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An all-electron LCGTO study of square and hexagonal plutonium monolayers

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Abstract. The linear combinations of Gaussian type orbitals fitting function (LCGTO-FF) method is used to study the electronic and geometrical properties of plutonium monolayers with square and hexagonal symmetry. The effects of several common approximations are examined: (1) scalar-relativity *vs.* full-relativity (*i.e.*, with spin-orbit coupling included); (2) paramagnetic *vs.* spin-polarized; and (3) local-density approximation (LDA) *vs.* generalized- gradient approximation (GGA). The results indicate that spin-orbit coupling has a much stronger effect on the monolayer properties compared to the effects of spin-polarization. In general, the GGA is found to predict a larger lattice constant and a smaller cohesive energy compared to LDA predictions. We also find a significant compression of the monolayers compared to the bulk, contradicting the only other published result on a Pu monolayer. The current result supports the existence of a δ-like surface on α-Pu.

PACS. 71.15.Mb Density functional theory, local density approximation, gradient and other corrections – 71.15.Nc Total energy and cohesive energy calculations

1 Introduction

During the past two decades, considerable theoretical effort has been devoted to studying the electronic and geometric structures and related properties of surfaces to high accuracy. One of the many motivations for this burgeoning effort has been a desire to understand the detailed mechanisms that lead to surface corrosion in the presence of environmental gases; a problem that is not only scientifically and technologically challenging but also environmentally important. Such efforts are particularly important for systems like the actinides for which experimental work is relatively difficult to perform due to material problems and toxidity.

Among the actinides, plutonium is particularly interesting in two respects [1]. First, Pu has, at least, six stable allotropes between room temperature and melting at atmospheric pressure, indicating that the valence electrons can hybridize into a number of complex bonding arrangements. Second, plutonium represents the boundary between the light actinides, Th to Pu, characterized by itinerant $5f$ electron behavior, and the heavy actinides, Am and beyond, characterized by localized $5f$ electron behavior. In fact, the high temperature fcc δ-phase of plutonium exhibits properties that are intermediate between the properties expected for the light and heavy actinides. These unusual aspects of the bonding in bulk Pu are apt to be enhanced at a surface or in a thin layer of Pu adsorbed on a substrate, due to the reduced atomic coordination of a surface atom and the narrow bandwidth of surface states. For this reason, Pu surfaces and films may provide a valuable source of information about the bonding in Pu.

The present work focuses on a theoretical investigation of the simplest possible model for a Pu surface or film, *i.e.*, an isolated monolayer. Although, in general, a metal monolayer provides a rather poor approximation to the one-electron properties of a surface, monolayer calculations can produce useful information about the bonding that is not readily accessible from calculations on thicker slabs or a surface. In particular, the relaxation of an isolated monolayer, relative to its bulk analog, provides an indication of the stress that the remainder of the solid exerts on the outer layer of atoms. It also may provide guidance in selecting substrates to be used for epitaxial deposition of a single monolayer under laboratory conditions.

This investigation has concentrated on square and hexagonal Pu monolayers that correspond to the (100) and (111) surfaces of δ-Pu. Although the monoclinic α-phase of Pu is more stable under ambient conditions, there are advantages to studying δ-like monolayers. First, small amounts of impurities can be used to stabilize δ-Pu at room temperature. Second, grazing-incidence photoemission studies combined with the calculations of Eriksson, *et al.* [2] suggest the existence of a small-moment δ-like

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surface on α-Pu. Finally, it may be possible to study $5f$ localization in a Pu monolayer as a function of lattice spacing through adsorption on a series of carefully selected substrates; in which case, the adsorbed monolayers are more likely to be δ-like than α-like.

2 Results and discussions

The properties of the square and hexagonal Pu monolayers have been determined here with a new relativistic version [3] of the linear combinations of Gaussian type orbitals fitting function (LCGTO-FF) method, as embodied in the program GTOFF [4–6]. This technique is distinguished from other variants of the LCGTO method by its use of two auxiliary GTO basis sets to expand the charge density and the exchange-correlation (XC) integral kernels. The charge fitting function coefficients are determined variationally, by minimizing the error in the Coulomb energy, while the XC coefficients are obtained with a least squares fit. In its non-relativistic form, the LCGTO-FF method is known to yield results that are comparable to results produced by other all-electron, full-potential DFT methods. Unlike many other electronic structure methods, however, the LCGTO-FF method is directly applicable to such diverse systems as isolated clusters of atoms [7], polymers [8], ultra-thin films [4,5], and crystalline solids [6]. Thus, the present calculations do not invoke the repeated slab approximation often required in other methodologies.

