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Reply: Comment on “Correlation and relativistic effects in U metal and U-Zr alloy: Validation of *ab initio* approaches”

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Abstract

In the Comment [Söderlind *et al.*, Phys Rev B 90, 157101 (2014)], Söderlind *et al.* argue that 1) density functional theory (DFT), especially with all electron methods already models U metal and U-Zr alloy accurately and 2) DFT + U results calculated at $U_{\text{eff}} = 1.24$ for volume, enthalpy and magnetic moments that they select from our study [Xie *et al.*, Phys. Rev. B 88, 235128 (2013)] suggest adding the Hubbard U potential in DFT + U reduces accuracy. With respect to Söderlind *et al.*'s argument 1) we argue 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)] still models the bulk modulus and elastic constants of α U with errors considerably larger than other related elements, e.g., most transition metals. In addition, we demonstrate that Söderlind *et al.*'s claim that our DFT results are not satisfactory because deficiency exists in our PAW calculation is unfounded. With respect to Söderlind *et al.*'s argument 2) we argue that they have inappropriately focused on just one phase (the BCC phase $\gamma(\text{U,Zr})$), neglecting the other phases which represent the majority of our evidence, made overgeneralization based on results at only one U_{eff} value of 1.24 eV, and supported their argument with inaccurate claims that DFT + U predicts for $\gamma(\text{U,Zr})$ an unprecedentedly large positive volume of mixing and an enthalpy of mixing that is inconsistent with the experimental miscibility gap. We therefore hold to our original conclusion that the accuracy of DFT for modeling U and U-Zr has room for improvement and DFT + U is a good candidate.

On the topic of applicability of DFT + U for modeling U metal and U-Zr alloy, Söderlind *et al.* have objected to our view first in a Letter¹ corresponding to our first article Xiong *et al.*², and then later in a Comment³ to our second article Xie *et al.*⁴. To avoid redundancy and potential confusion caused by similar objections and responses scattered in multiple articles in different journals, we have replied in detail in one place⁵ to all objections of Söderlind *et al.* from both their Letter¹ and Comment³. Here we outline the main points of our reply to only those arguments in the Comment³ and refer the reader to Ref. 5 for detailed results and discussion.

For clarity we summarize here Söderlind *et al.*'s arguments in their Comment³. Following our practice in Ref. 5, we label the two major claims a) and b) and their individual arguments (a1)-(a2) and (b1)-(b5). Note (b2) is only in Söderlind *et al.*'s Letter¹ and not discussed in the Comment³ to which we are replying here so it will be skipped in the following discussion. Söderlind *et al.* argue that a) DFT already models the U and U-Zr systems accurately by citing about ten references in Ref. 3, of which an exemplary one is the previous study by Söderlind⁶ 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 phase of elemental U metal, and (a2) our DFT results are not satisfactory because deficiency exists in our PAW calculation as they “seriously underestimates the volume of α -U” comparing to that from the FPLMTO calculation of Söderlind⁶. Söderlind *et al.* also argue that b) adding Hubbard U potential in DFT + U deteriorates rather than improves DFT, because at $U_{\text{eff}}=1.24$ eV, DFT + U from our PAW calculations gives (b1) worse volume for α U compared to the DFT value from Söderlind's FPLMTO calculations⁶, and overestimates the volume for γ (U,Zr) in terms of deviation from linear composition dependence (FIG 1 of Ref. 3) and expansion due to spin-orbit coupling (SOC) (FIG 2 of Ref. 3); (b3) gives enthalpy of mixing for γ (U,Zr) that is inconsistent with the miscibility gap in the experimental phase diagram (FIG 3 of Ref. 3); and (b4) gives “significant spin and orbital magnetic moments for most phases of uranium and all γ -U-Zr alloys”. Also Söderlind *et al.* argue that (b5) DFT + U is “incomplete or inappropriate” because it needs the use of the model parameter U_{eff} that they believe is “greatly different depending on the studied properties” for γ (U,Zr).

