Electronic structure of Pu and Am metals by self consistent relativistic GW method

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Abstract

We present the results of calculations for Pu and Am performed using an implementation of self–consistent relativistic GW method. The key feature of our scheme is to evaluate polarizability and self–energy in real space and Matsubara’s time. We compare our GW results with the calculations using local density (LDA) and quasiparticle (QP) approximations and also with scalar–relativistic calculations. By comparing our calculated electronic structures with experimental data, we highlight the importance of both relativistic effects and effects of self–consistency in this GW calculation.

PACS numbers: 71.27.+a, 71.15.Rf, 71.20.Gj
I. INTRODUCTION

During the last two decades we have been witnessing a surge of activity in many–body–
theory based methodologies applied to condensed matter physics. Here we are concerned
with one of them, the Hedin’s GW method\textsuperscript{1}. This particular approach has not only been
applied to many different materials but it has also been formally developed with an intent
to enhance its own applicability or to diagrammatically extend it.

First applications of GW were of ”one–shot” type when one starts with local density ap-
proximation (LDA) to get one–electron eigenstates and construct the corresponding Green’s
function which is then used as an input to perform only one GW iteration. Commonly, such
an approach is called G\textsubscript{0}W\textsubscript{0}. It usually improves LDA band gaps in semiconductors\textsuperscript{2} but has
an obvious drawback because the absence of self–consistency makes it depending on input
and not conserving\textsuperscript{3,4}.

To make the approach independent on the input, the quasi–particle self–consistent GW
method (QSGW) was introduced a few years ago\textsuperscript{5,6}. In this method the Green’s function is
found self–consistently with approximate Hermitian form of self–energy which is constructed
to minimize the perturbation while keeping a quasi–particle picture. The approach was
successfully applied to a wide class of materials including simple metals, semiconductors,
wide band gap insulators, transition metals, transition metal oxides, magnetic insulators,
and rare earth compounds. First calculations for actinide metals using this approximation
and neglecting spin–orbit interaction have also been reported\textsuperscript{7,8}. Recently a scheme based on
Löwdin’s orthogonalization was proposed\textsuperscript{9} which removes an ambiguity in the construction
of the effective self–energy in QSGW. The method has also been extended to treat finite
temperatures\textsuperscript{10} and to calculate spin wave dispersions\textsuperscript{11}. However, similar to the ”one–
shot” variants of GW, QSGW method is not Φ-derivable\textsuperscript{3}, and, as a consequence, it is not
conserving. This, for example, results in difficulties to calculate total energy.

Applications of fully self–consistent GW schemes are not numerous. They have been
applied for weakly correlated solids\textsuperscript{12–15} and for free atoms and molecules\textsuperscript{16,17}. General con-
clusion seems to be that for weakly correlated simple solids full self–consistency deteriorates
spectra as compared to ”one–shot” or QSGW approximations but improves total energies.
For free atoms the conclusion clearly favors fully self–consistent calculations. Based on these
facts one can expect that in solids the spectra obtained by fully self–consistent GW might
be competitive with spectra from QSGW if the corresponding physics is local enough, i.e. similar to free atoms. Besides, the fully self-consistent GW is \( \Phi \)-derivable and so it is conserving. Also, it is important to mention the works aimed to enhance the accuracy of GW based schemes, their robustness, performance, and convergency issues\(^{18-24}\).

Another very active field related to the GW method is its diagrammatic extensions. We mention here the approaches which use LDA-based vertex correction\(^{25-28}\), the approaches which use direct diagrammatic representation for the vertex\(^{29-33}\), and the approach which combines GW and dynamical mean field theory (GW+DMFT)\(^{34,35}\). Hedin’s equations and correspondingly the GW method have also been formally extended to spin-dependent interactions\(^{36,37}\), to treat the electrons residing in a subspace of the full Hilbert space\(^{38}\), and onto the Keldysh time-loop contour\(^{39}\).

