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ARTICLE

Reply to the ‘Comment on “Density functional theory analysis of structural and electronic properties of orthorhombic perovskite $\text{CH}_3\text{NH}_3\text{PbI}_3$ ”’ by J. Even *et al.*, *Phys. Chem. Chem. Phys.*, 2014, 10.1039/C3CP55006K

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Perovskite $\text{CH}_3\text{NH}_3\text{PbI}_3$ materials were theoretically investigated using density functional theory (DFT) since they are an important component in novel perovskite-based solar cells. One of the challenges is to accurately describe their electronic structures. As stated in our original paper, the accidental agreement of band gap energies between the traditional DFT calculations and the experimental measurement is “fortuitous”. The disadvantage of traditional DFT can be partially solved by the recent progress made by Even *et al.* with the consideration of spin-orbital coupling and many-body self-energy corrections. However, the C-N bonding mechanisms in CH_3NH_3^+ cations cannot be deduced from the Bader charge analysis.

We appreciate Even’s comments on our recent work entitled “Density functional theory analysis of structural and electronic properties of orthorhombic perovskite $\text{CH}_3\text{NH}_3\text{PbI}_3$ ”.¹ We would also like to thank the editor of Physical Chemistry Chemical Physics for giving us an opportunity to present our views.

Even *et al.* made three key points in their comments. One is related to the effects of spin-orbital coupling (SOC) and many-body self-energy corrections. Due to the cancellation between these effects in the calculations, the bandgap energies obtained from our calculations were very close to the experimental values, which could be misinterpreted by a non DFT-expert. To avoid such effect, we have stated in our original paper that “*Previous DFT studies demonstrate that the bandgap energies of solid-state semiconductors are seriously underestimated by using pure DFT functionals. In some cases, the deviation is about 30%. This is because good band gaps are not normally to be expected from functionals of the types tested here, which do not have hybrid characters. This successful match is likely to be fortuitous, which is also observed in other Pb-based materials.*”¹ We hope such a statement could provide non DFT-experts a warning regarding the problems associated with DFT calculations. While we are currently working on the accurate electronic structures of Pb-based perovskite materials using the methods beyond traditional DFT, we are glad to know that the considerations of the effects of SOC and many-body GW self-energy correction by Even *et al.* have improved the calculation accuracy.² Their results are a great supplement to ours. We believe that the recent progress made by Even *et al.* will stimulate further theoretical

studies on the precise understanding of electronic structures of Pb-based materials.

Another key point raised is why we did not focus on the tetragonal phase as it is more important for the practical applications.³⁻⁴ The reasons we focused on the orthorhombic phase in this study is from a theoretical perspective. Firstly, the temperature for traditional DFT calculations is 0K. At low temperature, the orthorhombic phase of perovskite $\text{CH}_3\text{NH}_3\text{PbI}_3$ is more stable from the XRD experiments.³ The studies on the orthorhombic perovskite $\text{CH}_3\text{NH}_3\text{PbI}_3$ enable us to do meaningful comparison between the theoretical and experimental data. Secondly, the structural change from orthorhombic phase to tetragonal or cubic phase at high temperature are experimentally demonstrated to relate to the fast dynamic movement of CH_3NH_3^+ cations within the Pb-I framework.³ As a result, the rationalization of atomic structures of tetragonal perovskite $\text{CH}_3\text{NH}_3\text{PbI}_3$ materials is currently difficult using traditional DFT calculations because the locations of CH_3NH_3^+ cations in this phase are thermally disordered. Therefore, we targeted the orthorhombic phase in this study, as suggested in the title.¹

The third key point raised is about the Bader charge analysis. According to Bader’s theory, the atoms are separated from each other at the place where the charge density reaches a minimum between atoms. After the atoms are divided, the charge distribution can be analysed.⁵⁻⁶ Based on its definition, Bader charge analysis method cannot be used to give direct evidence

for the bonding mechanisms between atoms. The suggestion made by Even *et al.* to analyse the structural properties of $\text{CH}_3\text{NH}_3\text{PbI}_3$ crystals to understand the bonding mechanisms is helpful. Based on our optimized structures, the C-N bond length in orthorhombic $\text{CH}_3\text{NH}_3\text{PbI}_3$ crystals is 1.49 Å, which is close to that in CH_3NH_2 molecules (1.47 Å). Thus, there is no C-N bonding break in CH_3NH_3^+ cations. The atomic structures of CH_3NH_3^+ cations can be found in Fig 1 in our original paper, which show that the CH_3 moiety is still tetrahedral and not planar.¹ The optimized structure of orthorhombic perovskite $\text{CH}_3\text{NH}_3\text{PbI}_3$ materials is given in the supplementary information.

Notes and references

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