree with the Referee that for systems without spin polarization singlet and triplet can be treated separately. However, we choose to maintain a more general discussion to encompass a broader range of materials (including those for which the spin-orbit interaction cannot be discarded).

Referee *The authors could remark on the connection between the exciton polarization in Eq. (15), which is derived from the disconnected part of the two-particles Green's function, and photoabsorption spectra. This could be useful since in most textbook derivations of the BSE, which are in the context of linear response and Hedin's equations, photoabsorption spectra are obtained starting from the Dyson's equation for L instead of GG . [See e.g. Strinati, Rivista del Nuovo Cimento, 11, 12 (1988)]*

Author We have inserted a discussion on the connection between ρ_{cv} and the photoabsorption spectrum at the beginning of Section 3.

Referee *The theory is formulated in the Tamm-Dancoff approximation, in which the Coulomb couplings between resonant and antiresonant valence-conduction transitions are neglected in the BSE kernel. It is presently unclear how much these terms are important out of equilibrium (even for a semiconductor), but I suspect that if they are included in the phonon-assisted kernel, they will also lead to the explicit appearance of the interband valence-conduction (screened) electron-phonon couplings inside additional exciton-phonon contributions. Do the authors have any comments on this?*

Author This is certainly an interesting point, though it is rather challenging to address. We can say that phonon-induced valence-conduction transitions should be taken into account when their contribution to the recombination time becomes comparable to the radiative recombination time. This finite (high?) excitation-density correction has not been accounted for. Other corrections are the renormalization of the exciton energies and wavefunctions due to Pauli blocking factors as well as the update of the screened Coulomb interaction W during the time evolution. Unfortunately, all these corrections would considerably complicate the formulation, making practical implementations unfeasible. In the revised version we clarify that the excitonic Bloch equations derived in this work are applicable for small excitation densities [containing effects up to second order], and state that the aforementioned finite-density corrections have been discarded, see end of Section 2.3.

Referee *The authors distinguish between the coherent exciton regime, where the exciton-phonon coupling is “irreducible”, and the incoherent regime, where it is “reducible”. Excitonic polarizations are then converted to populations again via the irreducible exciton coupling with phonons. The overscreening discussion in the coherent case, along with the identification of the correct electron-phonon self-energy and irreducible ex-ph coupling, is equivalent to the findings in Ref. [50] starting from linear response. The discussion of the exciton-phonon BSE kernel and relative reducible ex-ph coupling for the incoherent case is equivalent to Refs. [75] and [Cudazzo, PRB 102, 045136 (2020)] starting from an extension of the static BSE kernel (here I propose that the latter reference may be cited in the text). However, while these cited papers assumed that either the irreducible or reducible couplings should be used in all cases, the present paper makes the case for both formulations being correct, albeit in different regimes. It could be useful to explicitly state this in the text in order to make the points of convergence and departure with previous works clearer. I do have some additional comments on this.*

Author We thank the Referee for this suggestion. At the beginning of Section 6 we have inserted the following sentence: “It is noteworthy that the irreducible exciton-phonon coupling $\underline{\mathcal{G}}$ governs the dynamics of coherent excitons, while the reducible exciton-phonon coupling \mathcal{G} governs the dynamics of incoherent excitons. The XBE reconciles previous works that advocate

for either $\tilde{\mathcal{G}}$ [50] or \mathcal{G} [53,71-74], by clarifying that both are essential, though relevant in different regimes (or equivalently at different timescales).”

We have also added a citation to the work of Cudazzo, before Eq. (46) and in the discussion of the kernel K^c in Section 5.

Referee *The authors emphasize that the coherent part of the theory could be expressed in terms of reducible excitons if bare el-ph couplings were used. In the text they write $g^s \tilde{L} = gL^{(v)}$, but the implication seems to be – by looking at Appendix B – that actually the v -reducible L could be replaced with L^{HSEX} , i.e. only the first term in Eq. (67). Is this correct? This means that the exciton-phonon self-energy obtained with the irreducible ex-ph coupling and the irreducible \tilde{L} should be equivalent to the one obtained with the bare ex-ph coupling and the reducible – actually HSEX – L . But L^{HSEX} and \tilde{L} have different poles. How can Eq. (88) still be valid (including in the low-density regime) in the gL^{HSEX} formulation? In particular, in Ref. [50] it is pointed out that the $g^s \tilde{L}$ treatment gives rise to intrinsic nonzero phonon-mediated linewidths also for the lowest-lying excitonic state. I don't understand how a treatment with gL^{HSEX} could give the same.*