Very recently the importance of spin–orbit interaction was highlighted for the elements with large atomic numbers and it was perturbatively included in ”one–shot” GW calculations for \( Hg \) chalcogenides\(^{40}\). In this work we generalize the GW method to solve equations explicitly based on 4–component Dirac’s theory, which is important to get meaningful results for such elements as actinides. This fact together with uncertainty in respect to what kind of self-consistency is better to use for actinides defines the scope of the present work in which we apply self-consistent GW method based on Dirac equation to study the electronic structure of Plutonium and Americium metals.

These two metals (especially Pu) have been a subject of intensive studies during last two decades. From theoretical point of view the best understanding\(^{41-46}\) was achieved using a combination of LDA and dynamical mean field theory\(^{47}\) (DMFT) known as LDA+DMFT method. LDA+DMFT calculations have resolved the puzzle of false magnetism in Pu and Am metals which appears in density-functional based calculations\(^{48,49}\) but contradicts with the experiment\(^{52,53}\).

However, there is a problem with LDA+DMFT type of calculations as the approach is not parameter–free and requires the input matrix of on-site Hubbard interactions. On top of that there is an uncertainty with double counting correlation effects that are present both in LDA and DMFT theories. Therefore there is a significant interest to develop diagramatically based approaches such as GW and its extensions that offer the possibility to overcome both problems. In respect to Plutonium, our study can be considered as the extension of previous work by Chantis et al\(^{8}\) who have studied this metal with QSGW without spin–
orbit interaction and concluded that correlation effects included in GW make the \( f \)-bands narrower and decrease the crystal-field splittings as compared to the LDA results. We extend the work in three ways: i) include spin–orbit interaction by using Dirac form for kinetic energy operator, ii) perform fully self–consistent GW calculation and compare it with self–consistent quasi–particle (QP) and local density approximations, and iii) apply self–consistent GW method to Am metal.

II. RELATIVISTIC GW METHOD

Although, a truly relativistic treatment of the problem would require the use of rather complicated equations of Quantum Electrodynamics, we use a simplified approach. First, we neglect relativistic retardation effects in the Coulomb interaction. In this case, Hedin’s original derivation of his famous system of equations still holds with the only extension that all fermionic functions (Green’s function and self energy) become \( 4 \times 4 \) matrices for every pair of space coordinates. Also, in order to perform self–consistent GW calculation we need only scalar parts of the bosonic functions (polarizability \( P \) and screened interaction \( W \)) in the space of products of bi–spinors which is similar to the non–relativistic theory with collinear spin structures. So, in our method which is described below only the fermionic functions (Green’s function and self–energy) have bi–spinor arguments. Second, we exclude positron states and represent the coordinate dependence of Green’s function in terms of electron states only

\[
G(\alpha \mathbf{r}, \alpha' \mathbf{r}'; \tau) = \frac{1}{N_k} \sum_k \sum_{\lambda' \lambda} \psi_{\lambda}(\alpha \mathbf{r}) G_{\lambda' \lambda}(\tau) \psi_{\lambda'}^{\dagger}(\alpha' \mathbf{r}'),
\]

where \( \mathbf{k} \) runs over Brillouin zone, \( N_k \) is the number of \( \mathbf{k} \)-points, indexes \( (\lambda, \lambda') \) denote the electronic Bloch band states, as obtained from relativistic LDA or Hartree–Fock (HF) problem, \( (\alpha, \alpha') \) are the bi–spinor arguments, and \( \tau \) is Matsubara’s time. Thus, in the coordinate–space representation, Green’s function is generally \( 4 \times 4 \) matrix for every \( \mathbf{r}, \mathbf{r}' \) pair.

Inside the muffin–tin (MT) spheres the Bloch states can conveniently be represented as linear combinations of 4–component solutions \( \varphi_{LE}^{\dagger}(\alpha \mathbf{r}) \) of radial Dirac equation taken with the spherical symmetric part of Hamiltonian inside the sphere
\[ \Psi_k^t(\alpha r)|_t = \sum_{LE} Z_{tLE}^k \varphi_{LE}^{t}(\alpha r), \quad (2) \]

where \( t \) is the specific atom in the unit cell, \( L \) combines all spin–angular quantum numbers, and index \( E \) differs between \( \varphi, \dot{\varphi} \), and local orbitals. Coefficients \( Z_{tLE}^k \) ensure the smooth mapping between the muffin–tin spheres and the interstitial region as it is standardly done in the linear augmented plane wave (LAPW) method.

