Response to Letter “Electron correlation and relativity of the 5f electrons in the U-Zr alloy system”

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Abstract

In the Letter [Söderlind *et al.*, J. Nucl. Mater. 444, 356 (2014)], Söderlind *et al.* state their interpretation that 1) we view electron correlation to be strong and including spin-orbit coupling (SOC) to be necessary for U metal and U-Zr alloys in our article [Xiong *et al.*, J. Nucl. Mater. 443, 331 (2013)]. Further, they argue that 2) density functional theory (DFT) without adding the Hubbard U potential, especially when solved using all electron methods, already models U metal and U-Zr alloys accurately, and 3) adding the Hubbard U potential to DFT in DFT + U models U and U-Zr worse than DFT according to volume, bulk modulus, and magnetic moments predicted from their calculations of the γ U phase of elemental U metal. With respect to Söderlind *et al.*'s interpretation 1), we clarify that our opinions are that U and U-Zr are not strongly, but weakly to moderately correlated and that including SOC is beneficial but not necessary for modeling ground state properties of U and U-Zr. With respect to Söderlind *et al.*'s argument 2) we demonstrate that previously neglected and very recent experimental data suggest that DFT in Söderlind's full-potential linear muffin-tin orbital (FPLMTO) calculations [Söderlind, Phys. Rev. B 66, 085113 (2002)] in fact models the bulk modulus and elastic constants of α U with errors considerably larger than other related elements, e.g., most transition metals. With respect to Söderlind *et al.*'s argument 3) we argue that they have inappropriately focused on just one phase (the BCC γ U phase of U metal), neglecting the other phases which represent the majority of our evidence, and made overgeneralizations based on results at only one U_{eff} value of 2 eV. We therefore maintain our original conclusion that the accuracy of DFT for modeling U and U-Zr has room for improvement and DFT + U shows some evidence of providing better results than DFT alone.

Recently, Söderlind *et al.* objected to a number of points in our work, first in a Journal of Nuclear Materials (JNM) Letter[1] corresponding to our JNM article Xiong *et al.*[2] on CALPHAD and later in a Physical Review B (PRB) Comment[3] corresponding to our later PRB article Xie *et al.*[4] on *ab initio* modeling of the thermodynamics of U metal and U-Zr alloy. Both the JNM Letter and PRB comment criticized our hypothesis that adding the Hubbard U potential to the standard functional of density functional theory (DFT)[5,6] in the so-called DFT + U approach[7,8] could better model the energetics for the U metal and U-Zr alloy. Söderlind *et al.*'s Letter[1] and Comment[3] share the same major claims and to a large extent similar supporting arguments. To avoid redundancy and potential confusion that may be caused by similar responses scattered in multiple articles in different journals, we have replied in one extensive arXiv article[9] to all objections of Söderlind *et al.* from both their Letter[1] and Comment[3]. Here, as this is a JNM Letter, we outline the main points of our reply[9] to only those arguments in Söderlind *et al.*'s JNM Letter[1] and refer the reader to Ref.[9] for detailed data and discussion.

For clarity we summarize here Söderlind *et al.*'s arguments in the Letter[1]. Following our notation in Ref. [9], we label the two major claims a) and b) and their supporting arguments (a1)-(a2) and (b1)-(b5). Note (a2), (b3) and (b5) are only in Söderlind *et al.*'s Comment[3] and not discussed in the Letter[1] to which we are replying here. These points will therefore be skipped in the following discussion. In their Letter Söderlind *et al.*[1] argue that a) DFT, especially when solved using all electron methods already models the U and U-Zr systems accurately. To support this opinion, they cite in Ref.[1] seven previous DFT studies of the α U phase of U metal, of which an exemplary one is the study by Söderlind[10] arguing that (a1) DFT solved with full potential linearized muffin-tin orbital (FPLMTO) method accurately reproduces the structural and elastic properties of the α U. Söderlind *et al.* also argue that b) adding Hubbard U potential in DFT + U deteriorates rather than improves DFT for modeling U and U-Zr. To support this opinion, Söderlind *et al.*[1] perform DFT + U calculations at $U_{\text{eff}} = 2$ eV on the body-centered cubic (BCC) γ U phase of U metal and argue that DFT + U (b1) leads to "a grossly overestimated equilibrium volume", (b2) "substantially underestimates the bulk modulus", and (b4) predicts unphysical magnetic moments for γ U.

