PROJECTOR AUGMENTED-WAVE POTENTIAL FOR URANIUM

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1. Why should we want to create such a horror?

Actinides are specific elements with valence f-orbital. That means electrons in their valence band behave differently from other commonly simulated elements. However, their application in science and industry is quite important. Due to radioactivity and rarity (which mean also high prize) of many of them simulations seem to be a good means to test whether the ideas of use of these rare earth elements are reasonable.

In this work we would like to introduce our solution to the initial complex problem for anyone who wants to begin with *ab initio* simulations – creation of the potential. In the case of uranium there was a need to start (more or less) from scratch and design the potential of our own, because there is no suitable one in public repositories.

This paper is organized as follows. In the Section 2 we briefly introduce basic theoretical concepts of *ab initio* methods and show two important kinds of potentials. Short view to theoretical background of projector augmented-wave method can be found in Section 3. The implementation of this theory in ATOMPAW [1] is mentioned in Section 4. Section 5 shows our methods of testing potentials. In Section 6 the results of tests are presented. Finally in Section 7 you can find the conclusion of our work.

2. A short look to Latin dictionary: *ab initio*

Let's start from the beginning. In Latin '*ab initio*' means 'from the beginning' but in our field it is often translated as 'from the first principles'. The term stands for numerical methods that (ideally) do not use any parameters, because accurate description of elementary interactions (in the form of Schrödinger or Dirac equation) enables them to accurately predict macroscopic properties. In practice many approximations have to be introduced and the idea of zero parameters is somehow cloudy. However, with well-defined approximations and good set of settings this approach works interestingly well.

The exhibition piece of *ab initio* approach is density-functional theory (DFT). It is based on an idea that ground energy of electronic system is a functional of electron density. That means when we know electron density we can compute all ground-state properties. The idea is great. There is only one problem – we have no idea how is the electron density $\rho(r)$ distributed.

Here comes DFT which maps the ground state of interacting electron system into the ground state of non-interacting electron in the effective field. Then our problem with $\rho(r)$ is reduced to finding the effective field. At this moment an approximation comes to the scene. When the Schrödinger equation for the electron system is written

$$\boldsymbol{\hat{H}\Psi(\vec{r}) = E\Psi(\vec{r})} \tag{1}$$

the Hamiltonian can be divided into three parts

$$\boldsymbol{\left(\hat{E}_K + \hat{E}_C + \hat{E}_{XC}\right)\Psi(\vec{r}) = E\Psi(\vec{r})} \tag{2}$$

where $\hat{E}_K$ stands for kinetic energy, $\hat{E}_C$ for Coulombic interaction and $\hat{E}_{XC}$ is an exchange-correlation energy operator. The exchange-correlation energy is the part for which the exact mathematical formulation is unknown. But for the last fifty years people tirelessly try to approximate it.

One very successful approximation was proposed by Kohn and Sham [2]. They assumed $\rho(r)$ to be the local. That means the exchange-correlation energy in given point depends only on $\rho(r)$ in that same point. The name of this method is self-explaining – local density approximation (LDA).

The natural next step from the local $\rho(r)$ is using gradient. In practice it is not that straightforward, but it is possible and now there are a few implementations of generalized gradient approximation (GGA). It works better than LDA especially if gradients of electron density are large (e.g. in cohesion energy calculations or in treating actinide compounds).

Now we have all the operators in our Schrödinger equation and we would like to compute the ground-state energy. However, we still do not know electronic wave functions. To obtain them two branches of approaches have been developed: all-electron methods (LMTO, LAPW) and pseudopotential methods. The main difference between them is in treatment of core electrons. Pseudopotential methods work with *frozen* core – the electrons on inner shells (not valence) are treated together with the nucleus as an effective ion core. Only the valence electrons are treated self-consistently. To allow computationally affordable calculations the wave functions in the core region (near to frozen core) are approximated by smooth functions that can be represented in small basis. On the contrary all-electron methods treat all electrons self-consistently. The trick used there is to divide the elementary cell into two parts – so called muffin tins around atomic cores, where the electronic wave functions are atomic-like – and the interstitial region where the wave functions are represented by plane waves.