In the interstitial region we neglect by relativistic effects, i.e. we assume the small components to be zero and represent the large components of Bloch states as linear combinations of two–component spinors

\[ \Psi_{\lambda}^k(\alpha r)|_{Int} = \frac{1}{\sqrt{\Omega_0}} \sum_{Gs} A_{Gs}^{k\lambda} u_s(\alpha) e^{i(k+G)r}, \quad (3) \]

where \( G \) runs over reciprocal lattice vectors; \( s \) is spin index, \( \Omega_0 \) is the unit cell volume, \( u_s(\alpha) \) is a two–component spin function, and \( A_{Gs}^{k\lambda} \) are the variational coefficients in the LDA eigenvalue problem. We keep the same bi–spinor argument \( \alpha \) here with understanding that two of four components at every \( r \) point in the interstitial region are approximated to zero. Such an approximation greatly reduces computational time for GW but is still well justified because relativistic effects are mostly confined near the nuclei. We have checked the quality of this approximation by performing LDA calculations with and without relativistic treatment of the interstitial region, and the differences appear to be very small.

In our implementation of the GW method we have taken an advantage of the well known fact that polarizability and self–energy in Hedin’s GW system of equations are most easily evaluated in \((r; \tau)\)–representation while the equations for Green’s function and screened Coulomb interaction are most easily solved in \((k; \omega/\nu)\)–representation where \( \omega/\nu \) denote fermionic/bosonic Matsubara’s frequencies. So, in our approach we switch from one representation to another using Fast Fourier Transform (FFT) algorithm whenever needed.

Below we give the most important formulae as they appear in the course of one loop of the self–consistency. The expressions (2) and (3) allow us to express \( G(\alpha r, \alpha' r'; \tau) \) for both \( r \) and \( r' \) being inside the MT spheres as follows (due to the symmetry of the solid we can restrict \( r \) to be inside the unit cell with \( R = 0 \) whereas \( r' \) may be inside the unit cell with \( R' \neq 0 \)).
Here \( \mathbf{r} \) is inside of atom \( t \) in the central unit cell, \( \mathbf{r}' \) is inside of atom \( t' \) in the unit cell \( \mathbf{R}' \), and the number of different \( \mathbf{R}' \) is exactly equal to the number of \( \mathbf{k} \)-points inside the Brillouin zone.

In case when both \( \mathbf{r} \) and \( \mathbf{r}' \) are in the interstitial region we have three different representations for Green’s function: i) numerical values on regular mesh \( G(\alpha \mathbf{r}, \alpha' \mathbf{r}'; \tau) \), ii) band states representation \( G^{\mathbf{k}}_{\lambda, \lambda'}(\tau) \) which follows from (1), and iii) representation in terms of plane waves

\[
G^{\mathbf{R}'}(\alpha \mathbf{r}, \alpha' \mathbf{r}'; \tau) = \frac{1}{N_k} \sum_k e^{-i\mathbf{k} \cdot \mathbf{R}'} \times \sum_{sG:s'G'} e^{i(\mathbf{k} + \mathbf{G}) \cdot \mathbf{r}} u_s(\alpha) G^{\mathbf{k}}_{sG:s'G'}(\tau) u_{s'}(\alpha') e^{-i(\mathbf{k} + \mathbf{G}) \cdot \mathbf{r}'},
\]

We can easily transform between the representations i) and iii) using FFT while the representation ii) is connected to iii) by the formula [3]. Finally, when one of the arguments (say \( \mathbf{r} \)) is inside the MT space and another one belongs to the interstitial region the representations for Green’s function are obtained as obvious combinations of the formulae above.

