

# Non-Monotonic Size-Dependent Exciton Radiative Lifetime in CsPbBr<sub>3</sub> Nanocrystals

Corresponding Author: Professor A. Paul Alivisatos

This manuscript has been previously reviewed at another journal. This document only contains information relating to versions considered at Nature Communications.

**This file contains all reviewer reports in order by version, followed by all author rebuttals in order by version.**

**Attachments originally included by the reviewers as part of their assessment can be found at the end of this file.**

Version 0:

Reviewer comments:

Reviewer #1

(Remarks to the Author)

Please see attached referee report

Reviewer #2

(Remarks to the Author)

This manuscript focused on the radiative lifetime of different size of CsPbBr<sub>3</sub> nanocrystal and authors claimed their size regime variation non-monotonic trend. Nanocrystals in the weak and strong quantum confinement regimes of smaller and larger sizes displayed longer radiative lifetimes where the intermediately confined nanocrystals exhibited the shortest radiative lifetimes.

I carefully read the manuscript, comments of both reviewers, references discussed in the manuscript, authors rebuttal, and still confused to agree with the claim. The finding indeed provides something unique among nanocrystals and states the vulnerability of the decay systems in these halide perovskite nano systems. However, something I could not understand why did authors focus in three size regimes and found such unlikely trend even though this was compared with CdSe QDs. Authors also stated the phase matters here and if so, that can be focused here rather than highlighting size regime. Further, they have avoided to run the 4K data which were indeed required here to validate the big claim. These suggests that (1) authors may relate the size regime with phase and in this case and one more size in orthorhombic phase may be considered to be added. In second (2) to reduce the surface interference as shape varied with size, low temperature data may be added. These two data/clarifications are indeed missing.

Summary: This revised manuscript still shows confusion and has too little data to provide the conclusion of Non-Monotonic Size-Dependent Exciton Radiative Lifetime in CsPbBr<sub>3</sub> Nanocrystals. Novelty is still a question here.

Hence, in its current form, this is also unclear why it will be considered for NC.

1. What are the noteworthy results? : Stated above
2. Will the work be of significance to the field and related fields? How does it compare to the established literature?
3. If the work is not original, please provide relevant references. N/A
4. Does the work support the conclusions and claims, or is additional evidence needed? Additional evidences needed.
5. Are there any flaws in the data analysis, interpretation and conclusions? Do these prohibit publication or require revision? Partially and needs revision
6. Is the methodology sound? Does the work meet the expected standards in your field? Yes
7. Is there enough detail provided in the methods for the work to be reproduced? Ye

Version 1:

Reviewer comments:

Reviewer #1

(Remarks to the Author)

Please see attached PDF file with my review.

Reviewer #2

(Remarks to the Author)

Authors addressed my comments satisfactorily and now the Editor can take decision.

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## Note to the reviewers:

We are grateful to the reviewers for their thoughtful and constructive feedback, which has led to significant improvements in the manuscript. In this revised version, we have addressed all reviewer comments carefully and made substantial clarifications and additions. Additions made directly in response to the reviewers' comments are included in this document. Additional material that arose from follow-up investigations prompted by the reviewers' suggestions has been incorporated into the manuscript and is highlighted in blue.

In particular, we have expanded our analysis of the role of crystal symmetry in the observed non-monotonic size dependence of radiative lifetimes. This was enabled by the development of new computational tools, which allowed for a more nuanced understanding of how structural transitions influence excitonic behavior. We have also clarified the language used to describe quantum confinement regimes, ensuring it more accurately reflects the physical properties of the nanocrystals studied in both experiment and theory.

Below, we provide a detailed, point-by-point response to each reviewer comment. Reviewer remarks are shown in **bold**, followed by our responses and references to the corresponding changes in the manuscript.

## Synopsis of Author's response to the first report (Referee-1):

- 1) Referee-1 made five comments/criticisms on the original submission to which the Authors have responded.