The relativistic implementation of the LCGTO-FF method has progressed through several stages over the years. Scalar-relativity was initially implemented [3] in GTOFF using a nuclear- only Douglas-Kroll-Hess transformation [9,10] that neglected relativistic terms involving cross- products of the momentum operator. Subsequently [11], all scalar-relativistic cross product terms, and spin-orbit coupling terms (nuclear-only) have been included in the current fully- relativistic version of GTOFF. This version, however, does not yet allow simultaneous inclusion of spin-polarization and spin-orbit coupling effects. In addition, GTOFF does not calculate orbital moments; a limitation that should be of little consequence here, since previous calculations suggest that orbital polarization has little effect on properties of the Pu monolayers [2].

The overall precision of any LCGTO-FF calculation is, to a large extent, determined by the selection of the three basis sets. In this work, the orbital basis set used for Pu started with a $23s20p15d11f$ uncontracted basis set derived from an atomic basis set [12]. This basis set was contracted into a $17s14p11d7f$ basis with coefficients taken from scalar-relativistic atom calculations using the same DFT models as were used in the film calculations. The basis set was then augmented with an s-type function with an exponent of 0.07, a p_z type function with an exponent of 0.08, and a d-type function with an exponent of 0.12. The charge and XC basis sets were $25s2d$ and $21s2d$, respectively. The two-dimensional Brillouin zones for the hexagonal and square monolayers were sampled on uniform meshes with 19 and 28 irreducible points, respectively. For each calculation, the SCF cycle was iterated until the total energy was stable to within 0.01 mRy.

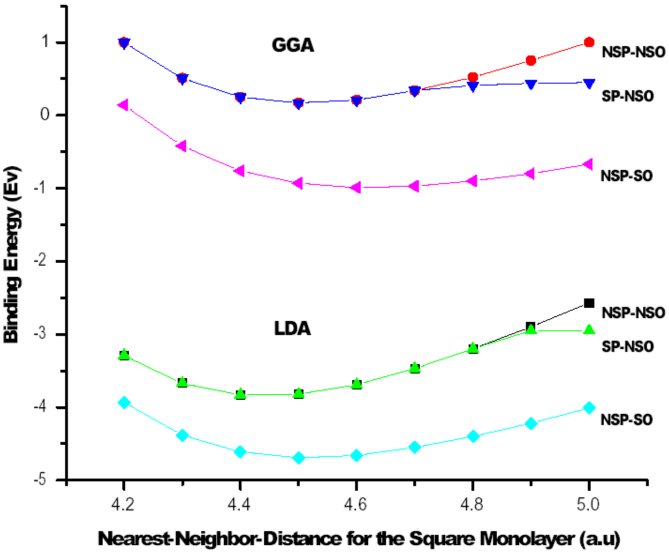

Fig. 1. Binding energy (eV) *vs.* nearest-neighbor-distance (a.u.) for the square monolayer in the generalized-gradient-approximation (GGA) and the local-density-approximation (LDA).

For the Pu monolayers, the effects of several approximations have been studied: (1) scalar-relativity *vs.* full-relativity (*i.e.*, spin-orbit coupling included); (2) paramagnetic *vs.* spin-polarized; and (3) local density approximation (LDA) [13] *vs.* generalized gradient approximation (GGA) [14]. First, non-spin-polarized local-density-approximation (NSP-LDA) and generalized gradient approximation (NSP-GGA) calculations were carried out at both the scalar-relativistic (SR) and fully-relativistic (FR) levels. Spin-polarized (SP) calculations were then carried out for the LDA and GGA models, assuming a ferromagnetic ordering, without spin-orbit coupling. (Recall that simultaneous spin-polarization and spin-orbit coupling is not yet implemented in GTOFF.) For each combination of approximations, total energies, work functions, and spin-moments were calculated on a uniformly spaced mesh of lattice parameters near the energy minimum. For the square monolayer, the lattice constant (nearest neighbor distance) was varied from 4.2 to 5.0 bohr in steps of 0.1 bohr. The lattice constants (nearest neighbor distances) for the hexagonal monolayer were chosen to produce the same unit cell areas as were used for the square monolayer. Binding energies were obtained for each lattice constant by subtracting atomic energies calculated using an orbital basis set formed by augmenting the monolayer basis with several diffuse GTOs. Finally, equilibrium lattice parameters and energy minima were determined by fitting the binding energies to a cubic polynomial. The LDA and GGA binding energy curves for the square and hexagonal monolayers are plotted in Figures 1 and 2, while the spin moments for the two monolayers are given in Figures 3–4. The equilibrium lattice constants,