Author The attempt of formulating the theory in terms of excitons and bare electron-phonon coupling is developed in Appendix B. Relegating this formulation to an appendix was intentional. As we have explicitly written in the last sentence of the Appendix, the fact that bare interband (valence-conduction) couplings come into play “complicates the whole theory as the equations of motion can no longer be closed solely on exciton numbers”. The point we wanted to emphasize is that a formulation in terms of excitons only is problematic.

No complications arise if the *bare* intraband electron-phonon couplings are zero – in this case the equations of motion close on ρ_λ and $N_{\lambda Q}^{inc}$. If such a physical system exists, then Eq. (109) would be a legitimate alternative to Eq. (55), and the accuracy of each should be further investigated. We emphasize that the $gL^{(v)}$ formulation is *alternative* but not *equivalent* to the $g^s \tilde{L}$ formulation. Indeed, the diagrammatic content of the self-energy and, more important, the way the electron-phonon couplings are screened (static versus dynamic) are different [compare Fig. 1 with Fig. 4].

Referee *About the incoherent excitons. In this case, the authors do not start from an electronic self-energy, but rather from the BSE for L (the correlated part of the two-particles Green's function) with a general interaction kernel, which is then approximated to HSEX for the Coulomb part, and to first order in D (the phonon Green's function) for the phonon part. Are these choices compelled by consistency with the previous coherent treatment (such as: approximating \tilde{L} as L^{SEX} requires L to become L^{HSEX}) and/or compliance with state-of-the art simulations (since BSE calculations are usually done in the HSEX approximation)? Is it not possible to obtain an electronic self-energy whose functional derivative with respect to the Green's function would yield this HSEX+ph kernel? And if not, can there be consistency issues (such as missed cancellations) between terms arising from the dressing of the electron Green's functions (quasiparticle corrections) and those appearing in the incoherent exciton-phonon kernel?*

Author Given the intricate diagrammatic structure of the kernel, addressing the Referee's questions poses significant challenges. The question on the existence of a self-energy leading to the kernel in Fig. 3 has been asked by Referee 1 as well. We invite the Referee to read our reply to the third point of Referee 1, where we provide a partial answer to the question.

Regarding the consistency issues, the Referee is probably referring to the violation of the Ward identities. Such violation is rather common in many-body approximations, and its significance depends on the physical system. Unfortunately, we are unable to provide a precise answer to this point.

Referee *On a related note: does Eq. (66) for the conservation of the total exciton number remain valid independently of the approximation chosen for N^{inc} in Eq. (65), that is, the type of incoherent kernel employed?*

Author The answer is negative. Equation (66) [now Eq. (68)] holds true only when all four diagrams of the kernel shown in Fig. 3 are included. Any approximation that omits one or more diagrams would violate the conservation law.

Referee *Does $N^{inc}(t)$ tend to relax to a Bose-Einstein distribution after long times? What about $\tilde{N}(t)$? In other words, can this theory provide some hints at the form of the “exciton” occupation function after they have relaxed to the bottom of their dispersion curves, before recombination?*

Author We thank the Referee for this comment. $N^{inc}(t)$ relaxes to a Bose-Einstein distribution with the same temperature of the phonon bath. This follows from the fact that the r.h.s. of Eq. (85) [now Eq. (87)] vanishes if f^{ph} and N^{inc} are both a Bose distribution, and from the fact that $\rho_\lambda \rightarrow 0$ in the long time limit – thus the whole r.h.s. of the third equation in Table 1 approaches zero. Since both N^{inc} and f^{ph} are described by a Bose distribution when $t \rightarrow \infty$, then $\tilde{N} \rightarrow N^{inc}$ in the same limit. Indeed, for $\tilde{N} = N^{inc}$ the r.h.s. of the second equation in Table 1 is zero. In the revised manuscript we have added a discussion on the long-time limit behavior of the XBE at the end of Section 6.

Referee Spotted typos:

- Eq. (7): the last z^+ should be z'^+
- Before Eq. (50): N^{HSEX} in the text should be \tilde{N}^{SEX}

Author Thank you, we have corrected both typos.