The most important question posed pertained to the number of samples measured in the study; it seemed to be rather small (3) in the first version, which raised a doubt about the validity of the main reported result –namely, the non-monotonic trend in the radiative decay rate with respect to nanocrystal size. The Authors have clarified this point - a large number of independent samples (34) were measured, which in my view addresses that concern fully.

Given that, the work is convincing to me and in my opinion the results will be interesting in the nanocrystal community especially as it bears on the importance of electron/hole correlation effects and the fact that these evidently persist to room T.

**Response:** We are glad that our clarification fully addressed the concerns and thank the reviewer for their support of publishing our work.

- 2) I am sympathetic that adding measurements over temperature would comprise a lot of work and would entail a significant delay. While it would be nice to see in future a test of the Authors' theoretical interpretation in a temperature series, on reflection, I think that their

results should be published at the *current* stage, since the experimental finding reported is surprising/interesting.

**Response:** We thank the reviewer for their thoughtful comment and for agreeing that our work should be published at the current stage.

- 3) The Authors' response is an explanation why they wrote what they did but does not actually respond to original comment.

Their use of the terms strong/weak confinement is oversimplified and not consistent with literature usage (e.g., I checked the *ACS Nano* 2021 reference they provided, I didn't check the others) and as a result, I think it could create (or perpetuate) misunderstanding.

The Authors still identify the largest and smallest nanocrystals as corresponding to the weak and strong confinement regimes, writing this in the Abstract and the Conclusions; in the Conclusions for example they write that "Larger and smaller nanocrystals in the weak and strong quantum confinement regimes displayed longer radiative lifetimes." But that characterization is not correct. The weak confinement regime ( $L \gg a$ ) is never realized within the size range studied, nor is the strong confinement regime as it is understood in the literature ( $L \ll a$ ).

I suggest that the Authors simply add a few words to explain what they wrote in their response. Instead of writing statements as they did such as "Larger and smaller nanocrystals in the weak and strong quantum confinement regimes" they could make the statement strictly correct by rephrasing along these lines: "Larger and smaller nanocrystals **respectively approaching** the weak and strong quantum confinement regimes ..."

**Response:** We apologize for misunderstanding the original question of the reviewer and agree with his/her classification. Before detailing the changes, we have made to the manuscript, we would like to clarify that the strong and weak confinement regimes are strictly defined by the limits  $L \ll 2a$  and  $L \gg 2a$ , respectively. Given that CsPbBr<sub>3</sub> (CsPbI<sub>3</sub>) has a Bohr diameter of  $2a \approx 7$  (12) nm, strictly speaking, all particle sizes in our simulations fall within  $L \leq 2a$ , thereby covering the strong confinement regime and approaching intermediate confinement for the largest system analyzed. Experimentally, the size studied are above  $2a$  and enter the weak confinement limit. In response to the Reviewer's comment, we have revised the manuscript to adopt the suggested phrasing of "approaching" intermediate and weak confinement. We would like to note in passing, that our calculations do not assume weak, intermediate, or strong confinement. Instead, we directly diagonalize the BSE matrix and achieve convergence of the excitonic states, independent of the confinement regime.

- 4) The Authors' response addresses a different question than the one I asked. Their response conflates electron/hole exchange with correlation in the electron and hole position

coordinates. These are different things. For example, excitons in a nanocrystal characterized strictly by strong confinement have no correlation in the electron and hole position coordinates (i.e., in strong confinement the exciton envelope function can be understood strictly as a product of uncorrelated electron and hole wavefunctions), but such a system certainly has fine structure splitting due to electron-hole exchange.

I suggest they clarify this distinction. In any event, the additional calculations in Suppl Fig 7 are useful since for example, the model in Kreig did not include fine structure splitting.

