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Assessing a solids-biased density-gradient functional for actinide metals

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Recent developments of new electron exchange and correlation functionals within density-functional theory include a solids-biased modification of the popular Perdew-Burke-Ernzerhof (PBE) functional and is referred to as PBEsol. The latter is claimed to remove a bias toward free-atom energies in the former and is therefore better suited for equilibrium properties of densely packed solids and surfaces. We show that PBEsol drastically worsens the equilibrium properties of the actinide metals compared to PBE and produces results closer to that of the local density approximation. The PBEsol atomic volume of δ-Pu is 12% and 14% smaller than PBE and experimental values, respectively. Also, iron is predicted to have the incorrect ground-state phase within PBEsol. These results illustrate the difficulties and limitations in improving the gradient approximations of the electron exchange and correlation functional in a general fashion even when the application is restricted to solids. We comment on the possibility of formulating a unique functional without these limitations that is applicable to solids as well as to finite-sized systems such as atoms and molecules.

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Efficient calculations of ground-state properties for solids and molecules using density-functional theory (DFT) (Refs. 1 and 2) coupled with approximations of the electron exchange and correlation functionals (E_{xc}) have been very practical for several decades. Although the approach has some fundamental problems, which we discuss below, its successes when comparing to experimental data are too numerous to list. Generally DFT predicts realistic lattice constants and binding energies for many elements, alloys, and compounds including the transition metals.[3]

It was discovered early that the more primitive approximation of the E_{xc}, that depends explicitly on the local electron density (local density approximation, LDA), has a tendency toward overbinding. This deficiency is reflected in too small LDA atomic volumes for all transition metals[3] as well as the early actinides.[4] An advanced form of the E_{xc} includes gradient terms of the electron density as well. The first widely used general gradient approximation (GGA) is due to Perdew *et al.*,[5] which we will call PW91 hereafter. Ozolinš and Körling[3] found PW91 to substantially improve on the LDA for equilibrium volumes and bulk moduli of nonmagnetic transition metals. It was also discovered[6] that PW91 predicts the correct body-centered-cubic (bcc) ferromagnetic ground state of iron, something that the LDA fails to do. For both α-cerium and the actinide metals[4,7] PW91 was further shown to be far superior to the LDA as well. PW91 was "made simple "in the so-called PBE (Ref. 8) which retains the general features of the PW91 while having a less complex formulation at the cost of not fulfilling some nonessential exact conditions.

These GGA's certainly improve upon the LDA in many instances but over time it has become clear that they overcorrect the chronic LDA overbinding for some simple metals, ionic solids, and transition elements.[9] The overcorrection for the solids is attributed to an inherent bias toward the description of free-atom energies and a remedy for eliminating this bias has been proposed in a new functional, PBEsol.[9] PBEsol includes adjustments of the PBE to better correspond to the LDA in the sense that it restores the electron-density gradient expansion of the exchange energy[2] that is accurate for slowly varying densities. Consequently, the performance of PBEsol is closer to that of the LDA and is therefore producing better lattice constants for some 18 solids.[9]

The new PBEsol is a hopeful candidate for a more accurate E_{xc} and an aid for a better DFT description of solids in general. One worry is, however, that it might do worse in metals where PW91 strongly improve upon the LDA. The present Brief Report explores this risk by focusing on the light actinide metals thorium through plutonium (atomic numbers 90–94) for which the PW91 indeed is a great improvement over the LDA.[4]

The early actinides are similar to the early d-transition metals in that valence electrons occupy chemically bonding band states that are contracting the lattice when proceeding through higher atomic numbers. For the actinides the major difference in terms of bonding is the much narrower $5f$ bands compared to the d bands of the transition metals. These narrow $5f$ bands support distortions of the lattice giving rise to increasingly complex and deformed crystal structures traversing the series.[10] The narrow bands also depart more strongly from the concept of slowly varying electron densities to which PBEsol is explicitly tuned.

In Fig. 1 we show calculations of the atomic volumes (V) for the elemental solids Th-Pu together with room-temperature experimental data. The computations are performed for the correct crystal structures, are nonmagnetic, and include spin-orbit interaction, which are experimentally known to be highly important for the actinide $5f$ states.[11] The technical details are similar to calculations for the actinides we have carried out in the past[12] with an all-electron electronic-structure code without geometrical restrictions to charge density and potential.[13] We have chosen the Janak *et al.*[14] parameterization of the von Barth and Hedin (BH) (Ref. 15) E_{xc} to represent the LDA treatment although there are newer LDA formulations. Our purpose, however, is not to assess the performance of the LDA which is rather well established. Here we choose one of the early LDA expressions to compare with the most recent GGA to highlight these functionals progress over time.

The calculations in Fig. 1 account for thermal expansion.