We used projector augmented-wave method which combines both approaches. It uses frozen core but the valence electrons are treated differently inside the augmentation radius around cores and outside of it.

3. Terrifying math behind the scene

It is quite fascinating story to follow when you see how projector augmented-waves can be created. It was originally shown by Blöchl [3]. In the beginning we realize we need to transform real wave function in the basis of function we can easily represent (plane waves). Let’s start with physical wave function $\Psi_n(r)$ (In fact we use DFT, so $\Psi_n(r)$ is Kohn-Sham one electron wave function) which can be transformed by operator $\hat{\mathcal{U}}$ to auxiliary (pseudo) wave function $\tilde{\Psi}_n(r)$.

$$\boldsymbol{\tilde{\Psi}_n(r) = \hat{\mathcal{U}}\Psi_n(r)} \tag{3}$$

However, we would like to express physical wave function by pseudo wave function, so we need inverse transformation.

$$\boldsymbol{\Psi_n(r) = \hat{\mathcal{U}}^{-1}\,\tilde{\Psi}_n(r) = \hat{\mathcal{T}}\,\tilde{\Psi}_n(r)} \tag{4}$$

Then the expression for total energy can be written as follows.

$$\boldsymbol{E = E[\Psi_n(r)] = E\big[\hat{\mathcal{T}}\,\tilde{\Psi}_n(r)\big]} \tag{5}$$

Our task is to find such operator $\hat{\mathcal{T}}$ that the auxiliary wave functions are well behaved.

As a consequence of this three requirements on the operator $\hat{\mathcal{T}}$ can be formulated:

- the physical wave functions shall be transformed onto numerically convenient auxiliary wave functions
- the operator shall be linear so the algebraic operations are valid
- the operator shall be local so there is no interaction between different atomic sites in pseudo wave functions ($\boldsymbol{R}$ runs over each atomic site and $\boldsymbol{S_R}$ is a local atom-centred contribution within one augmentation region)

$$\hat{\boldsymbol{\mathcal{T}}} = \mathbf{1} + \sum_{\boldsymbol{R}} \boldsymbol{S_R} \tag{6}$$

Now when we know what the operator $\hat{\mathcal{T}}$ should do we find its definition. At first we have to point out that each wave function can be expanded into partial waves. Then we have to define a complete set of initial and final states for the transformation.

$$\forall \boldsymbol{i} \qquad |\boldsymbol{\phi_i}\rangle = \hat{\boldsymbol{\mathcal{T}}}|\tilde{\boldsymbol{\phi}}_{\boldsymbol{i}}\rangle \tag{7}$$

where $|\phi_i\rangle$ are final states – all-electron valence partial waves, which solve Schrödinger equation for all-electron atomic potential for a set of energies and $|\tilde{\phi}_i\rangle$ are initial states – auxiliary partial waves which are pairwise identical with all-electron outside the augmentation radius r_c. The index i stands for different atomic sites R, quantum numbers connected to angular momentum (l,m) and index n to distinguish different partial waves concerning one orbital.

After definition of initial and final states a closed expression for the transformation operator is found. It can be derived from the combination of Eq. 6 and Eq. 7. Let's assume the situation in one augmentation region:

$$|\boldsymbol{\phi_i}\rangle = |\tilde{\boldsymbol{\phi}}_{\boldsymbol{i}}\rangle + \boldsymbol{S_{R_i}}|\tilde{\boldsymbol{\phi}}_{\boldsymbol{i}}\rangle \tag{8}$$

In this case contribution S to linear transformation is:

$$\boldsymbol{S_{R_i}}|\tilde{\boldsymbol{\phi}}_{\boldsymbol{i}}\rangle = |\boldsymbol{\phi_i}\rangle - |\tilde{\boldsymbol{\phi}}_{\boldsymbol{i}}\rangle \tag{9}$$