**Response:** We appreciate the reviewer for clarifying their comment, as it was not entirely clear to us in the first round. We agree with the referee's perspective. In our work, we employ the Bethe-Salpeter equation (BSE) to describe excitons using an electron-hole pair basis. It is important to emphasize that the BSE approach is suitable in the weak, intermediate, or strong confinement regimes as pointed out in the previous comment. In the BSE framework, the spatial noncorrelated limit is achieved by neglecting the direct and exchange integrals. Spatial correlations are included by computing direct and exchange terms thus providing a clear link between exchange and spatial correlations.

To prevent further confusion, we have revised the caption of Fig. S7 to clarify this point. The new caption reads: **“Figure S1: Contrasting Size Dependent Radiative Lifetime Trend Without Electron-Hole Correlation. a,b,** Exciton energy level diagrams as a function of CsPbI<sub>3</sub> nanocube edge length for (a) uncorrelated and (b) correlated excitons. Uncorrelated excitons are taken as a product of an electron and hole state, and correlated excitons are obtained by solving the BSE. For uncorrelated electron-hole pairs, the lowest energy states are quadruply degenerate bright states, with higher lying dim states becoming thermally accessible for larger systems in which the DOS is increased. The fine structure changes when we solve the BSE and include electron-hole correlations. The lowest energy state is a dim singlet below a manifold of bright triplet excitons. **c,** Size-dependent Boltzmann population of the lowest energy bright state for uncorrelated (orange triangles) and correlated (blue circles) excitons. For small nanocrystals, there is opposing size dependent behavior. Thermal population of higher lying states decreases the emissive ground state population for uncorrelated excitons, while for correlated excitons the emissive triplet state increases in population for larger nanocrystals, until the inflection point where thermal population of higher lying dim states decreases the triplet population. **d,** Predicted radiative lifetimes of uncorrelated excitons increase monotonically due to decreased Boltzmann population of the emissive manifold. Contrastingly, for correlated excitons, reduced confinement in larger nanocrystals lowers the energy of the bright triplet states with respect to the dim ground state, increasing the Boltzmann population of emissive states and decreasing the lifetime (Fig. 5).”

5) I accept the argument made by the Authors.

**Response:** We thank the reviewer for their comment.

**Recommendation:**

I recommend publication of the manuscript with minor revisions as noted in points 2 and 3 above.

The work convincing to me and in my opinion the results will be interesting in the nanocrystal community.

**Response:** We thank the reviewer for their thorough and insightful evaluation of our manuscript and their recommendation for publication. We appreciate their positive feedback that helped strengthen our manuscript.

## Reviewer 2:

This manuscript focused on the radiative lifetime of different size of CsPbBr<sub>3</sub> nanocrystal and authors claimed their size regime variation non-monotonic trend. Nanocrystals in the weak and strong quantum confinement regimes of smaller and larger sizes displayed longer radiative lifetimes where the intermediately confined nanocrystals exhibited the shortest radiative lifetimes. I carefully read the manuscript, comments of both reviewers, references discussed in the manuscript, authors rebuttal, and still confused to agree with the claim. The finding indeed provides something unique among nanocrystals and states the vulnerability of the decay systems in these halide perovskite nano systems.

- 1) However, something I could not understand why did authors focus in three size regimes and found such unlikely trend even though this was compared with CdSe QDs.

**Response:** We thank the reviewer for their helpful evaluation of our manuscript. We apologize for the confusion regarding the size regimes. A similar comment has been made by referee 1 (comment 2). Please see our response above.

Regarding the comparison to CdSe, we would like to note that a nonmonotonic behavior has also been reported by others for CdSe. (see manuscript ref. 22) [*J. Semicond.* **44**, 032702 (2023)]. The manifestation of a nonmonotonic transition in the lifetimes depend sensitively on the details of the excitonic level structure, oscillator strengths, and confinement effects. Therefore, depending on these specific outcomes, different materials may show a minimum radiative lifetime occurring in different size regimes, or there is the possibility of the radiative lifetime decaying monotonically to the bulk value without any extremum.