We begin our GW self–consistent cycle by transforming Green’s function from \((\mathbf{k}, \tau)\)–representation to the real–space. Then we calculate the polarizability in \((\mathbf{r}, \tau)\)-variables. For the \( \mathbf{r}, \mathbf{r}' \) pair of indexes within the MT spheres we have the following expression

\[
P^{\mathbf{R}'}_{tLK;L'K'}(\tau) = \\
- \sum_{E_1L_1 E_2L_2} \sum_{A} \langle M^\mathbf{t}_{LK} \psi^\mathbf{t}_{E_1L_3}(\alpha) | \psi^\mathbf{t}_{E_1L_1}(\alpha) \rangle \\
\times \sum_{E_2L_1} G^{\mathbf{R}'}_{tE_1L_1;E_2L_1}(\tau) \sum_{E_4L_4} G^{\mathbf{R}'}_{tE_3L_3;E_4L_4}(\beta - \tau) \\
\times \sum_{\alpha'} \langle \psi^\mathbf{t}_{E_2L_2}(\alpha') | \psi^\mathbf{t}_{E_4L_4}(\alpha') M^\mathbf{t}_{L;L'}(\alpha') \rangle,
\]

where indexes \( k \) and \( k' \) distinguish bosonic basis functions \( M^\mathbf{t}_{LK} \) (product basis functions which are scalars in bi–spinor space) with the same angular symmetry and we have omitted
argument $r$ of all functions in the integrands. For the MT–interstitial and interstitial–interstitial combinations of $r,r'$ we obtain:

\[
P^{R'}_{tLk}(\tau) = - \sum_{E_1 L_1} \sum_{E_2 L_2} \sum_{\alpha} \langle M^t_{Lk} \varphi^t_{E_2 L_2}(\alpha) | \varphi^t_{E_1 L_1}(\alpha) \rangle 
\times \sum_{\alpha'} G^{R'}_{tE_1 L_1; \alpha' r'}(\tau) G^{r_r' R'}_{tE_2 L_2; \alpha' r'}(\beta - \tau).
\]

(7)

\[
P^{R'}_{r r'}(\tau) = - \sum_{\alpha \alpha'} G^{R'}_{\alpha r \alpha' r'}(\tau) G^{r_r' R'}_{\alpha' r}(\beta - \tau).
\]

(8)

Having calculated the polarizability we transform it to the reciprocal $q$–space and boson–frequency $\nu$–representation, which schematically is given as

\[
P^{R'}_{r r'}(\tau) \rightarrow P^{q}_{ij}(\nu),
\]

(9)

where indexes $i$ and $j$ refer to the product basis functions. Transformation (9) is performed similar to the Green’s function which was specified earlier.

After that, we calculate the screened Coulomb interaction $W$. It is convenient to divide $W$ into the bare Coulomb interaction $V$ and the screening part $\widetilde{W}$:

\[
W^{q}_{ij}(\nu) = V^{q}_{ij} + \widetilde{W}^{q}_{ij}(\nu).
\]

(10)

In the $(q, \nu)$–representation we have to solve the following linear equation system for $\widetilde{W}$:

\[
\sum_k \left\{ \delta_{ik} - \sum_l V^{q}_{il} P^{q}_{lk}(\nu) \right\} \widetilde{W}^{q}_{kj}(\nu) = \sum_k V^{q}_{ik} \sum_l P^{q}_{kl}(\nu) V^{q}_{lj}.
\]

(11)

Having found it, we switch back from $\nu$–representation for $\widetilde{W}$ to $\tau$–representation and from $q$ space to $r$ space.

Next we find the self–energy. This is subdivided onto three steps: i) we solve an effective Hartree–Fock band structure problem which is similar to the familiar Hartree–Fock problem but with matrix elements of Hartree and exchange interaction calculated using full GW Green’s function from the previous iteration. To speed up the process, we calculate exchange interaction in real space and then transform it to the reciprocal space and band
representation. The solution of the effective Hartree–Fock problem gives us a new exchange part of the Green’s function $G^x$. In step ii) we calculate the correlated part of the self energy $\Sigma^c$ in $(\mathbf{r}, \tau)$–representation. Again there are three different cases depending on where $\mathbf{r}$ and $\mathbf{r}'$ belong to:

$$
\Sigma^{c, \mathbf{R}}_{tE_1L_1; t'E_2L_2}(\tau) = - \sum_{E_3L_3} \sum_{E_4L_4} \sum_{kLk' L'} \sum_{\alpha} \langle \varphi_{E_1L_1}^t(\alpha) | \varphi_{E_3L_3}^t(\alpha) M_{kL}^t \rangle \\
\times G_{tE_1L_1; t'E_4L_4}(\tau) \tilde{W}_{\mathbf{R}}^{R'}_{tkL, t'k' L'}(\beta - \tau) \\
\times \sum_{\alpha'} \langle \varphi_{E_4L_4}^t(\alpha') | \varphi_{E_2L_2}^t(\alpha') M_{k'L'}^t \rangle,
$$