Remember that the wave functions with tilde stand for auxiliary partial waves and these without tilde represent all-electron partial waves. Each wave function can be expanded into partial waves. Hence we can write:

$$\boldsymbol{\Psi_n} = \sum_{\boldsymbol{i}} \boldsymbol{\phi_i c_i} = \hat{\boldsymbol{\mathcal{T}}}\tilde{\boldsymbol{\Psi}}_{\boldsymbol{n}} = \hat{\boldsymbol{\mathcal{T}}}\sum_{\boldsymbol{i}} \tilde{\boldsymbol{\phi}}_{\boldsymbol{i}}\boldsymbol{c_i} = \sum_{\boldsymbol{i}} \boldsymbol{c_i}\hat{\boldsymbol{\mathcal{T}}}\tilde{\boldsymbol{\phi}}_{\boldsymbol{i}} = \sum_{\boldsymbol{i}} \boldsymbol{\phi_i c_i} \tag{10}$$

From Eq. 10 we see that coefficients $\mathbf{c_i}$ must be the same for real and auxiliary waves. Since we require transformation $\hat{\boldsymbol{\mathcal{T}}}$ to be linear $\mathbf{c_i}$ can be expressed as scalar product of the pseudo wave function and some fixed function. These fixed functions are called projector functions $\tilde{p}_i$ and there are as many projectors as many partial waves.

$$\boldsymbol{c_i} = \langle\tilde{\boldsymbol{p}}_{\boldsymbol{i}}|\tilde{\boldsymbol{\Psi}}\rangle \tag{11}$$

Projectors have to be localized within an augmentation region

$$\sum_{\boldsymbol{i}} |\tilde{\boldsymbol{\phi}}_{\boldsymbol{i}}\rangle\langle\tilde{\boldsymbol{p}}_{\boldsymbol{i}}| = \mathbf{1} \tag{12}$$

That means expansion of pseudo wave function in one augmentation region into projectors must be identical to that wave function.

$$\sum_{\boldsymbol{i}} |\tilde{\boldsymbol{\phi}}_{\boldsymbol{i}}\rangle\langle\tilde{\boldsymbol{p}}_{\boldsymbol{i}}|\tilde{\boldsymbol{\Psi}}\rangle = \tilde{\boldsymbol{\Psi}} \tag{13}$$

Analysis of Eq. 13 leads to another condition for the projector functions:

$$\langle \tilde{\boldsymbol{p}}_{\boldsymbol{i}} | \tilde{\boldsymbol{\phi}}_{\boldsymbol{j}} \rangle = \boldsymbol{\delta}_{\boldsymbol{ij}} \tag{14}$$

The reader interested in practical process of choosing projectors and partial waves can find more details in the original work of Blöchl [3]. The others can skip the details and move forward to the result. Linear transformation between auxiliary and physical wave function has been found.

$$\hat{\boldsymbol{\mathcal{T}}} = \mathbf{1} + \sum_{\boldsymbol{i}} \big(|\boldsymbol{\phi}_{\boldsymbol{i}}\rangle - |\tilde{\boldsymbol{\phi}}_{\boldsymbol{i}}\rangle \big) \langle \tilde{\boldsymbol{p}}_{\boldsymbol{i}} | \tag{15}$$

Using this transformation, physical wave function can be obtained from known projectors, partial waves around the atomic centres and the pseudo partial waves.

$$|\boldsymbol{\Psi}\rangle = |\tilde{\boldsymbol{\Psi}}\rangle + \sum_{\boldsymbol{i}} \big(|\boldsymbol{\phi}_{\boldsymbol{i}}\rangle - |\tilde{\boldsymbol{\phi}}_{\boldsymbol{i}}\rangle \big) \langle \tilde{\boldsymbol{p}}_{\boldsymbol{i}} | \tilde{\boldsymbol{\Psi}} \rangle \tag{16}$$

Note that right-hand side of eq. 16 consists of three components. The first is the auxiliary wave function (expandable to plane waves) that is correct in the interstitial region. The second term is the sum of partial waves (solutions of Schrödinger equation for isolated atom) that is correct in the augmentation region around the atomic cores. The last term is the sum of pseudo partial waves (but on the radial grid) that must be subtracted inside the augmentation region to reach valid results.