- 2) Authors also stated the phase matters here and if so, that can be focused here rather than highlighting size regime.

**Response:** We agree with the referee that the crystal structure is important to find qualitative match between theory and experiments. This is now emphasized in our work, by comparing the radiative lifetimes for the cubic, orthorhombic, and relaxed structures (see Figure 5). We also expanded our simulations to include additional nanocrystal sizes and better converged the excitonic fine structure of the larger nanocrystals. We find that, in addition to the dim state thermal population mechanism, symmetry lowering to the relaxed and orthorhombic structures lifts degeneracies, spreads the excitonic spectrum, and closes the bright-dim gap. In fact, we find that the competition between oscillator strength and thermal depopulation only produces non-monotonicity for the low symmetry structures where the bright-dim gap is sufficiently small to compete with the size-dependent oscillator strength increase. We have updated the manuscript Results section to include the following language:

*“The nanocrystal crystal structure influences the exciton level details. The cubic geometries host degenerate excitons and large bright-dim gaps, while symmetry lowering to the relaxed and orthorhombic structures lifts degeneracies, spreads the excitonic spectrum, and closes the bright-dim gap. In fact, we find that the competition between oscillator strength and thermal depopulation*

*only produces non-monotonicity for the low symmetry structures where the bright-dim gap is sufficiently small to compete with the size-dependent oscillator strength increase”*

- 3) Further, they have avoided to run the 4K data which were indeed required here to validate the big claim. These suggests that (1) authors may relate the size regime with phase and in this case and one more size in orthorhombic phase may be considered to be added. In second (2) to reduce the surface interference as shape varied with size, low temperature data may be added. These two data/clarifications are indeed missing.

**Response:** We thank the reviewer comments. The major claim of this work is that the exciton level details and thermalization at room temperature explain the observed non-monotonicity in the radiative lifetimes. For these claims, we do not find it necessary to perform analyses at 4K. We will address this more specifically in future work. Additionally, we assessed the influenced of crystal structure on radiative lifetime by calculating an additional nanocrystal with 6.3 and 6.9 nm edge lengths for all symmetries considered (Fig. 5a), finding that the increased anisotropy of larger orthorhombic structures leads to a decrease in the bright-dim gap and an increase in the density of lower energy dim states. This depopulates the emissive manifold and generates the non-monotonic trend. These findings suggest that the observed non-monotonicity is a feature unique to ambient conditions in CsPbBr<sub>3</sub> nanocrystals, driven by size-dependent excitonic properties that parametrically depend on the crystal symmetry.

- 4) Summary: This revised manuscript still shows confusion and has too little data to provide the conclusion of Non-Monotonic Size-Dependent Exciton Radiative Lifetime in CsPbBr<sub>3</sub> Nanocrystals. Novelty is still a question here.

Hence, in its current form, this is also unclear why it will be considered for NC.

**Response:** We hope that based on response the referee will change their minds and support the publication of our novel findings.

1. What are the noteworthy results? : Stated above
2. Will the work be of significance to the field and related fields? How does it compare to the established literature?
3. If the work is not original, please provide relevant references. N/A
4. Does the work support the conclusions and claims, or is additional evidence needed? Additional evidences needed.
5. Are there any flaws in the data analysis, interpretation and conclusions? Do these prohibit publication or require revision? Partially and needs revision
6. Is the methodology sound? Does the work meet the expected standards in your field? Yes
7. Is there enough detail provided in the methods for the work to be reproduced? Ye