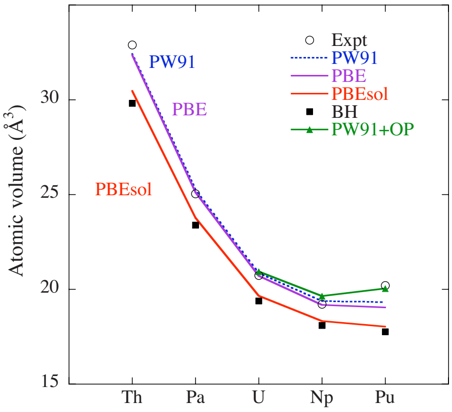

FIG. 1. (Color online) Calculated atomic volumes, corrected for room temperature (see text) for the light actinides using various E_{xc} functionals. The calculations include spin-orbit coupling but no spin polarization. OP is important for Pu and non-negligible for Np but can be ignored for Th-U.

This is done by using the experimental linear coefficient of thermal expansion, α, so that $V(T)=V(0)[1+3\alpha T]$ where the temperature (T) is chosen to be 300 K. Notice that the PBEsol results are relatively close to that of the BH but very far from the experimental data and on average 6.6% too small. PBE and PW91 are nearly identical and much closer to experiment. The PW91+OP treatment also includes orbital polarization (OP) that is an electron correlation similar to the spin-orbit interaction and a generalization of Hund's second rule of an atom.[16] The OP is known to be important for plutonium[17] but has a small effect on Np and is negligible for uranium and the lighter actinides (not shown). The PW91 has an average error of about 1.6% which reduces to 1.2% when OP is taken into account.

Although experimentally plutonium has not been proven to be a magnetic material,[18] conventional DFT predicts formation of spin and orbital magnetic moments in Pu and the high-temperature δ phase, in particular. We have argued recently that within the DFT model δ-Pu is best described as a paramagnet with disordered spin and antiparallel orbital moments of similar magnitude.[19] In Fig. 2 we show calculations assuming this model with the same functionals as in Fig. 1. The experimental equilibrium volume (V_{expt}) for δ-Pu is 25 Å^3 and is used to scale the x axis in Fig. 2. Notice also that the x axis is contracted to better display all total-energy curves within the same plot. As is the case for the light actinides, the new PBEsol dramatically worsens the agreement with experiment for δ-Pu, although it represents a slight improvement over the LDA. Nevertheless, the predicted PBEsol volume is almost 15% too small while both

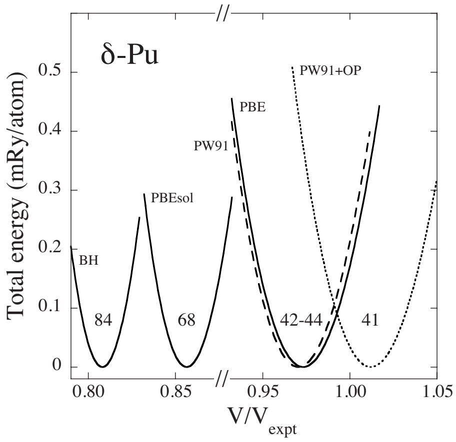

FIG. 2. Calculations similar to those in Fig. 1 but allow spin polarization in a paramagnetic (disordered) phase (see text and Ref. 19). The volumes (V) are scaled with the experimental (25 Å^3) value. The bulk modulus for each treatment is shown in units of GPa. Notice that the x axis has been contracted to better display the curves.