(12)

$$
\Sigma^{c, \mathbf{R}}_{tE_1L_1; \alpha' \mathbf{r}'}(\tau) = - \sum_{E_2L_2} \sum_{kL} \sum_{\alpha} \langle \varphi_{E_1L_1}^t(\alpha) | \varphi_{E_2L_2}^t(\alpha) M_{kL}^t \rangle \\
\times G_{tE_1L_1; \alpha' \mathbf{r}'}(\tau) \tilde{W}_{kkL, r'}^{R'}(\beta - \tau),
$$

(13)

$$
\Sigma^{c, \mathbf{R}}_{\alpha \alpha' \mathbf{r}'} = - G_{\alpha \alpha' \mathbf{r}'}(\tau) \tilde{W}_{\mathbf{r} \mathbf{r}'}^{R'}(\beta - \tau),
$$

(14)

In iii) we transform the self–energy back to the band representation in $\mathbf{k}$–space, using the formulae similar to Green’s function. We also transform it from $\tau$ to Matsubara’s $\omega$–frequency.

The last part is to solve Dyson’s equation in order to find new correlated part of the Green’s function $G^c$. We perform this step using band representation in $\mathbf{k}$–space:

$$
\sum_{\lambda \lambda'} \{ \delta_{\lambda \lambda'} - G^e_{\lambda}(\mathbf{k}; \omega) \Sigma^{c}_{\lambda \lambda'}(\mathbf{k}; \omega) \} G^c_{\lambda' \lambda}(\mathbf{k}; \omega) = G^e_{\lambda}(\mathbf{k}; \omega) \Sigma^{c}_{\lambda \lambda'}(\mathbf{k}; \omega) G^e_{\lambda'}(\mathbf{k}; \omega).
$$

(15)
mention that we completely avoid convolutions in $k$–space, which saves a lot of computer
time as compared to pure $k$–space implementation.

We can also perform quasiparticle self–consistent calculations. Different from the QP-
quasGW method by Kotani et al.\textsuperscript{6}), our method is based exclusively on imaginary axis data:
We approximate frequency dependence of the self–energy by a linear function near zero
Matsubara’s frequency and reduce the problem to the solution of Dyson’s equation to one
matrix diagonalization. Then, as justified in [Ref.6] we neglect by $Z$–renormalization of
Green’s function and use it as an input for the new self–consistent iteration.

To get single–particle densities of states (DOS) from the full self–consistent GW approx-
imation we perform similar linear approximation to the self–energy and compute spectra
as the final step after the self–consistency is reached. For the low energy behavior of the
spectral functions this kind of analytical continuation is a lot more stable and produces
essentially the same DOS as the traditional Pade approximation.

III. DETAILS OF CALCULATIONS

Parameters of our calculations are as follows: We use mesh $7 \times 7 \times 7$ in the Brillouin zone.
Green’s function was expanded over Bloch states obtained from LDA based full potential
LAPW band structures. The number of bands in this expansion varies between 142 and
168 depending on the $k$–point in the Brillouin zone. Note that such large number of states
is only possible only when using real–space based implementation of the GW method while
using reciprocal space, it is very hard to handle more than 40–50 bands in the LAPW based
GW method.

Inside the MT spheres we expand the functions of fermionic type (Green’s function and
self–energy) in spherical harmonics up to $l_{\text{max}} = 5$. Bosonic functions (polarizability and
interaction) are expanded up to $l_{\text{max}} = 6$. In the interstitial region each function is expanded
in plane waves. We use more plane waves for bosonic functions (250–300) than for fermionic
ones. Our full basis size to expand bosonic functions both inside the MT spheres and in the
interstitials is about 600 depending on the particular $k$–point.