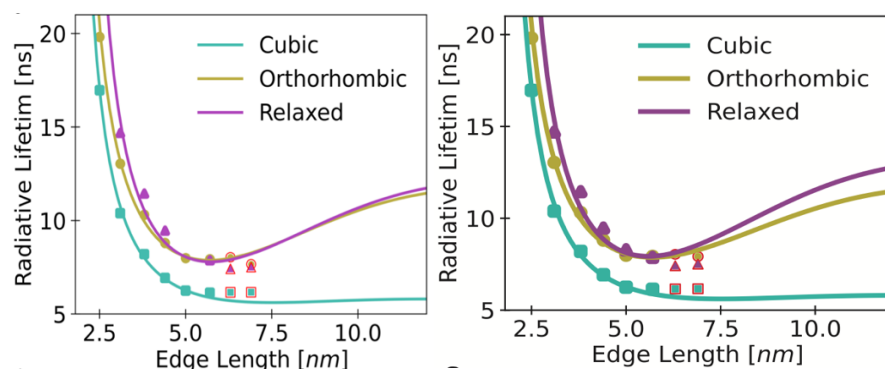
**Manuscript No:** NCOMMS-24-58403A:

**Title:** Non-Monotonic Size-Dependent Exciton Radiative Lifetime in CsPbBr<sub>3</sub> Nanocrystals

**Authors:** Abdullah S. Abbas, Daniel Chabeda, Daniel Weinberg, David T. Limmer, Eran Rabani, A. Paul Alivisatos

**Note to all reviewers:**

Figure 5 has been updated without change to the main text or conclusions. Previous (left) and current (right) figure 5a is shown side-by-side below:



**Synopsis:**

In my last review of NCOMMS-24-58403T I had already recommended publication after consideration of a few minor comments.

The Authors responded appropriately to these minor suggestions.

The Authors also made substantial additions in addressing the remarks of the other Reviewer: They have added calculations comparing the radiative lifetimes for the cubic, orthorhombic, and relaxed structures in the substantially revised and more informative Fig. 5 and the discussion of it, and have revised their description of the findings from their computational study as follows:

*The nanocrystal crystal structure influences the exciton level details. The cubic geometries host degenerate excitons and large bright-dim gaps, while symmetry lowering to the relaxed and orthorhombic structures lifts degeneracies, spreads the excitonic spectrum, and closes the bright-dim gap. In fact, we find that the competition between oscillator strength and thermal depopulation only produces non-monotonicity for the low symmetry structures where the bright-dim gap is sufficiently small to compete with the size-dependent oscillator strength increase"*

This is an interesting finding, I like the revised Figure 5; and it's a great discussion.

**I do find one statement in the updated discussion which I think should be clarified or re-thought**, namely the following added statement by the Authors:

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It is important to note a distinguishing feature of the electron and hole DOS emerging from atomistic models compared to effective mass/ $kk \cdot pp$  models: atomistic models reveal many more orbitals within a given energy range than the  $kk \cdot pp$  approach because angular momentum restrictions are relaxed<sup>38</sup>.

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Here the Authors state that as a general rule, that, “effective mass/ $kk \cdot pp$  models: atomistic models reveal many more orbitals within a given energy range than the  $kk \cdot pp$  approach because angular momentum restrictions are relaxed”.

No effective mass model was presented here. So the Authors have not shown this “rule” within this work in *any* way. They support the statement by citing Ref 38, Wang& Zunger, High-energy excitonic transitions in CdSe quantum dots. *Journal of Physical Chemistry B* **102**, 6449 (1998). This is a sloppy basis for the Authors’ statement: Ref 38 was comparing effective mass models conducted on spherical nanocrystals within a spherical band approximation to realistic atomistic models. It was an “apples to oranges” comparison.

In the Wang/Zunger comparison there was a vast difference in the model symmetries, so the larger number of distinct states in the atomistic calculation is certainly due to the breakdown of angular momentum as a good quantum number in the atomistic case.

But that is not a general rule or requirement on effective mass models. It is not generally the case for effective mass models that have been performed on perovskite nanocrystals, which typically model accurate non-spherical shapes and in some cases have accounted for departures of the underlying crystal structure from cubic to lower symmetry phases.

So the general rule that the Authors state here is based on the Ref 38 comparison that doesn’t apply in the perovskite context; in fact the general rule that was stated is not a general rule at all.

