Pseudopotential for ab initio calculations of uranium compounds

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Abstract. The density functional theory (DFT) is a research tool of the highest importance for electronic structure calculations. It is often the only affordable method for ab initio calculations of complex materials. The pseudopotential approach allows reducing the total number of electrons in the model that speeds up calculations. However, there is a lack of pseudopotentials for heavy elements suitable for condensed matter DFT models. In this work, we present a pseudopotential for uranium developed in the Goedecker–Teter–Hutter form. Its accuracy is illustrated using several molecular and solid-state calculations.

1. Introduction
Materials properties can be calculated by density functional theory (DFT) in a parameter-free way. DFT is successfully applied to a wide variety of systems [1–6]. Computational tools for DFT modelling have been under active development during last 30 years. Now there are many well-developed free and commercial codes. For a particular model different choices are available with respect to the type of a basis set, an exchange-correlation functional and a pseudopotential for a given element. Recently the systematic comparison of the accuracy of different codes has got a special attention [7]. A pseudopotential model is among the major factors that determines the accuracy of DFT calculations.

The pseudopotential approach was introduced by Hans Hellmann [8] for molecular models and became an important tool for condensed matter electronic structure calculations since the paper of Heine and Abarenkov [9]. Since actinide atoms have many electrons, all-electron calculations are possible only for small molecules. Pseudopotentials are needed to successfully model condensed actinide-bearing materials. However, there is only a limited set of properly described pseudopotentials suitable for DFT calculations with actinides. Relativistic effects and strong electron correlation effects in the 5f states are important for building reliable pseudopotentials of actinides [10].

The projector augmented-wave (PAW) method model for a uranium pseudoatom included in the VASP [11] code was used for creation of the empirical EAM (embedded atom model) potential for classical atomistic models of uranium [12]. This EAM model shows good accuracy for different properties [12] that supports the accuracy of the PAW model [11] used for building the reference data-base for fitting [12].

Since the pseudopotential is crucial for the accuracy of DFT calculations, all subtle details of its generation should be properly controlled. On the way to make DFT precision higher, it
is instructive to compare different alternative pseudoatom models. In this work we describe the
 generation of a pseudopotential for a uranium atom in the format suitable for the ABINIT and
 CP2K codes (free alternatives to VASP). The accuracy of this pseudopotential is illustrated by
 a series of molecular and solid-state calculations. We also compare our model with available
 pseudopotentials for QuantumEspresso [13] and VASP codes.

2. Pseudopotential development
Such free DFT codes as CP2K and ABINIT can use the norm-conserving, separable, dual-
 space Goedecker–Teter–Hutter (GTH) pseudopotentials [14,15]. The GTH pseudopotentials are
available for the whole periodic system up to Rn. The pseudopotential for uranium was created
by Rabone and Krack [16] but its coefficients were not published.

The CP2K code uses the hybrid Gaussian and plane wave (GPW) basis. The ABINIT code
uses pure plane wave (PW) basis. The GPW method is highly accurate and allows CP2K to
perform faster calculations for fairly large systems. However, tests are required to avoid errors
connected with the Gaussian basis set parameters, and PW calculations can serve as a reference.
The GPW and PW methods require nuclei to be described using pseudopotentials. In this paper
we use CP2K for pseudopotential development and benchmark calculations.

The local part of a GTH pseudopotential is the sum of the long-ranged and short-ranged
terms:

\[ V_{\text{loc}}(r) = \frac{-Z_{\text{ion}}}{r} \text{erf} \left( \frac{r}{\sqrt{2} r_{\text{loc}}} \right) + \exp \left[ -\frac{1}{2} \left( \frac{r}{r_{\text{loc}}} \right)^2 \right] \times \left[ C_1 + C_2 \left( \frac{r}{r_{\text{loc}}} \right)^2 + C_3 \left( \frac{r}{r_{\text{loc}}} \right)^4 + C_4 \left( \frac{r}{r_{\text{loc}}} \right)^6 \right], \]  