All calculations are performed for the temperature 1000K. The LDA calculations use
exchange–correlation parametrization after Perdew and Wang\textsuperscript{54}. 

TABLE I: $5f$ occupation numbers for $\delta$–Pu (taken at the volume of its $\delta$–phase) obtained within scalar relativistic (SR) and fully relativstic (FR) approaches.

| Method | $5f_{5/2}$ | $5f_{7/2}$ | $5f_{5/2} + 5f_{7/2}$ |
|--------|------------|------------|----------------------|
| LDA, SR| 5.17       |            |                      |
| LDA, FR| 4.15 0.92  | 5.07       |                      |
| GW, SR | 4.82       |            |                      |
| QP, FR | 4.26 0.56  | 4.84       |                      |
| GW, FR | 4.45 0.44  | 4.89       |                      |

TABLE II: $5f$ occupation numbers for $\delta$–Pu (taken at the volume of its $\alpha$–phase) obtained using fully relativstic (FR) approach.

| Method | $5f_{5/2}$ | $5f_{7/2}$ | $5f_{5/2} + 5f_{7/2}$ |
|--------|------------|------------|----------------------|
| LDA, FR| 3.72 1.38  | 5.10       |                      |
| GW, FR | 4.05 0.81  | 4.86       |                      |

IV. RESULTS

We first discuss our results obtained by various methods for the number of $5f$ electrons, $n_{5f}$, as given in Tables I, II, and III. As follows from experiment, the $5f$ occupation in Pu is close to 5, and the corresponding occupation in Am is close to 6. Our scalar–relativistic GW result (4.82) is very close to the value 4.85 obtained in the calculation performed by

TABLE III: $5f$ occupation numbers for fcc–Americium obtained using fully relativstic (FR) approach.

| Method | $5f_{5/2}$ | $5f_{7/2}$ | $5f_{5/2} + 5f_{7/2}$ |
|--------|------------|------------|----------------------|
| LDA, FR| 5.36 0.84  | 6.2        |                      |
| QP, FR | 5.66 0.26  | 5.92       |                      |
| GW, FR | 5.67 0.27  | 5.94       |                      |
FIG. 1: (Color online) Total density of states (DOS) of δ–Plutonium as obtained in self consistent relativistic calculations. Comparison is made between GW, QP, and LDA approaches.

FIG. 2: (Color online) Total density of states (DOS) of Americium as obtained in self consistent relativistic calculations. Comparison is made between GW, QP, and LDA approaches.

Chantis et al. As it is seen from the calculated data our GW results are consistently less than the experimental ones, which may be attributed in part to the fact that we count $5f$ electrons only inside the MT spheres. In this respect, the LDA results, which are a little too large, look less consistent with experiment. There is also a noticeable difference between LDA and GW in the separation of $n_{5f}$ onto $5f_{5/2}$ and $5f_{7/2}$ contributions where the GW approximation produces more $5f_{5/2}$ electrons and less $5f_{7/2}$ electrons. An interesting trend is seen when one looks at the volume dependence of $5f$ counts for Plutonium (Tables I and III). Full $5f$ occupation is amazingly unchanged but the distribution between $5f_{5/2}$ and $5f_{7/2}$ states changes a lot.
We next describe our calculated total densities of states (DOS) (Figures 1-4) and partial densities of states (PDOS) (Figures 5-8). In all plots chemical potential is set to zero. For δ–Pu (Fig. 1) we notice that the occupied part of the spectrum as obtained using GW, LDA, or QP is practically indistinguishable while the unoccupied part is different. Here, the GW method spreads the spectrum over a wide energy interval while the LDA produces features mostly near the Fermi level.

The spectrum of Americium (Fig. 2) shows no similarity between different methods even for the occupied part of the DOS. Here we clearly see the advantage of using the GW method which gives the lowest position of the peak at minus 2 eV in much better agreement with the experimental value\textsuperscript{59} (minus 2.8 eV) than the LDA or QP approaches do. The unoccupied part of the spectrum gets progressively wider when we go from LDA to QP and then to full GW calculation.