A proper statement should be something like,

*“models with unrealistically high symmetry (whether using effective mass theory or atomistic models) will have unrealistic density of states”.*

I recommend striking the statement made or making it more precise and defensible along the lines that I suggested above.

### **Recommendation:**

I recommend publication of the manuscript after revision in consideration of my remarks above.

**Response:**

We agree with the referee regarding their comment and have removed that statement from the manuscript. In addition, we have revised the surrounding section according to the referee's suggestion. The revised section on pages 14-15 now reads:

[Uniquely, our atomistic calculations capture this behavior across the size range, showing excellent agreement with experiment for both small and larger perovskite nanocrystals. The lifetime decreases between 2 – 5 nm, and we rationalize this decrease in radiative lifetime by analyzing the size-dependent oscillator strength of bright states. We find an increase in the oscillator strength of the lowest bright state as the nanocrystals size increases, independently of crystal symmetry (Fig. 5c). However, this does not cause the large nanocrystals approaching weak confinement to exhibit a reduced radiative lifetime. Instead, due to the increasing density of states (DOS) in larger nanocrystals, high-lying states exhibiting weak oscillator strength (i.e., dim states) become thermally accessible and lead to a decreased Boltzmann population of the bright triplet manifold of states (Fig. 5b). We underscore that the non-monotonic behavior depends sensitively on the exciton level details and ambient temperature conditions. We find that at lower temperatures, our model predicts a monotonically decreasing size-dependence of the radiative lifetimes (Fig. S8) because the high-lying dim states become thermally inaccessible, in alignment with previously reported experimental findings.<sup>13,15]</sup>

**Manuscript No:** NCOMMS-24-58403-T:

**Title:** Non-Monotonic Size-Dependent Exciton Radiative Lifetime in CsPbBr<sub>3</sub> Nanocrystals

**Authors:** Abdullah S. Abbas, Daniel Chabeda, Daniel Weinberg, David T. Limmer, Eran Rabani, A. Paul Alivisatos

**Synopsis of Author's response to the first report ( Referee-1):**

Referee-1 made five comments/criticisms on the original submission to which the Authors have responded.

The most important question posed pertained to the number of samples measured in the study; it seemed to be rather small (3) in the first version, which raised a doubt about the validity of the main reported result –namely, the non-monotonic trend in the radiative decay rate with respect to nanocrystal size. The Authors have clarified this point - a large number of independent samples (34) were measured, which in my view addresses that concern fully.

Given that, the work is convincing to me and in my opinion the results will be interesting in the nanocrystal community especially as it bears on the importance of electron/hole correlation effects and the fact that these evidently persist to room T.

I outline here the other comments made originally, the Author's responses, and my comment on each response.

- 1) Ref-1's second comment was that to be truly convincing, the measurements would need to be done at more than one temperature, because in the Authors' model, the "inflection point" size where the radiative lifetime is minimized would be temperature dependent.

Authors' response: The Authors agreed that this would be desirable but state "However, obtaining PLQY data on ensemble level at lower temperatures is experimentally challenging and beyond the scope of this work" and noted that "we addressed this limitation by using simulations to explore the radiative lifetimes behavior at lower temperatures, which corroborate our findings".

Referee-1 comment on this response:

I am sympathetic that adding measurements over temperature would comprise a lot of work and would entail a significant delay. While it would be nice to see in future a test of the Authors' theoretical interpretation in a temperature series, on reflection, I think that their results should be published at the *current* stage, since the experimental finding reported is surprising/interesting.

- 2) Ref-1's third comment was that the use of the terms strong, intermediate, and weak confinement was oversimplified relative to correct usage. Since the exciton radius  $a \sim 3\text{nm}$ ; the ratio of the nanocrystal size  $L/a$  varies from 1.5 to 2.5 across the full range of sample sizes, so that all samples are characterizable as within intermediate confinement. None approach the weak confinement regime ( $L \gg a$ ) and none approach the strong confinement regime as it is understood in the literature ( $L \ll a$ ).

