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The effect of exact calculation of exchange interaction upon calculated electronic structure of actinides

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Abstract

An account is given on the results of quantum-mechanical calculations of electronic structure for delta-plutonium and americium within relativistic Hartree–Fock approach. The comparison with the results obtained within density functional theory is presented. Based upon this work, one can say that a correct description of both screening and dynamical correlation effects is important for the detail analysis of electronic structure of actinides.

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Beginning with 1960s, density functional theory (DFT) has been a principal instrument for modelling the structural, electronic and magnetic properties of crystalline solids. Undisputable advantage of this scheme in its local approximation (LDA) or in generalized gradient approximation (GGA) is a comparative simplicity of the theory and low requirements to calculational resources. The epochal works by Kohn, Sham, and Hohenberg [1,2], also favored to the popularity of DFT. It was proved in these works that the true functional of DFT attains its minimum at the distribution of the electronic density corresponding to the ground state of the system. However, the functional, going much further than LDA, has not been found. At the same time a number of solids have been discovered (first of all these are the elements with partially filled d- or f-shells and their compounds), the properties of which appeared to be not describable within LDA.

First applications of DFT to the actinides [3,4], were concerned primarily with structural properties and seemed to be relatively successful. However, followed them more detailed investigations into electronic and magnetic structure [5,6], have shown a number of inconsistences in LDA-based results. For example, the equilibrium volume of δ-Pu was obtained in calculations only with spin-polarization included. It yielded in the magnetic moments in plutonium which, however, have not been found in this metal, despite the careful analysis [7]. It is evident, that the approximation for exchange-correlation energy, which is calculated in LDA via the formulas from the interacting electron gas theory, allows us to describe with comparative success some integral characteristics (like the dependence of total energy on volume), but it fails completely when one tries to apply it for thorough analysis.

At the same time and in parallel with DFT, the strict many-body approach has been developing. This approach, the foundation of which was given by Hedin [8], is based on the one-particle Green's function formalism. Up to very recently, the applications of many-body theory to the real materials were prohibited by their high requirements to computer power. However, great improvements in computer capabilities during last decade have made the applications realistic. The dynamical mean field theory (DMFT) [9], greatly elaborated by many scientists and which seems to be capable (at least in principle) to describe strong one-site correlations, have also favored to the interest in many-body theories. One believes DMFT explains (at least qualitatively) the problem of electronic and magnetic structure in plutonium [10]. At the same time, it needs to be mentioned that all up to present day applications of DMFT were based upon LDA + U Hamiltonian (the combination of LDA and Hubbard model)instead of true multi-electron Hamiltonian of the system. Thus, all disadvantages of LDA + U approach (such as obvious non-first-principleness and the problem of double counting of f-f interaction) are passed automatically to DMFT. Besides, the

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magnetic moments in Pu disappear already in LDA + U calculations [11,12], and the role of DMFT in their diminishing is not clear. So, it is evident, that the developing of true ab initio many-body approaches, which are not based on model parameters, is very desirable.

The strict, i.e. non screened, Hartree–Fock (HF) method can be considered in this respect as a first step, because many technical components which are needed for many-body calculations are presented already in HF approach (HFA). HF-based calculations are useful at least due to their capability to say us directly something about the importance of correlation in the material, because HF approach by definition treats everything but correlation exactly while the correlation is completely missed in it.

In the present work the new developed code realizing the relativistic Hartree–Fock method (Dirac–Hartree–Fock) has been applied to study the electronic structure of fcc plutonium and americium at their experimental equilibrium volumes. Full potential linear method of muffin-tin orbitals (FPLMTO) has been used for numerical solution of HF equations. The Methfessel's idea [13], of interpolation and integrating in interstitial region has been applied also for calculating the exchange integrals. For the purposes of comparison, GGA calculations have been performed within the same computer code.

The unscreened exchange in HFA leads to strongly localized 5f states in Pu and Am. This fact appeared to be a reason that the final self-consistent configuration was found to be dependant on the initial one. However inconvenient it is, this circumstance is useful when one wants to study the configurational energy differences. In the present work the configuration $5f^5$ ($M_S = 1.7\mu_B$, $M_L = -3.9\mu_B$) has been found to be the HF ground state for δ-Pu. It bears some resemblance with GGA $5f^{5.3}$ configuration ($M_S = 4.5\mu_B$, $M_L = -2.0\mu_B$) obtained with the same computer code, but strongly contradicts with the recent LDA + U results (nonmagnetic $5f^{5.4}$ [11], or $5f^6$ [12]). Another magnetic $5f^5$ configuration ($M_S = 5.1\mu_B$, $M_L = -4.5\mu_B$) appeared to be 10 mRy higher in energy, which can be within the numerical uncertainty of the method. The energy of nonmagnetic $5f^6$ configuration has been found to be 80 mRy higher. For Am all calculations have converged to $5f^6$ configuration. The ground state appeared to be magnetic ($M_S = 6.2\mu_B$, $M_L = -4.0\mu_B$) and the energy of nonmagnetic $5f^6$ was found to be 50 mRy higher.