4. Getting mathematical golem into life

Having the beautiful theoretical concept from the previous chapter in mind we move to implementation. The first thing to mention is the need for approximations. We required complete basis of plane waves, but they can be included only up to the specified cut-off. Another restriction is that number of partial waves (and also pseudo partial waves and projector functions) is finite. However these three types of functions can be matched, so for each partial wave there is one pseudo partial wave and one projector function.

In fulfilling our task of creating the potential for Uranium we used tool ATOMPAW [1]. Valence configuration was used as follows (the same as Dorado [4] used): $6s^2$, $6p^6$, $6d^2$, $5f^2$, $7s^0$. Two partial waves for each value of l were used. Radius of the augmentation region was chosen to 2.5 a. u. considering many core electrons in uranium atom. Pseudo partial waves are created by RRKJ scheme [5]. They are constructed as a sum of two Bessel functions. Matching radius for *s* orbital pseudo partial waves was chosen to value 2.0 a. u.

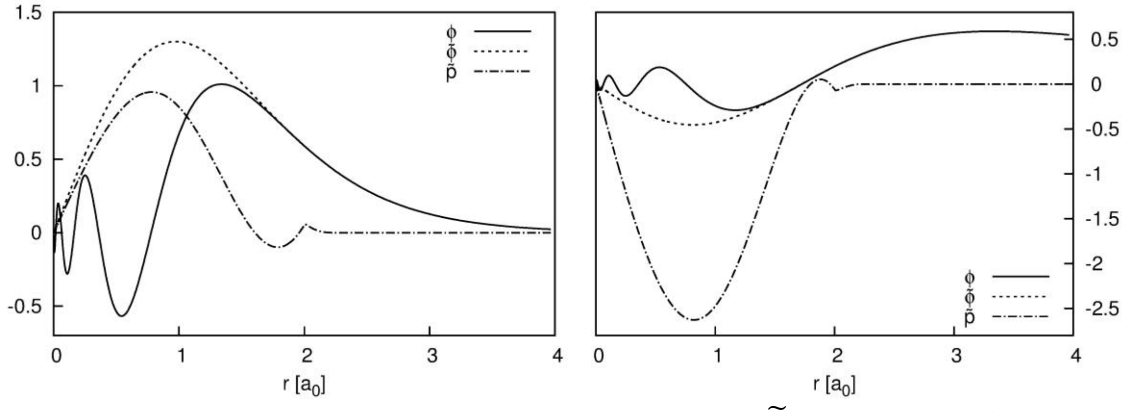

Fig.1: *Here all (two) partial waves* $\boldsymbol{\phi}$, *pseudo partial waves* $\tilde{\boldsymbol{\phi}}$ *and projector functions* $\tilde{\boldsymbol{p}}$ *for quantum number l=0 are shown. Note that pseudo partial wave is identical with partial wave outside the matching radius. Sharp peak of projectors at 2 a. u. is caused by difference between matching and augmentation radius.*

5. Why do you think it is correct?

Two potentials were constructed – one for LDA and the other for GGA approximation. Both were extensively tested on α-U lattice. Crystalline α-U is an orthorhombic structure with space group $Cmcm$. We introduce two types of tests we used:

- Unit cell volume relaxation – lattice parameters are set free so that lattice can reach minimal total energy.
- Computation of bulk modulus B_0 – a few slightly non-ideal energetic states are computed by moving lattice parameters and simulating changes of volume – then Murnaghan fit is used to find bulk modulus.

6. I believe the test results!

Test results were compared with other calculations and also with experimental values. LDA is presently quite rarely used to describe actinides, so the data for it are not complete.

Tab. 1. *Test results for α-U.*

	This work		Previous calculations		Experiment [6,7]
	LDA	GGA	LDA [6]	GGA [6]	
a [Å]	2.81	2.94	2.76	2.84	2.85
B_0 [GPa]	154	113	182	143	107
b/a	2.08	2.00	-	2.02	2.06
c/a	1.76	1.75	-	1.74	1.73

7. Conclusion

According to principles presented in the first three sections we managed to make our own PAW potentials for uranium with acceptable test results. Numerical parameters in ATOMPAW were meticulously set and our potentials belong among the best in modelling bulk modulus of α-U. The further use of potentials is to compute positron lifetimes in UO_2.

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