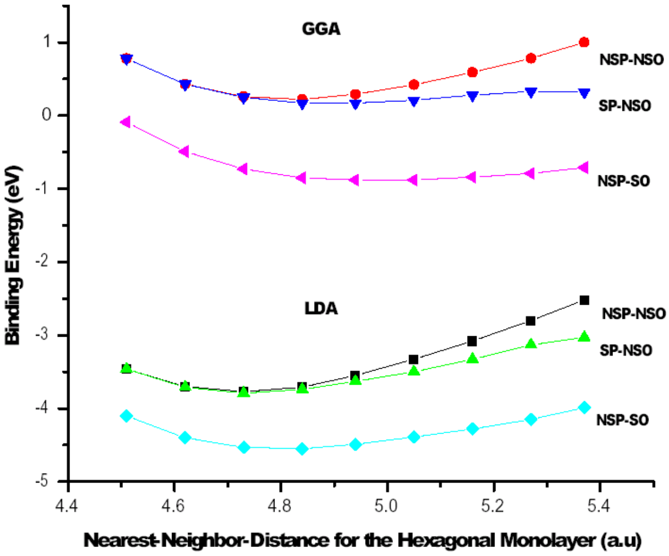

Fig. 2. Binding energy (eV) *vs.* nearest-neighbor-distance (a.u.) for the hexagonal monolayer in the generalized-gradient-approximation (GGA) and the local-density-approximation (LDA).

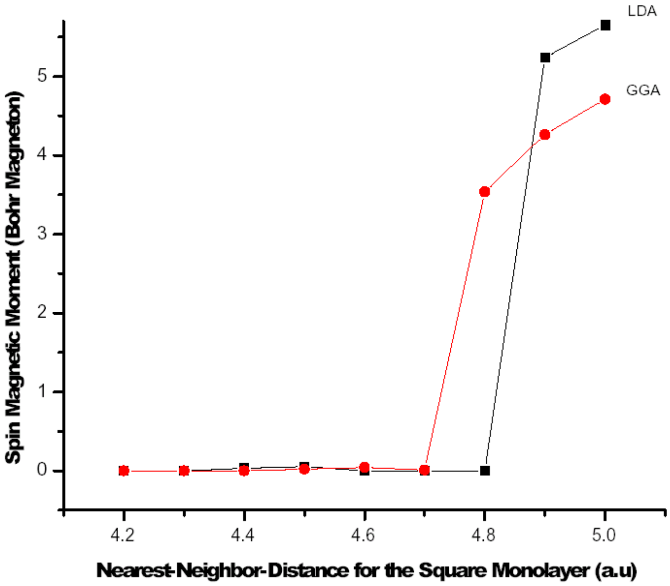

Fig. 3. Spin magnetic moment (Bohr magnetons) *vs.* nearest-neighbor-distance (a.u.) for the square monolayer in the generalized-gradient-approximation (GGA) and the local-density-approximation (LDA).

cohesive energies, and work functions found here are listed in Table 1.

For the square monolayer, spin-polarization does not significantly affect the cohesive energy or the lattice constant regardless of the model, LDA *versus* GGA. This result is due to the rather small lattice constants found here for the square monolayer, which enhance hybridization and inhibit spin-polarization. For the hexagonal monolayer, the effect of spin- polarization on the lattice constant is highly dependent on the model being used, LDA *vs.* GGA. For the LDA, the lattice constant (and cohesive energy) of the hexagonal monolayer is only slightly affected by spin-polarization. For the GGA, however, the hexagonal lattice constant is increased by roughly 1.5 percent. Again, this result can be understood in terms of the effect that the lattice constant has on hybridization. In general, gradient corrections increase lattice

