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Importance of full Coulomb interactions for understanding the electronic structure of δ-Pu

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Understanding the electronic structure of materials containing elements from the end of the periodic table represents a challenge due to a complex interplay of a number of physical phenomena occurring in these systems. In the plutonium metal, a fraction of the valence electrons is at the turning point between joining the conduction cloud, which occupies the whole crystal, and staying bound to a particular atom. This delicate boundary can be probed by photoemission experiments. Here we employ a very accurate computational method—the quantum Monte Carlo simulations—to describe the electronic states in the material achieving previously inaccessible resolution. We show that in order to successfully analyze the experimental photoemission spectra, it is essential to include the complete form of the electron-electron interaction into the Schrödinger equation, otherwise the spectral features near the Fermi level are not correctly reproduced.

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The solid-state properties of the most elements are now well understood on the basis of quantum physics—with few exceptions, notably the element number 94, plutonium. Plutonium has six crystalline phases at ambient pressure, some of which are separated by unusual phase transitions with large discontinuities in volume, exhibit negative thermal-expansion coefficients, or form exotic low-symmetry structures.[1,2] The main challenge to explain these anomalous properties is that the characteristic ingredient of actinides, the $5f$ electronic states, are in a crossover regime between the localized and delocalized (itinerant) behavior in Pu.[3,4] The early part of the actinide series with the $5f$ states being itinerant, i.e., part of the metallic bond, culminates with low-temperature (dense) phases of Pu; starting with its high-temperature (expanded) phases, the $5f$ states are localized, nonbonding, and resemble the $4f$ states in lanthanides. Both itinerant and localized regimes are well covered by existing theories, but they cannot be simply interpolated due to the importance of dynamical electron-electron correlations.[5,6]

In the last few years there has been intense research, theoretical as well as experimental, aimed to understand properties of the metallic plutonium. The low-temperature monoclinic α phase is stable up to 395 K while the face-centered-cubic (fcc) δ phase is stable between 593–736 K. The δ-Pu phase, which received a significant interest in the metallurgical community because of its high ductility, is quite different from the brittle ground-state α-Pu phase. For instance, (i) δ-Pu has an atomic volume of about 25% greater than α-Pu; (ii) the thermal expansion of δ-Pu is small and negative whereas it is very large and positive for α-Pu; and (iii) the electronic specific-heat coefficient of δ-Pu is substantially larger than in α-Pu while the magnetic susceptibility stays almost unchanged. For all plutonium phases, local magnetic moments are absent[7] but the Pauli-type magnetic susceptibility and resistivity are an order of magnitude larger than for simple metals.

Strong correlations among electrons in Pu result in a failure to predict the equilibrium volume of nonmagnetic δ-Pu within the conventional local-density approximation (LDA).[8] Attempts to account for f-electron correlations within the LDA+U technique result in a nonmagnetic ground state close to f^6 configuration when the so-called "fully localized" double counting is employed.[9] The use of a different form of the double counting, the "around-the-mean-field" (AMF) expression, results in quenching of the spin and orbital magnetic moments and leads to an admixture of the f^5 and f^6 configurations in the ground state.[10,11] The δ-Pu equilibrium volume is calculated in good agreement with experiment.[9–11] However, this static mean-field approach is not able to reproduce experimental photoemission spectra (PES) of Pu, where a high peak, attributed to the f states, is clearly observed in the vicinity of the Fermi level.[12,13]

The LDA+U technique takes into account only the static part of the self-energy, which is not sufficient to correctly reproduce spectral properties of strongly correlated systems. The full frequency dependence of the self-energy requires improved methods such as dynamical mean-field theory (DMFT) (Ref. 14) that enables treatment of bandlike and atomiclike behavior of electrons on the same footing. The first application of DMFT to Pu was done by Savrasov *et al.*[5] who explained the origin of volume expansion between α and δ phases in terms of competition between Coulomb repulsion and kinetic energy. The authors assumed that Pu has a $5f^5$ configuration with an open $j=5/2$ subshell resulting in a local magnetic moment that is further screened by valence electrons via Kondo mechanism. Although the double minimum on the energy versus volume curve, derived in this paper, provided a possible explanation for the volume collapse that accompanies the $\alpha \rightarrow \delta$ transition in Pu, the calculated density of states (DOS) did not capture the multiplet structure seen in photoemission experiments.[13] Taking into consideration that the DMFT calculations[5] were actually performed only for the fcc lattice, a more realistic interpretation of this double minimum as an origin of the negative thermal expansion (Invar effect) in δ-Pu was presented later.[15]