(1)

where \( Z_{\text{ion}} \) is the core charge (the ion charge minus the total charge of the valence electrons),
\( r_{\text{loc}} \) and \( C_i \) are the fitting parameters.
Table 1. The differences in eigenvalues (E) and charges (Q) between the all-electron DFT model and the pseudopotential DFT model of a uranium atom.

| Energy level | Spin | \( E_{ae} - E_{pseudo} \) (Ha) | \( Q_{ae} - Q_{pseudo} \) (Ha) |
|--------------|------|---------------------------------|---------------------------------|
| 6s           | 0.5  | \( 2.22 \times 10^{-5} \)      | \( -2.94 \times 10^{-6} \)      |
| 7s           | 0.5  | \( -3.44 \times 10^{-5} \)     | \( -1.92 \times 10^{-7} \)      |
| 8s           | 0.5  | \( 4.41 \times 10^{-6} \)      | \( -5.59 \times 10^{-5} \)      |
| 6p           | 0.5  | \( -1.10 \times 10^{-6} \)     | \( -6.74 \times 10^{-7} \)      |
| 6p           | 0.5  | \( -7.23 \times 10^{-6} \)     | \( -2.21 \times 10^{-6} \)      |
| 7p           | -0.5 | \( -9.56 \times 10^{-4} \)     | \( 1.21 \times 10^{-5} \)       |
| 7p           | 0.5  | \( 3.25 \times 10^{-4} \)      | \( -1.25 \times 10^{-3} \)      |
| 8p           | -0.5 | \( -1.05 \times 10^{-4} \)     | \( -1.42 \times 10^{-3} \)      |
| 8p           | 0.5  | \( 1.08 \times 10^{-4} \)      | \( -2.36 \times 10^{-4} \)      |
| 6d           | -0.5 | \( -1.03 \times 10^{-5} \)     | \( -8.23 \times 10^{-6} \)      |
| 6d           | 0.5  | \( -1.69 \times 10^{-5} \)     | \( -1.36 \times 10^{-5} \)      |
| 7d           | -0.5 | \( -1.27 \times 10^{-5} \)     | \( 1.42 \times 10^{-4} \)       |
| 7d           | 0.5  | \( -1.28 \times 10^{-5} \)     | \( 1.56 \times 10^{-4} \)       |
| 5f           | -0.5 | \( -2.62 \times 10^{-4} \)     | \( -1.76 \times 10^{-5} \)      |
| 5f           | 0.5  | \( 3.97 \times 10^{-4} \)      | \( 1.84 \times 10^{-5} \)       |
| 6f           | -0.5 | \( -1.57 \times 10^{-8} \)     | \( -9.69 \times 10^{-6} \)      |
| 6f           | 0.5  | \( -2.29 \times 10^{-6} \)     | \( 2.64 \times 10^{-6} \)       |

The nonlocal contribution \( V_l(r, r') \) has the following form:

\[
V_l(r, r') = \sum_{i=1}^{3} \sum_{j=1}^{3} \sum_{m=-l}^{l} Y_{l,m}(\hat{r}) p_l^i(r) h_{l,j}^m(r') Y_{l,m}^*(\hat{r}),
\]

where \( Y_{l,m} \) are the spherical harmonics, \( l \) is the angular momentum quantum number, \( p_l^i(r) \) are the Gaussian-type projectors and \( h_{l,j}^m \) are the fitting parameters.

All terms in GTH pseudopotential are given analytically without tabulated functions. The set of parameters is optimized with respect to atomic all-electron wave functions and energies.

The pseudopotential generation is tricky. The general procedure is known well but the final result depends strongly on the initial values of the pseudopotential coefficients.

Starting with a relativistic all-electron calculation for a uranium atom, we determine radial wave functions and corresponding energy levels. We use the Perdew–Burke–Ernzerhof (PBE) exchange-correlation density functional. The inner 78 electrons of uranium atom are included in the core (described by the pseudopotential). The outer 14 electrons (6s^2 6p^6 5f^6 6d^1 7s^2) are treated explicitly. The fitting of coefficients is done by minimizing the penalty function which includes the differences of eigenvalues and charges between the all-electron and pseudoatom models.