The DOSs obtained for the ground state configurations are presented in Fig. 1. As it can be seen, the electronic structure of the above mentioned actinides calculated within HFA appears to have little common with the electronic structure cal-

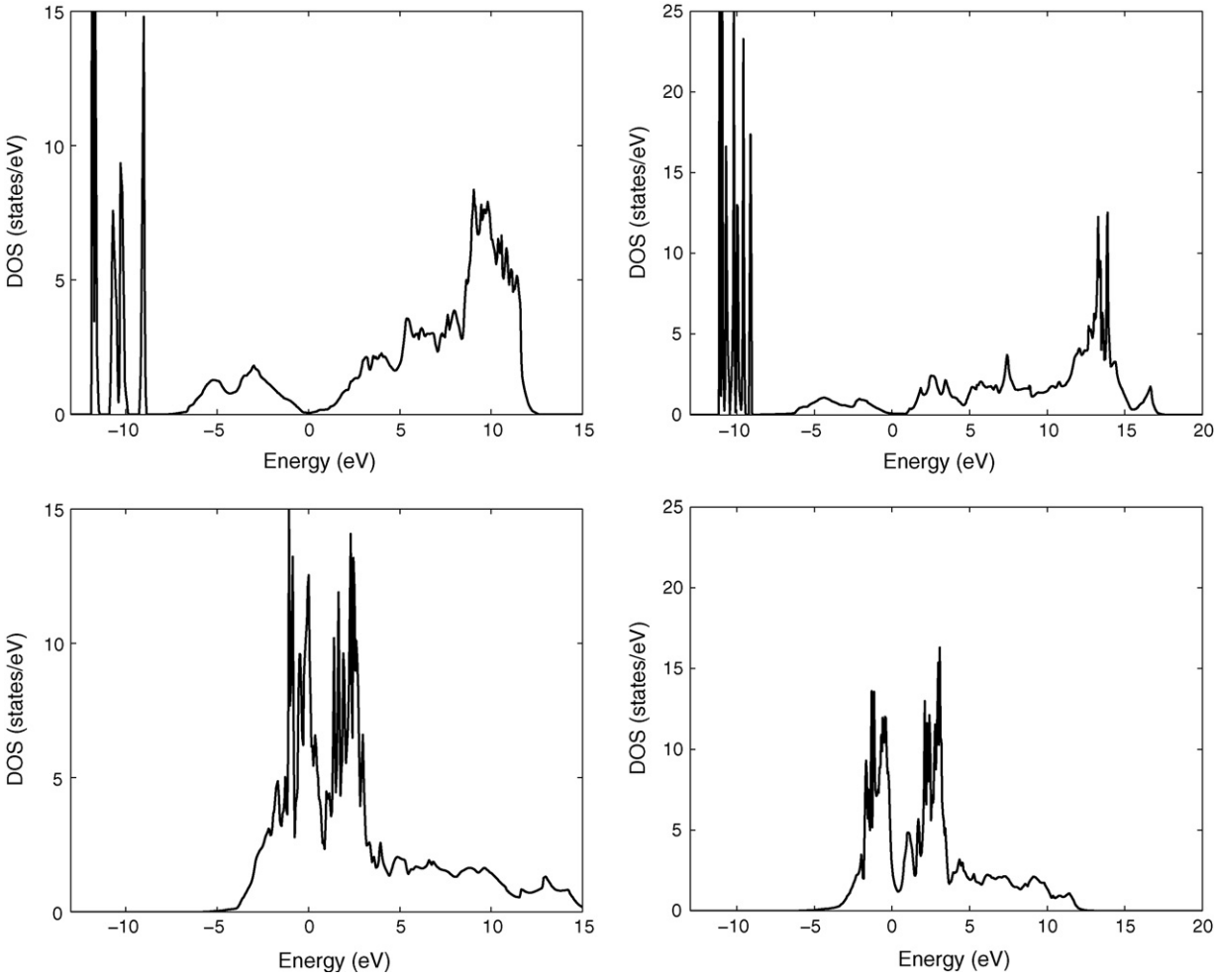

Fig. 1. Total densities of states (DOS) for delta-plutonium (left column) and americium (right column). In the upper row of pictures the results from HF calculations are presented, in the lower row—from DFT (GGA). Fermi level is placed at zero energy.

culated within density functional theory (in generalized gradient approximation, GGA). Orbital dependence of the potential in HF method leads to a strong splitting between occupied and empty f-bands. It needs to stress also that GGA calculation without correlation (exchange only) gave almost the same DOS as GGA with correlation. Thus, the big difference between HFA and GGA DOS stems mostly from the different description of the exchange, which is exact in HFA but is very simplified in GGA.

Despite the obvious disagreement of HF DOS with experiment (which, however, can be easily explained by absence of screening and other correlation effects in the present Hartree–Fock calculations) the results obtained let us draw some conclusions and they also give rise some questions.

- In view of the fact that Hartree–Fock calculation (i.e. exact treatment of exchange interaction) leads to zero DOS at Fermi level, the experimental peak of DOS at Fermi level can be explained only as coming from dynamical correlation effects. But as it is clear from the presented results the correlation in GGA has nothing common with this peak. It is just some approximations made in exchange treatment which lead to the peak. So, the success of GGA in describing the above peak and obviously connected with it the success in describing the equilibrium properties, can just be attributed to some happy fortuity. Based on these considerations one can ask: Why GGA appears to be so good in describing the equilibrium properties? Also, should we say that formulas from homogeneous gas theory effectively take into account the screening in actinides?
- We have the same magnetic configuration in two different methods (Hartree–Fock and LDA(GGA)), i.e. the issue which contradicts with nonmagnetic one obtained within LDA + U approach. This difference can be explained either by absence of screening in the present Hartree–Fock calculations or by inadequacy of LDA + U Hamiltonian (which clearly is not obtained ab initio) for studying the plutonium electronic structure. Obviously, this question has to be studied further within some approach that describes the screening with minimum of approximations.
- Occurrence of different configurations with close energies (especially in Pu) means that there is a strong configuration interaction in the system. Apparently, this work can serve as some additional evidence of the fact that electronic structure of actinides can be described only within some many-body picture, like DMFT, which is capable to take into account the mixing of configurations. But, applying the DMFT one should be careful, using LDA + U as a starting point (which is common approach presently).

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