Authors' response: "Our classification of the samples into strong, intermediate, and weak confinement regime was intended to provide a clear and practical framework for illustrating the variations in optical properties across different sizes. By using these categories, we aimed to highlight the impact of size on optical properties in a manner that aligns with broader context of similar studies, despite the nuanced boundaries of confinement regimes[*ACS Nano* 2016, 10, 9, 8603–8609, *Nano Lett.* 2016, 16, 4, 2349–2362, *ACS Nano* 2021, 15, 10775–10981]."

Referee comment: The Authors' response is an explanation why they wrote what they did but does not actually respond to original comment.

Their use of the terms strong/weak confinement is oversimplified and not consistent with literature usage (e.g., I checked the *ACS Nano* 2021 reference they provided, I didn't check the others) and as a result, I think it could create (or perpetuate) misunderstanding.

The Authors still identify the largest and smallest nanocrystals as corresponding to the weak and strong confinement regimes, writing this in the Abstract and the Conclusions; in the Conclusions for example they write that "Larger and smaller nanocrystals in the weak and strong quantum confinement regimes displayed longer radiative lifetimes." But that characterization is not correct. The weak confinement regime ( $L \gg a$ ) is never realized within the size range studied, nor is the strong confinement regime as it is understood in the literature ( $L \ll a$ ).

I suggest that the Authors simply add a few words to explain what they wrote in their response. Instead of writing statements as they did such as "Larger and smaller nanocrystals in the weak and strong quantum confinement regimes" they could make the statement strictly correct by rephrasing along these lines: "Larger and smaller nanocrystals **respectively approaching** the weak and strong quantum confinement regimes ..."

- 3) Ref-1 fourth comment was that the Authors' model doesn't address the full context of cited prior models; (it considers only thermal population effects but not possible temperature related decoherence).

The Authors' response (which I won't fully reproduce) was to add additional calculations (Supp. Fig 7) which they characterize as a comparison of uncorrelated vs. correlated exciton lifetimes, but in reality comprise a comparison of excitons with the electron/hole

exchange interaction versus excitons without exchange interaction. They wrote: **For uncorrelated electron-hole pairs, the lowest energy states are quadruply degenerate bright states... The fine structure changes when electron exchange is included”**

Referee comment: The Authors’ response addresses a different question than the one I asked. Their response conflates electron/hole exchange with correlation in the electron and hole position coordinates. These are different things. For example, excitons in a nanocrystal characterized strictly by strong confinement have no correlation in the electron and hole position coordinates (i.e., in strong confinement the exciton envelope function can be understood strictly as a product of uncorrelated electron and hole wavefunctions), but such a system certainly has fine structure splitting due to electron-hole exchange.

I suggest they clarify this distinction. In any event, the additional calculations in Suppl Fig 7 are useful since for example, the model in Kreig did not include fine structure splitting.

4. Ref-1 also commented that modelling contains the major assumption of thermalization whose validity is not discussed.

Authors’ response acknowledged the issue at low temperature but argued that the assumption of thermalization in the higher temperature regime that they modelled is legitimate on the basis of the timescales of the relevant relaxation processes.

Referee comment: I accept the argument made by the Authors.

#### **Recommendation:**

I recommend publication of the manuscript with minor revisions as noted in points 2 and 3 above.

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This is an interesting finding, I like the revised Figure 5; and it’s a great discussion.

**I do find one statement in the updated discussion which I think should be clarified or re-thought**, namely the following added statement by the Authors:

It is important to note a distinguishing feature of the electron and hole DOS emerging from atomistic models compared to effective mass/ $k \cdot p$  models: atomistic models reveal many more orbitals within a given energy range than the  $k \cdot p$  approach because angular momentum restrictions are relaxed<sup>38</sup>.

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