Our replies are as follows: Argument (a1) is spurious because issues exist in the experimental data against which Söderlind⁶ benchmarks the theoretical values. Section 2.1 of Ref. 5 demonstrates that previously neglected and very recent experimental data indicate that DFT, even solved with all electron methods like FPLMTO⁶ still models the bulk modulus and elastic constants of α U with errors considerably larger than most transition metals. Argument (a2) is unreasonable. Section 2.2 of Ref. 5 shows quantitatively that the discrepancies in the volume of α U from DFT between our PAW and Söderlind's FPLMTO⁶ are caused also by different GGA functionals, structural relaxations, and implementations of SOC used between the two sets of calculations, which dominates the difference due to the PAW approximation, so our PAW calculations do not suffer from the claimed deficiency and are valid. Argument (b1) is not generally sound. First, for α U the comparison between our PAW DFT + U and Söderlind's FPLMTO⁶ DFT results cannot draw meaningful conclusion because the two sets of calculations involve other factors—for example, those just mentioned above—that are entangled with the effect of the Hubbard U potential. Second, for γ (U,Zr)'s volume, Figure 2 b) of Ref. 5 shows that at $U_{\text{eff}} = 1.24$ eV, DFT + U with SOC actually gives volume for γ (U,Zr) that deviates from linearity to an extent that is very close to what DFT does and not abnormally large, contrary to the visual impression from Söderlind *et al.*'s FIG. 1³ created only by using a very small axis scale. In terms of volume expansion due to SOC, we agree with Söderlind *et al.*³ that DFT + U at $U_{\text{eff}} = 1.24$ indeed gives too large value for γ (U,Zr). However, Figure 2 c) of Ref. 5 shows that for all the other phases studied in Xie *et al.*⁴ it is in the expected range. Moreover, even for γ (U,Zr), DFT + U obtains good agreement with experiment at other more appropriate U_{eff} values than $U_{\text{eff}} = 1.24$ eV. As explained in Section 3.1 of Ref. 5, 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. $\gamma(\text{U,Zr})$ is a perfect example. While at $U_{\text{eff}} = 1.24$ eV, the multi-structure optimized U_{eff} for the overall U and U-Zr systems, DFT + U gives inaccurate volume for $\gamma(\text{U,Zr})$ as Söderlind *et al.* have rightfully criticized. However, Section 3.2.1 of Ref. 5 shows that at $U_{\text{eff}} = 1$ eV, which we argue is the single-structure optimized U_{eff} specifically for $\gamma(\text{U,Zr})$ and therefore the most appropriate value for use on $\gamma(\text{U,Zr})$, DFT + U still gives improved volume for $\gamma(\text{U,Zr})$ over DFT with both the deviation from linearity and the expansion due to SOC in the expected ranges, although uncertainty exists due to the thermodynamic and mechanical instability of this phase at the modeling temperature of 0 K. Argument (b3) is also unsound. Section 3.2.3 of Ref. 5 shows that our DFT + U enthalpy for $\gamma(\text{U,Zr})$ at $U_{\text{eff}} = 1.24$ eV can, despite being slightly negative on the Zr-rich end, still be consistent with the experimental range of compositions for the BCC miscibility gap, not to mention that at the single-structure optimized $U_{\text{eff}} = 1$ eV the mixing energies are positive and fully consistent with expectations of a typical miscibility gap. Argument (b4) is addressed in Section 3.2.4 of Ref. 5. We agree in general with the observation that using sufficiently large U_{eff} DFT + U can give spurious moments. However, we disagree with the suggestion that we should as a result avoid DFT + U completely. Our extensive results and discussion in Refs. 4,5 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. Also relating to this issue, Söderlind, *et al.* state that we think a solution with cancellation of magnetic moments is nonmagnetic, which we clarify is not our intended opinion in Ref. 4. Finally, we disagree with argument (b5). As addressed in Section 3.2.5 of Ref. 5, at U_{eff} near 1 eV, which is $\gamma(\text{U,Zr})$ ’s single-structure optimized U_{eff} DFT + U gives optimal results for both enthalpy and volume of $\gamma(\text{U,Zr})$, so no excessive fitting depending on property is necessary. In summary, we maintain our original conclusion that the accuracy of DFT for modeling U and U-Zr has room for improvement and DFT + U is a good candidate.

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² W. Xiong, W. Xie, C. Shen, and D. Morgan, *J. Nucl. Mater.* **443**, 331 (2013).

³ P.A. Söderlind, A. Landa, and P.E.A. Turchi, *Phys. Rev. B* **90**, 157101 (2014).

⁴ W. Xie, W. Xiong, C.A. Marianetti, and D. Morgan, *Phys. Rev. B* **88**, 235128 (2013).

⁵ W. Xie, C.A. Marianetti, and D. Morgan, arXiv:1601.07959.

⁶ P.A. Söderlind, *Phys. Rev. B* **66**, 085113 (2002).