In this Letter, we will address the claims and arguments of Söderlind *et al.*[1] summarized in the previous paragraph that challenge the applicability of DFT + U to U metal and U-Zr alloy. Before that, we clarify our views on two more minor issues Söderlind *et al.* also bring up in Ref. [1] that relate to opinions expressed in our work. The first issue is the strength of electron correlation in U and U-Zr. Söderlind *et al.* improperly claim that we determine electron correlation in U and U-Zr to be strong, and then they proceed to refute their improper claim in their Letter[1]. We did not determine that electron correlation in U and U-Zr is strong and have not meant to suggest that this is the case. This misunderstanding may be due to our use of the term "strong on-site correlation" once in Xiong *et al.*[2] (p 334) to refer to Hubbard U potential in DFT + U , but may also be based on the deduction that because we argue that DFT + U can be of value for modeling U and U-Zr, we must also believe them to have strongly correlated electrons. We take this opportunity to clarify that the word "strong" is unwarranted when referring to Hubbard U potential in DFT + U and it is with regret that we have used it in Ref.[2]. We stress that DFT + U can be helpful for modeling materials that are not strongly correlated, for example FeAl[11]. In fact, based on the ratio of band width W over Coulomb U from our calculations, we have argued that U and U-Zr should be weakly to moderately correlated metals (p19 of Xie *et al.*[4]). The second minor issue is the importance of the relativistic effect of SOC in the U and U-Zr systems. In Xiong *et al.*[2], we present *ab initio* enthalpy results from both scalar relativistic and spin-orbit coupling calculations, demonstrating that including SOC can create small improvements of the accuracy of *ab initio* enthalpies. Söderlind *et al.* improperly claim that we have concluded SOC is necessary to include in all *ab initio* calculations of U and U-Zr, and then they proceed to refute their incorrect claim in their Letter[1]. To be clear, Xiong *et al.*[2] have not suggested that SOC must be included for accurate energetics of U and U-Zr given that the improvements are found to be modest and the study was limited in scope with respect to SOC. Furthermore, in Xie *et al.*[4] we have argued that SOC affects ground state properties of U and U-Zr only

marginally, a result supported by extensive validations. Next we reply to Söderlind *et al.*[1]’s major arguments, each in turn.

Argument (a1) is unsound because the experimental data against which Söderlind[10] benchmarks the theoretical values from DFT have inaccuracies. As detailed in Section 2.1 of Ref.[9], old but previously neglected and very recent experimental data indicate that DFT, even when solved using the all electron method FPLMTO[10], still models the bulk modulus and elastic constants of α U unsatisfactorily, with errors considerably larger than most transition metals. These results illustrate that claim a) is not correct and suggest that improvements to standard DFT approaches may be necessary for sufficiently accurate modeling of at least some ground state properties of U and U-Zr.