Calculated electronic structure of δ–Pu at a reduced volume, corresponding to the volume of α–phase (Fig. 3) in general shows broader features than the one obtained for the δ–Pu volume. The difference between LDA and GW calculations seems to be reduced.

The DOS of δ–Pu as obtained in scalar–relativistic calculation (Fig. 4) differs on a qualitative level from the relativistic result, therefore, it is quite clear that any serious calculation for this element should take into account spin–orbit interaction.

PDOS from all calculations performed in our work tell us that 5f states in Pu and Am
FIG. 4: (Color online) Total density of states (DOS) of $\delta$–Plutonium as obtained in self–consistent scalar–relativistic calculations. Comparison is made between GW and LDA approaches.

FIG. 5: (Color online) Partial densities of states (PDOS) for Plutonium (taken at the volume of its $\delta$–phase) as obtained in self–consistent relativistic GW calculation.

play a key role in energy region close to the Fermi level. We see the increase in hybridization between $5f_{5/2}$ and $5f_{7/2}$ states when we go from $\delta$–Pu (Fig.5) to $\alpha$–Pu (Fig.6), and we see practically perfect separation between these states in Americium metal (Fig.7).

The difference between QP and self–consistent GW electronic structures becomes more clear when we consider the quasiparticle renormalization factor $Z$ (Fig.9 and 10). We calculate $Z$ factor in band representation according to

$$Z_{\lambda\lambda'}^k = \left(1 - \frac{\partial \Sigma^k(\omega)}{\partial \omega}\right)^{-1}_{\lambda\lambda'}|_{\omega \to 0}.$$  \hfill (16)
FIG. 6: (Color online) Partial densities of states (PDOS) for Plutonium (taken at the volume of its α–phase) as obtained in self–consistent relativstic GW calculation.

FIG. 7: (Color online) Partial densities of states (PDOS) for Americium as obtained in self–consistent relativstic GW calculation

In our case, the indexes ($\lambda, \lambda'$) correspond to the effective Hartree–Fock band structure problem where Hartree and exchange interactions are calculated using full GW Green’s function. The more Z differs from 1 the stronger DOS differs from the effective Hartree–Fock band structure which usually has too broad spectral features. On Fig.9 and 10 we have plotted the diagonal components of Z factor matrices as functions of the band index for 80 lowest bands for the $k = (0,0,0)$ point of the Brillouin zone. In all cases the position of the Fermi level is between band 16 and band 17. Actually there are 6 distinguishable bands ($5f_{5/2}$) below $E_f$ and 8 bands ($5f_{7/2}$) above $E_f$ which have noticeably smaller Z’s than the rest of the spectrum. It is also clearly seen that Z’s for the $f$–bands in the QP
FIG. 8: (Color online) Partial densities of states (PDOS) for δ–Plutonium as obtained in self-consistent scalar–relativistic GW calculation.

FIG. 9: (Color online) Band renormalization factor $Z$ as a function of band index for fcc–Plutonium (taken at volumes of α– and δ–phases) and for fcc–Americium as obtained in self–consistent relativistic GW calculations for $\mathbf{k} = (0,0,0)$.

calculation ($0.55 \div 0.6$) are smaller than those obtained in the self–consistent GW calculation ($0.65 \div 0.75$). This explains why spectral features in the QP electronic structure are closer to the $E_f$. One can say that in case of Am and Pu the QP approximation looks like being overscreened similar to the LDA.

In conclusion, we have described our implementation of the relativistic self–consistent GW method and its application to the electronic structure for Plutonium and Americium metals. We have found that the inclusion of relativistic effects in GW is extremely important for the proper treatment of the actinides. We also discussed the differences in spectral
FIG. 10: (Color online) Band renormalization factor $Z$ as a function of band index for fcc–Plutonium (taken at volume of the $\delta$–phase) and for fcc–Americium as obtained in self–consistent relativistic QP calculations for $\mathbf{k} = (0, 0, 0)$.

functions obtained using the present approach with LDA and quasiparticle self–consistent GW approximations.

ACKNOWLEDGEMENTS

This work was supported by the United States Department of Energy Nuclear Energy University Program, Contract No. 00088708. We would like to thank V. Oudovenko for adapting our GW code to a computer cluster at Rutgers University.

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