

Comment on “Interplay of defect cluster and the stability of xenon in uranium dioxide from density functional calculations”

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Geng *et al.* [H. Y. Geng, Y. Chen, Y. Kaneta, M. Kinoshita, and Q. Wu, *Phys. Rev. B* **82**, 094106 (2010)] recently reported DFT + U calculations of xenon behavior in uranium dioxide UO_2 . One of the main conclusions of their work is that the quasiaannealing (QA) procedure allowed them to avoid metastable states created by the DFT + U approximation. However, based on a comparison of total energies, they stated that an incomplete implementation of occupation matrix control (OMC) had been done in our previous work [B. Dorado, G. Jomard, M. Freyss, and M. Bertolus, *Phys. Rev. B* **82**, 035114 (2010)] and that we failed to reach the ground state of the perfect UO_2 fluorite structure. In this Comment, we show that the discrepancy they observed does not stem from an incomplete implementation of OMC, but from the calculation of the compensation charge used in the projector augmented-wave formalism.

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Recently, Geng *et al.*¹ reported LDA + U calculations of xenon incorporation in uranium dioxide UO_2 , which is used as a standard nuclear fuel in pressurized water reactors. A significant part of Geng’s work is devoted to the assessment of the efficiency of the quasiaannealing (QA) approach compared to the occupation matrix control (OMC) scheme for the treatment of metastable states created by the DFT + U approximation.^{2–7} The latter approach (OMC) was used in our previous studies^{6–8} for the modeling of perfect and defective UO_2 and was proven to yield reliable energies. In their work, Geng *et al.* concluded that an incomplete implementation of OMC had been done in our work (Ref. 7) and that we failed to reach the ground state of UO_2 . In the present Comment, we show that our implementation of OMC is valid and that the discrepancy observed stems from the calculation of the compensation charge used in the projector augmented-wave (PAW) formalism.

To assess the efficiency of the QA approach with respect to the OMC scheme, Geng *et al.* calculated the total energy of the perfect UO_2 fluorite structure using similar calculation details as in Ref. 7 (VASP code, Dudarev’s approach of the DFT + U , $(U - J) = 3.99$ eV, 500 eV cutoff energy, $5 \times 5 \times 5$ k -point mesh, collinear antiferromagnetic order). Although it is well known that total energies cannot be directly compared unless *all* calculation parameters are strictly identical, Geng *et al.* did compare their calculated total energy with ours. They found that their total energy for bulk UO_2 is almost 0.5 eV/ U_4O_8 lower and, based on this result, they concluded that our implementation of OMC had failed to reach the true ground state of perfect UO_2 .

In our previous work, however, we took particular care in analyzing the form of uranium occupation matrices and testing all possible initial electronic occupancies. Given the systematic character of this search, it is very unlikely that we did not find the true ground state for perfect UO_2 . It would also be very surprising that we reached a metastable state as high as 0.5 eV above the ground state, as stated by Geng *et al.* We therefore performed additional calculations in order to investigate the origin of this discrepancy. We have found that

the calculation of the compensation charge used in the PAW formalism differs slightly in Geng’s study, compared to ours, therefore preventing a direct comparison of total energies.

According to Blöchl’s PAW formalism,⁹ the total [all electron (AE)] charge density $n(\mathbf{r})$ for valence electrons is decomposed in three terms as follows (using the same notations as in Ref. 9):

$$n(\mathbf{r}) = \tilde{n}(\mathbf{r}) + n^1(\mathbf{r}) - \tilde{n}^1(\mathbf{r}), \quad (1)$$

where $\tilde{n}(\mathbf{r})$ is the pseudo (PS) charge density calculated directly from PS wave functions. The exponent 1 indicates that these quantities are calculated inside the augmentation region (also called the PAW sphere). The crucial step in Blöchl’s decomposition is the introduction of a compensation charge \hat{n} added to reproduce the correct multipole moments of the AE charge density.⁹ In the VASP code, this compensation charge is expressed as a sum of one-center terms:¹⁰

$$\hat{n} = \sum_{(i,j),L} \rho_{ij} \hat{Q}_{ij}^L(\mathbf{r}), \quad (2)$$

where the sum goes over all $L = (l, m)$, ρ_{ij} are the occupancies of each augmentation channel (i, j) , and Q_{ij} is the difference between the AE and PS charge density. For the interested reader, extensive details of this formalism can be found in Refs. 9 and 10. What is important here is that in the DFT + U calculations we reported in Ref. 7, the sum in Eq. (2) is truncated up to $L = 4$. We have therefore investigated the dependence of our results with respect to the truncation of the compensation charge. Table I reports the total energies of the ground state and the first metastable state of perfect UO_2 , calculated with an expansion of the compensation charge up to $L = 6$, using the ground state and the first metastable state occupation matrices (as determined in Refs. 6 and 7) and the same calculations parameters as in Geng’s study.

It should be noted that the ground-state total energy calculated with $L_{\text{MAX}} = 4$ (−116.313 eV) differs slightly from the one that we reported previously (−116.505 eV) because the cutoff energy and the k -point mesh are slightly different in order to match perfectly Geng’s calculations. This does

TABLE I. Total energies (in eV) of perfect UO_2 in the fluorite structure, calculated with different truncation of the compensation charge \hat{n} .

	$L_{\text{MAX}} = 4$	$L_{\text{MAX}} = 6$
Ground state	-116.313	-117.136
1st metastable state	-116.129	-116.959

not affect the line of reasoning. We see from Table I that the total energy of the ground state of UO_2 is lower with $L_{\text{MAX}} = 6$ than with $L_{\text{MAX}} = 4$, and that our ground-state calculation using OMC and $L_{\text{MAX}} = 6$ yields a total energy that is very close to the total energy calculated by Geng *et al.* using the QA approach (-117.095 eV). A comparison of electronic occupancies between Geng's work and ours might further explain the 10 meV/ UO_2 difference, but unfortunately occupation matrices are not provided in Geng's work.

The above results therefore show that the difference between Geng's results and ours stems from the calculation of the compensation charge, rather than from an incomplete implementation of OMC. It should be noted that the fact that we used a lower L does not impact our previous DFT + U results. This approximation in our calculations induces a shift in the total energy that is the same for all calculations on the perfect or defective crystal.

It therefore cancels out in the calculation of point defect formation, migration, and activation energies. To check this, we have performed additional calculations using a larger expansion of \hat{n} , and all energy differences remain perfectly unchanged.

Finally, Geng *et al.* also concluded that the QA approach would outperform OMC for calculations in defective supercells, where a large number of metastable states are present. We agree that the QA approach could offer an interesting alternative method, as well as the U -ramping method developed by Meredig *et al.*¹¹ On a practical viewpoint, however, it is not necessary with OMC to perform a high number of calculations in order to find the ground state of point defect containing systems. Indeed, occupation matrices of atoms located far from the defects are those obtained in the perfect crystal while near the defect, the breaking of symmetries allows for an efficient optimization process that does not require any systematic search as in the perfect crystal. Also, OMC has two major advantages. The first one lies in the possibility to explore different valence configurations for the cations in the system, such as U^{3+} or U^{5+} cations in the case of UO_2 . The second advantage is that OMC allows us to impose the fluorite structure of UO_2 *via* the control of occupation matrices. This is very important in the case of UO_2 since it prevents the system from completely converging into the Jahn-Teller distorted phase, in which formation energies are slightly different.⁷

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