Arguments for claim b) suffer from two broad problems and thus do not undermine the applicability of DFT + U to U metal and U-Zr alloy. The first broad problem is that they have focused on the high temperature BCC phase γ U in the Letter[1], which is thermodynamically and mechanically unstable at the modeling temperature of 0 K, while neglected results for most of the other phases that are actually the primary evidence of our arguments in favor of DFT + U . In particular, our comparisons on enthalpies for the stable solid phases of U and U-Zr other than γ (U,Zr) are neglected in Söderlind *et al.*[1] due to their focus on γ U. The instability in γ U means both that it is difficult to model this phase and that reliable low temperature experimental references are usually lacking for benchmarking theoretical approaches. The other broad problem is an overgeneralization of results at selected U_{eff} values to argue that DFT + U in general suffers from issues that occur at those specific U_{eff} values or ranges of values. In their Letter[1], Söderlind *et al.* use only $U_{\text{eff}} = 2$ eV. Although this value is suggested from theoretical estimation of Hubbard U for U metal, it is too large because DFT + U is based on the Hartree-Fock approximation which is expected to overestimate the effects of the Hubbard U [12]. Use of this large value leads to many of the undesired results which lead Söderlind *et al.* to find fault with DFT + U . Section 3.1 of Ref. [9] has discussed in detail what U_{eff} we suggest should be used. We notice there has been some confusion regarding the difference between the “multi-structure optimized U_{eff} ” (previously called “statistical optimal U_{eff} ” in Ref. [4]), which gives the smallest *average* error when considering multiple structures together, and the “single-structure optimized U_{eff} ”, which gives the smallest error when considering just one structure. In some cases, for a given structure it is true that the multi-structure optimized U_{eff} does not work well, but its own single-structure optimized U_{eff} can still provide meaningfully improved results vs. DFT. Based on our fittings[4,9], we determined that the single-structure optimized U_{eff} varies approximately in the range of 1-1.5 eV for the 8 solid phases of U and U-Zr, while the multi-structure optimized U_{eff} for the overall U and U-Zr systems is 1.24 eV. γ U’s single-structure optimized U_{eff} should be around 1 eV, as is that for its associated alloy phase γ (U,Zr). Different from γ U and γ (U,Zr), α U’s single-structure optimized U_{eff} may be as large as 1.5 eV, and so is the value for δ (U,Zr). In general, to best describe an individual phase, the “single-structure optimized U_{eff} ” for that phase should be used, and that is why we use $U_{\text{eff}} = 1$ eV for γ (U,Zr) and $U_{\text{eff}} = 1.5$ eV for δ (U,Zr) in Ref.[2]. We unfortunately have neglected to report the two U_{eff} values used in Ref.[2]. This is an oversight we are glad to be able to correct here and it may have led to some confusion on the issue of the accuracy of DFT + U . Note we have been using $J = 0.51$ and the somewhat awkward values of 0.99 and 1.49 eV (from $U_{\text{eff}} = U - J = 1.50 - 0.51$ and $2.00 - 0.51$, respectively) are the exact values of U_{eff} ’s that are actually used, but more often their rounded values of 1 and 1.5 eV are used in our discussion. We now address arguments (b1), (b2) and (b4) more specifically.

Argument (b1) is discussed in Section 3.2.1 of our arXiv article, Ref. [9]. In that discussion we show that DFT + U with $U_{\text{eff}} = 2$ eV, the value used in Söderlind *et al.*’s Letter[1], and $U_{\text{eff}} = 1.24$ eV, the multi-structure optimized U_{eff} for the overall U and U-Zr systems, does indeed seem to give too large volume for γ U and the U-rich part of γ (U,Zr). However, at $U_{\text{eff}} = 1$ eV, which we argue is the single-structure optimized U_{eff} specifically for both γ U and γ (U,Zr) (and therefore the most appropriate value for use on these BCC phases), DFT + U still gives improved volume over DFT, although uncertainty exists due to the thermodynamic and mechanical instability of this phase at the modeling temperature of 0 K.

Argument (b2) is addressed in Section 3.2.2 of our arXiv article, Ref. [9]. After correcting the error due to non-hydrostatic stress in the experimental reference[13] and estimating the change from the experimental temperature of 1100 K to the modeling temperature of 0 K, we show that DFT + U also seems to reproduce the estimated 0 K experimental bulk modulus of γ U best near γ U's single structure optimized U_{eff} of 1 eV. Although the accuracy deteriorates at $U_{\text{eff}} = 1.24$ eV, which is the multi-structure optimized U_{eff} for the overall U and U-Zr systems, it is still better than DFT without U .

Argument (b4) is addressed in Section 3.2.4 of our arXiv article, Ref. [9]. We agree in general with the observation that using U_{eff} larger than about 0.75 eV DFT + U can give spurious moments for γ U, which we have clearly demonstrated in FIG 7 of Ref.[4] and discussed therein. However, we disagree with the suggestion that we should as a result avoid DFT + U completely. Our extensive results and discussion in Refs.[4,9] show that the magnetic moments, if present, do not appear to keep DFT + U from providing improvement on other properties like energetics, volume and bulk modulus. Furthermore, these artificial moments are not necessarily inherent to the Hubbard U modification and can potentially be avoided if one uses alternative double counting terms in DFT + U , or by going beyond the Hartree-Fock approximation and using DFT + DMFT, whereby the DMFT impurity problem is solved exactly, e.g., via quantum Monte-Carlo.

In summary, Söderlind *et al.*'s arguments in their Letter[1] against modeling U or U-Zr with DFT + U have not considered the issues we have outlined in this Letter and thus are not very well supported. Therefore, we maintain our original conclusion that the accuracy of DFT for modeling U and U-Zr has room for improvement and DFT + U can be one candidate for this purpose.

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