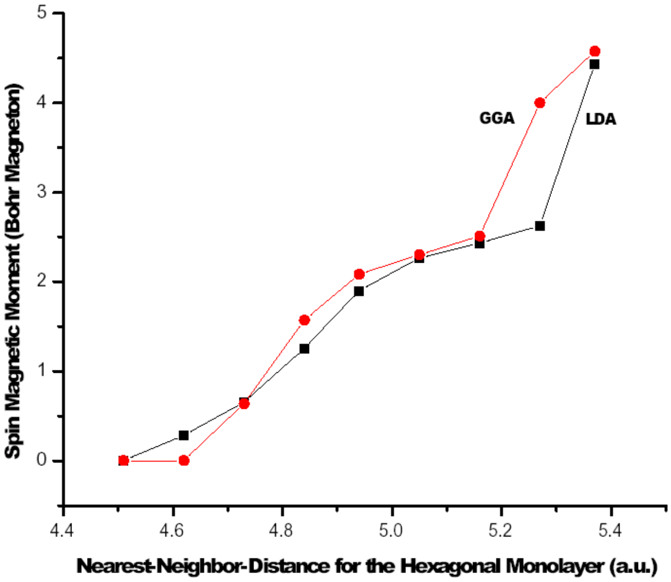

Fig. 4. Spin magnetic moment (Bohr magnetons) *vs.* nearest-neighbor-distance (a.u.) for the hexagonal monolayer in the generalized-gradient-approximation (GGA) and the local-density-approximation (LDA).

Table 1. Equilibrium nearest neighbor distances (bohr), cohesive energies (eV) and work functions (eV) for different levels of theory.

System	Theory	a(a.u)	$E_{\rm coh}$ (eV)	W_f (eV)
Square	LDA(NSP-NSO)	4.44	3.84	4.92
Monolayer	LDA(SP-NSO)	4.44	3.84	4.92
	LDA(NSP-SO)	4.51	4.70	4.87
	GGA(NSP-NSO)	4.51	−0.17	4.41
	GGA(SP-NSO)	4.50	−0.18	4.41
	GGA(NSP-SO)	4.62	0.99	4.36
Hexagonal	LDA(NSP-NSO)	4.73	3.77	4.85
Monolayer	LDA(SP-NSO)	4.73	3.78	4.75
	LDA(NSP-SO)	4.80	4.55	4.71
	GGA(NSP-NSO)	4.82	−0.21	4.74
	GGA(SP-NSO)	4.89	−0.16	4.39
	GGA(NSP-SO)	4.96	0.89	4.28
Pu Metal	LDA(NSP-NSO)	5.40	4.44	
	LDA(NSP-SO)	5.62	5.65	
	GGA(NSP-NSO)	5.56	0.31	
	GGA(NSP-SO)	5.85	1.98	
	Experiment	6.21		

constants, thereby reducing hybridization and favoring spin-polarization. In addition, even for a fixed value of the lattice constant, gradient corrections will tend to enhance spin-polarization.

Spin-orbit coupling, on the other hand, has a significant effect on the cohesive energies and lattice constants of both monolayers, regardless of the model used. For the square monolayer, spin-orbit coupling increases the lattice constant by roughly 1.6 percent using the LDA or 2.4 percent using the GGA. For the hexagonal monolayer, spin-orbit coupling increases the lattice constant by 1.5 percent using the LDA or 2.9 percent using the GGA. In all cases, spin-orbit coupling increases the cohesive energy by several tenths of an eV. In fact, for the GGA model, spin-orbit coupling effects must be included to achieve binding in either monolayer, as is evidenced by the local maxima that appear in the SP-GGA binding energy curves under expansion. It is well known also that, in general, LDA consistently overestimates cohesive energies and we also note that at the scalar-relativistic level, the Pu atom is spin-polarized and that at the fully-relativistic level, it is paramagnetic.

Comparison of the monolayer lattice constants found here with bulk lattice constants obtained at the same levels of theory [11] (Tab. 1) reveals that the monolayers are highly compressed. For the square monolayer, the compression varies from 17.8 to 21.0 percent, depending on the level of theory employed. For the hexagonal monolayer, the compression varies from 12.0 to 15.1 percent. All of these contractions are more than twice as large as the largest contraction found for any alkali-metal or alkaline-earth-metal monolayer using the LCGTO-FF technique; *i.e.*, 4.4 percent for Mg [15]. The anomalously large contractions found here for the Pu monolayers directly contradict the results of Eriksson *et al.* [2], who, using the film linearized muffin-tin orbitals (FLMTO) method, found that the paramagnetic monolayer exhibited a 4.3 percent expansion of the lattice constant. They interpreted this anomalous expansion as being due to a loss in the $5f$ cohesion, associated with the narrowing of the $5f$ partial DOS at the surface. This appears to be the only Pu monolayer calculation reported in the literature, though Hao *et al.* [16] have studied the (111) and (100) surfaces of δ-Pu, using a five-layer slab geometry and the FLMTO method. For the paramagnetic, fully-relativistic square monolayer, Eriksson *et al.* [2] found a lattice constant of 5.61 bohr, substantially larger than the 4.51 bohr found here. For the scalar-relativistic spin-polarized monolayer, Eriksson *et al.* predicted a lattice constant of 5.73 bohr *versus* the 4.44 bohr found in the present study.