The nonmagnetic configuration, suggested in the AMF-LDA+U calculations by Shick *et al.*,[10] served as a starting point for several DMFT studies. Pourovskii *et al.*[16] tried to correct the deficiency of the LDA+U density of states by adding dynamical fluctuations by means of DMFT in conjunction with the fluctuating exchange T-matrix technique (T-matrix FLEX).[17] A similar LDA+DMFT approach, but employing the Hubbard-I approximation (HIA) (Ref. 18) for the quantum impurity solver, was used by Shick *et al.*[19] to reproduce the distinct three-peak structure experimentally observed in PES of δ-Pu.[13]

Later, Pourovskii *et al.*[20] were able to reproduce the experimentally observed large increase in the electronic specific-heat coefficient of δ-Pu as compared to the α phase. In this study the T-matrix FLEX method was used for the quantum impurity solver. Shim *et al.*[21] employed a vertex corrected one-crossing approximation for the quantum impurity problem[14] and obtained $5f$ occupancy approximately 5.2 in calculations which also properly included multiplet effects. They concluded that plutonium becomes nonmagnetic due to Kondo screening below about 800 K. Moreover, they also confirmed the suggestion[10,19] that the fractional $5f$ occupancy in δ-Pu arises from a mixture of two different atomic configurations (f^5 and f^6) in the ground state. Finally, Zhu *et al.*[22] used both an exact quantum Monte Carlo (QMC) method within the Hirsch-Fye scheme[14] (for a truncated Coulomb interaction, without multiplet effects) and the Hubbard-I approximation[18] (with multiplet effects) for the quantum impurity solver. They demonstrated sensitivity of the spectral properties of Pu to the $5f$ occupancy and suggested on the basis of comparison to experimental data that the $5f^5$ open-shell configuration was more likely than the closed shell $5f^6$ configuration. Nevertheless, according to Refs. 19, 21, and 22, the three-peak multiplet structure observed in the DOS of bulk δ-Pu metal is induced by nonvanishing admixture of atomic f^6 configuration into the ground state.

Quantum Monte Carlo methods represent an exact tool to solve the quantum impurity problem. There are, however, several issues to be addressed when these methods are applied to systems like δ-Pu. The often employed auxiliary-field Hirsch-Fye QMC algorithm is computationally expensive for multiorbital calculations at low temperature,[14] since the required computer time scales as N_{orb}^2/T^3, where N_{orb} is the number of orbitals on the impurity and T is the temperature. Even more importantly, the Hirsch-Fye algorithm has an inherent limitation on the form of the electron-electron interaction that can be included in the Hamiltonian. Out of the full Coulomb interaction vertex

$$\hat{H}_U^{\text{full}} = \frac{1}{2}\sum_{ijkl\sigma\sigma'} U_{ijkl}\hat{c}^{\dagger}_{i\sigma}\hat{c}^{\dagger}_{j\sigma'}\hat{c}_{l\sigma'}\hat{c}_{k\sigma}$$

only the density-density contributions

$$\hat{H}_U^{\text{dens-dens}} = \frac{1}{2}\sum_{ij\sigma}[U_{ij}\hat{n}_{i\sigma}\hat{n}_{j-\sigma} + (U_{ij}-J_{ij})\hat{n}_{i\sigma}\hat{n}_{j\sigma}]$$

can be treated with this method. The matrix elements of the electron-electron potential $\hat{V}_{\text{ee}}$ that enter the above expressions are defined as $U_{ijkl}=\langle ij|\hat{V}_{\text{ee}}|kl\rangle$, $U_{ij}=\langle ij|\hat{V}_{\text{ee}}|ij\rangle$, and $J_{ij}=\langle ij|\hat{V}_{\text{ee}}|ji\rangle$. The particle-number density operator is $\hat{n}_{i\sigma}=\hat{c}^{\dagger}_{i\sigma}\hat{c}_{i\sigma}$. In the case of the plutonium f shell, the full vertex has 377 nonequivalent terms and only 91 of them have the diagonal density-density form. The remaining nondiagonal part consists of 42 spin-flip terms and 244 integrals of the most general four-index form. These nondiagonal contributions can reduce the effects of large spin-orbital splitting in relativistic density-functional calculations of δ-Pu and produce a multiplet structure near the Fermi level. Notably, T-matrix FLEX, Hubbard-I, and one-crossing approximations used in Refs. 16, 19, 21, and 22 examine the full f-f Coulomb interaction and its consequent term structure so that the Hund's rule exchange is included in these models.