Finally, we obtain a pseudopotential that describes fairly well atomic energies and charges. Results are summarized in table 1. An example of the comparison between all-electron and pseudo wavefunctions is shown in figure 1.

The parameters of the pseudopotential are determined from the atomic calculations, that is why accurate testing of the pseudopotential in different chemical environments is required. To check the transferability of the pseudopotential we calculated energy levels for several excited and ionised states (6s^2 6p^6 5f^6 6d^2 7s^3; 6s^2 6p^6 5f^6 6d^0 7s^2; 6s^2 6p^6 5f^5 6d^1 7s^1 7p^1; 6s^2 6p^6 5f^6 6d^0 7s^2). The
Table 2. Bond distances (Å) for the uranium-bearing molecular compound. Atoms numbering is illustrated in figure 2.

| Method          | U–F (UF₆) | U–Cl (UCl₆) | U–F (UF₅) | U–Cl (UCl₅) | U–Cl (UCl₃) | U–O (UO₂) | U–O (UO₃) |
|-----------------|-----------|-------------|-----------|-------------|-------------|-----------|-----------|
| PBE (our result)| 2.019     | 2.471       | 2.034     | 2.466       | 2.538       | 1.811     | 1.821     |
|                 |           |             | 2.036     | 2.492       |             |           |           |
|                 |           |             |           |             | (U–O₁)      |           |           |
|                 |           |             |           |             | (U–O₂)      |           |           |
|                 |           |             |           |             | (U–O₃)      |           |           |
| PBE [17]        | 2.024     | 2.469       | 2.034     | 2.509       | 1.815       | 1.828     |           |
| AE PBE [18]     | 2.024     | 2.469       | 2.034     | 1.815       | 1.828       | 1.863     |           |
|                 |           |             |           |             |             | 1.9       |           |
| RECP PBE [18]   | 2.023     |             |           | 1.818       | 1.856       |           |           |
|                 | 2.027     |             |           |             |             |           |           |
| Experiment      | 1.999 [19]| 2.46 [20]   | 1.996 [22]| 2.549 [21] | 2.549 [21] |           |           |

The difference in bond lengths is less than 1%. However, the experimental values are slightly lower. That is the well-known feature of the PBE functional. Uranium pentafluoride UF₅ and pentachloride UCl₅ have the C₄ᵥ symmetry with square-pyramidal geometry. In our calculations the apical U–F distance is slightly longer than the basal one. The all-electron calculations predict the same result. A uranium dioxide molecule is linear and a uranium trioxide molecule has the distorted planar T-shaped form. Their geometries are also in agreement with the previous calculations [24].

3. Ab initio calculations of γ-uranium

Finally we consider the crystalline γ-uranium with a body-centered cubic structure (two atoms in the unit cell). This phase of uranium is of primary interest to the nuclear fuel applications. All calculations were made with CP2K, VASP and QuantumEspresso packages with PBE exchange-correlation functional. Pseudopotential for QuantumEspresso was taken from PSLibrary 1.0 [25]. For zero-temperature optimizations 20 × 20 × 20 k-points mesh was used in all cases.

The difference in the optimized lattice constant between different codes is less than 1%. The results are 3.466 Å for CP2K, 3.432 Å for VASP and 3.430 Å QuantumEspresso, which are in a
Figure 2. Models of uranium-bearing molecules (from left to right and top to bottom): UCl$_3$, UCl$_5$, UCl$_6$, UF$_5$, UF$_6$, UO$_2$ and UO$_3$.

good agreement with the previous DFT study with VASP (3.427 Å) [26] and the experimental value (3.47 Å). The bulk modulus is 123 GPa for CP2K and 120 GPa for VASP. These results are also in agreement with previous work [26] (132 GPa) and the experimental value (113.3 GPa).

4. Conclusions
Thus the generation of the GTH pseudopotential for uranium atom has been described. The accuracy of the pseudopotential has been illustrated by calculations for uranium-bearing molecular compounds UF$_6$, UCl$_6$, UF$_5$, UO$_2$, UO$_3$ and γ-U. All results are in the agreement with the previous studies.

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