The large qualitative difference between the highly compressed monolayer lattice constants found here and the expanded lattice constants obtained by Eriksson *et al.* [2] has important implications for real systems. The present results suggest that the atoms in the outer layers of the (111)- and (100)-surfaces of δ-Pu would compress if it were not for a large opposing stress exerted by the remainder of the solid, whereas the earlier FLMTO results suggest the opposite. Similarly, the current results suggest that it should be possible to grow a thin film of δ-Pu on a substrate whose lattice constant is markedly smaller than that of bulk δ-Pu (such as α-Pu), while the FLMTO results indicate that a better match could be achieved by using a substrate with a slightly larger lattice constant. Thus, the LCGTO-FF results support the existence of a δ-like surface on α-Pu, whereas the FLMTO results do not.

The surprisingly large difference found here between the lattice constants obtained with two different all-electron, full-potential electronic structure methods warrants further discussion. Although the FLMTO method employed by Eriksson *et al.* has been used with considerable success on a number of systems, the overall quality of the results obtained with any method will be largely determined by the selection of the basis set. In their work on the Pu monolayer, Eriksson *et al.* employed a basis set of 16 muffin-tin orbitals (MTO); *i.e.*, the $7s$, $7p$, $6d$, and $5f$ states were each represented by a single MTO. In contrast, more recent work on the bulk actinides has utilized doubled-basis sets that include the semi-core $6s$ and $6p$ states [17]. It seems likely that the large differences between the LCGTO-FF results and the FLMTO results are due to the rather small basis set that was used in the latter work.

It should be noted that it is well-known that traditional electronic structure theory, such as is used here and in the FLMTO calculations, is ill-equipped to describe the highly-correlated $5f$ states of the actinide metals [18]. In addition, there has been a vigorous debate in recent years as to the correct LDA and GGA values for the lattice constants of the light-actinides [11,19–21]. For these reasons, the monolayer lattice constants obtained here should be viewed with some skepticism. This difficulty should not, however, affect the directions and approximate sizes of the shifts in the theoretical lattice constants.

The work functions for the square monolayers vary over a range of 4.36 eV to 4.92 eV, whereas for the hexagonal monolayer, the range is from 4.28 eV to 4.85 eV. The GGA values are always smaller than the corresponding LDA values, with the GGA (NSP-SO) values being the smallest for both monolayers. The work functions are near the values normally found in transition metals (5±1 eV). Here, for the paramagnetic square monolayer, the present value of 4.87 eV at the equilibrium lattice constant of 4.51 bohr is comparable to the FLMTO result of ~5.15 eV at an equilibrium lattice constant of 5.61 bohr [2]. For the scalar-relativistic spin-polarized case, the present work function value is 4.92 eV at the equilibrium lattice constant of 4.44 bohr whereas Eriksson *et al.* found a value of ~4.50 eV at their equilibrium lattice constant of 5.73 bohr. Eriksson *et al.* [2] also found that at a lattice constant corresponding to δ-Pu, the work function from the monolayer calculation was quite close to the value obtained from their five-layer calculation, claiming that their monolayer results may well represent the surface of an extended solid. For the (100) and the (111) faces of Pu, Hao *et al.* [16] estimated the FLMTO work function of Pu to be 3.68 and 4.14 eV, respectively. Given the differences between the lattice constants being considered in the various calculations, the differences in the predicted work functions are not unreasonable.

The spin moments, for the square and hexagonal monolayers respectively, are shown in Figures 3 and 4. For the square monolayer, the spin-moments at the equilibrium lattice constants are found to be nearly zero, regardless of the model used. However, as the lattice constant increases, the spin moments increase significantly, with the transition occurring earlier in the GGA. This might be due to the approximations inherent in GGA and the fact that gradient corrections are expected to be large because of the presence of the f-states. Eriksson *et al.* [2] found a significantly larger value for the spin moment of $\sim 6.0\ \mu_{\mathrm{B}}$ at their equilibrium lattice constant of 5.73 bohr. This discrepancy is most likely due to the large difference between the lattice constants in the two calculations. For the hexagonal monolayer, the spin moments are, in general, larger compared with the spin moments of the square monolayer because of the larger nearest neighbor distance for a given cell area.

In conclusion, we have studied the electronic and geometric properties of a Pu monolayer, using the LCGTO-FF method. Spin-orbit coupling is found to have a stronger effect on the electronic and geometric properties of the plutonium monolayer, square or hexagonal, compared to the effects of spin-polarization. Our results also indicate that the monolayer is significantly compressed compared to the "ideal" monolayer, contradicting the only other published result in the literature.

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