Preliminary report on Lucy Whalley’s PhD thesis

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In her thesis, the student uses theory and simulation to understand atomic and electronic properties of materials for solar cell applications. Overall, the thesis is well written and the quality of graphs is high. The PhD work has already led to several publications.

In the first chapter, the student introduces basic considerations and working principles of solar energy conversion. This chapter is very clear and a good introduction. The second chapter reviews the current state of the art in modelling hybrid halide perovskites, a novel class of solar absorber materials that have recently generated much excitement. Again, this chapter is well written and sets the stage nicely for the work presented in chapters 4, 5 and 6.

In Chapter 3, the student describes the methods that have been used. The focus is on the basic techniques, such as density functional theory, supercells, etc. Again, this chapter is clear and well written. The more specialized methods are discussed in the following chapters. However, these advanced methods are often introduced quite briefly and the viva should establish whether the student has a sufficiently deep understanding of these techniques to gauge their limitations and range of applicability.

In Chapter 4, the student studies different approaches to calculate the effective mass in solar absorber materials and also the effect of non-parabolicity of the band structure. The motivation for this chapter is clear, but I do not understand the fundamental motivation for using the Kane approach and not simply going to higher orders of the band energy in an expansion in powers of the crystal momentum. Also, the interplay of nonlinearity and anisotropy was not discussed clearly. Moreover, the influence of the electron-phonon interaction on the effective mass was not even mentioned. The results indicate that the model developed by the student is useful and helps to gain a deeper understanding of optical and transport experiments.

Chapter 5 discusses electron-phonon and phonon-phonon interactions in halide hybrid perovskites. Here, a clearer structure would have improved the chapter. In particular, different kinds of electron-phonon couplings are studied (deformation potential and Froehlich), but it is not clear how they relate to each other. The concept of polarons is introduced and their cooling mechanism is discussed. Here, a classical approach based on the heat equation is used, but it is not clear how this relates to the other electron-phonon technique and why the classical analysis is justified. Also, the use of linear and non-linear techniques is a bit mixed. Finally, the calculation of the phonon wave function is not described in any detail. Overall, this chapter contains many different concepts and techniques, but it is difficult to appreciate how they relate to each other. I suggest rewriting this chapter to give a better structure and also introduce the advanced techniques in more detail.

The final chapter investigates the capture of electrons and hole by defects in hybrid halide perovskites. This is a challenging and highly relevant problems and the techniques that are used are state of the art. However, again, more background on the methods would have been useful. Also, the discussion of the phonon modes of the defective system and the correspondence to the simpler model discussed before was not clear to me. The results in this chapter are very important to understand the observed defect tolerance of these new materials.

Overall, I think the thesis presents several novel insights and advances of the field of solar energy conversion in complex materials, in particular the halide hybrid perovskites. However, the structure of the results chapters could be improved and the relationship between the various concepts could be sharpened.



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