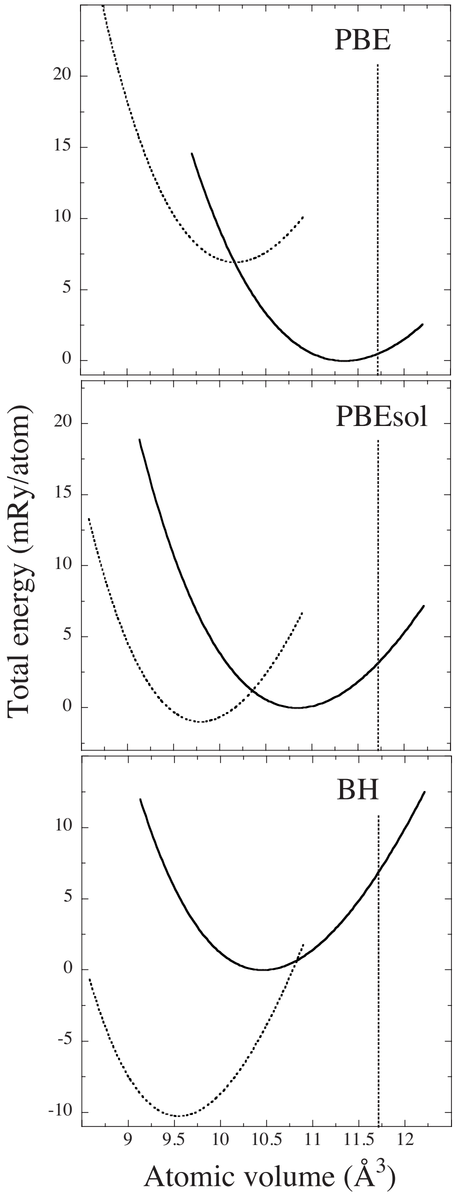

FIG. 3. PBE (upper panel), PBEsol (middle panel), and BH (lower panel) total energies for nonmagnetic hcp (dashed) and magnetic bcc (full) iron as functions of atomic volume. Vertical dashed line represents the experimental room-temperature atomic volume for iron. Only the PBE treatment (and PW91, not shown) predicts the correct ground state.

PBE and PW91 are much closer to the measured volume. Experiment and theory are very close when also OP is included (PW91+OP) but perfect agreement is not expected because temperature effects are difficult to include and are not modeled in these calculations. The PBEsol bulk modulus (68 GPa) is more than twice the experimental one ($\sim$30 GPa) while the PBE and PW91 bulk moduli are both considerably closer ($\sim$40 GPa).

Clearly, the recently proposed PBEsol (Ref. 9) is disappointing for the actinide metals. The very grave failure for the magnetic δ-Pu is particularly worrisome because one of the great successes of PW91 is the correct *magnetic* description of the important metal iron. We have therefore investigated also the magnetic bcc and nonmagnetic hexagonal close-packed (hcp, ideal c/a axial ratio) phases of iron with these same functionals. In the upper panel of Fig. 3 we show the PBE total energy for the magnetic bcc (full line) and nonmagnetic hcp (dotted) phases as a function of atomic volume. The PBE functional correctly predicts the ground state of iron as is expected from previous reports for PW91.[6] The theoretical zero-temperature equilibrium volume also compares favorably with experimental room-temperature data (vertical dashed line with no thermal-expansion correction). The transition pressure obtained from the PBE total energies (when the phases enthalpy coincide) is about 14 GPa which is a somewhat higher than the PW91 (12 GPa not shown) treatment. Experimentally this transition is rather sluggish with a significant hysteresis but the pressure is bracketed between 10 and 15 GPa.[20] Unfortunately, in the middle panel, PBEsol predicts the wrong nonmagnetic hcp phase as the ground state. The LDA (in the lower panel) also favors the incorrect nonmagnetic phase, which is a well-established failure of this functional.[21] The fact that PBEsol produces too small lattice constant for iron and thorium was also recently reported.[22]

Nearly two decades have passed since the widely used and rather successful PW91 functional was introduced. It improves the description of f-electron elements substantially and also predicts the correct ground state of iron. On these accounts and perhaps others the newly proposed PBEsol shows an unsatisfactory performance. PBEsol is reportedly better than previous GGA's for systems with slowly varying electron densities for which also the LDA assumption is a good choice. For the actinides, iron, and probably rare-earth systems the electron density is not sufficiently monotone for PBEsol or LDA to be appropriate which explains their failure. This revelation and the fact that any GGA formulation of the E_{xc} cannot satisfy, simultaneously, accurate atomic exchange energies and that of a slowly varying electron density[9,23] lead us to conclude that one must consider other avenues for an improved DFT in the future.

One approach consists of the most recently suggested and hence most advanced functionals that tend to be of the hybrid type.[24] Here one considers exchange terms determined by various procedures and includes each with weights deemed pertinent to particular applications. The exchange terms are needed in order to correct for the presence of self-interaction that is present in the Coulomb energy calculated in the form of the Hartree term. It appears, however, that this procedure often fails to produce reliable results for other systems than those dictating the nature of the hybrid.

We briefly also mention the meta-GGA that also considers the kinetic-energy density as a variable. The so-called TPSS functional is of this type[25] but unfortunately this functional does not generally improve[22] on the previous GGA's.

It is well known that self-interaction is exactly removed by a single exchange term constructed from the orbitals calculated by the Kohn-Sham equations. As in the methodology of exact exchange and the so-called optimized effective potential method[26] we suggest the inclusion of just this functional but with one difference. The functional is to be treated together with the Hartree term allowing the calculation of the Coulomb energy in terms of the pair density. This construction is fully consistent with the nature of the Coulomb energy as an expectation value of the Coulomb operator with respect to the wave function (Slater determinant) determined by the Kohn-Sham equations. We are currently investigating methodologies[27] for obtaining the functional derivative of the pair density with respect to the density and expect to report on our efforts as results are obtained.

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