Recently, a new class of continuous-time QMC (CT-QMC) impurity solvers has been developed.[23–25] These diagrammatic QMC approaches rely on a perturbation expansion of the partition function into Feynman diagrams and on resummation of these diagrams into determinants. The weak-coupling method[23] uses a perturbation expansion in the interaction part of the Hamiltonian and its determinantal formulation originates in the Wick's theorem. The strong-coupling or hybridization expansion method[24,25] treats the local interactions exactly and expands in the impurity-bath hybridization; the determinants emerge naturally from the trace over the bath states. Both weak- and strong-coupling CT-QMC methods can treat the full Coulomb interaction vertex and do not suffer from discretization problems inherent to the Hirsch-Fye QMC in the low-temperature regime. Therefore, the CT-QMC formalism has an essential advantage compared to auxiliary-field methods when complex systems like δ-Pu are considered. The application of hybridization expansion CT-QMC to the electronic structure of δ-Pu shows an importance of complete rotationally invariant Coulomb interaction among $5f$ electrons.[26]

In this paper we apply the weak-coupling CT-QMC scheme to investigate effects of full Coulomb interaction on the electronic spectrum of δ-Pu. We start with the relativistic LDA Green's function for the f electrons,[27] which is a 14×14 matrix. The LDA solution is found with the aid of the tight-binding linear muffin-tin orbital method based on the atomic-spheres approximation.[28,29] We take advantage of the rotational invariance of the Coulomb interaction and work in the natural relativistic basis of spherical harmonics in order to avoid the so-called three-orbital terms like $\hat{c}^{\dagger}_{i}\hat{c}^{\dagger}_{j}\hat{c}_{i}\hat{c}_{k}$ that cause a large fermion sign problem in the weak-coupling CT-QMC scheme. In low-temperature simulations, we still encountered a sign problem related to odd numbers of small but negative nondiagonal Coulomb matrix elements. Since these processes were very rare (on the order of 1% of accepted QMC steps) we simply restricted the QMC process to even numbers of nondiagonal Coulomb terms of the general form $\hat{c}^{\dagger}_{i}\hat{c}^{\dagger}_{j}\hat{c}_{l}\hat{c}_{k}$.

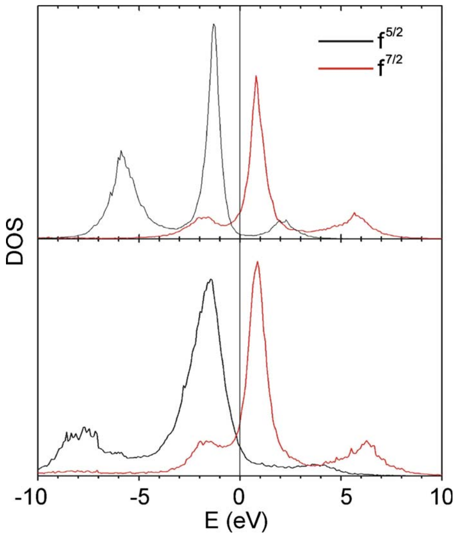

FIG. 1. (Color online) Orbital-resolved spectral function of Pu for high temperature with nondiagonal spin-flip Coulomb vertex (lower panel) and diagonal density-density interaction (upper panel).

We parametrize the matrix U_{ijkl} with the aid of four Slater integrals $F_0=4$ eV, $F_2=8.34$ eV, $F_4=5.57$ eV, and $F_6=4.12$ eV in concord with the general LDA+U scheme.[9–11] The numerical values correspond to the screened average Coulomb integral $U=4$ eV and the exchange interaction parameter $J=0.7$ eV. The CT-QMC simulations are computationally very demanding due to the presence of the full Coulomb vertex, and we therefore perform only a single solution of the impurity problem with the LDA Green's function (the first iteration of the DMFT procedure). In order to increase accuracy of analytical continuation of the CT-QMC data to the real-energy axis, we use a stochastic approach starting directly from Matsubara frequencies and not from the imaginary-time axis.[30]

We investigate first the influence of spin-flip terms in the Coulomb vertex and compare the spectral function of δ-Pu with results of diagonal-only Coulomb vertex for relatively high temperature of about 5000 K (Fig. 1). The main effect of the spin-flip terms is related to much stronger interaction between the $j=5/2$ and $j=7/2$ subbands at the same energy. It is manifested as an increase of the $j=7/2$ signal around -2 eV where the $j=5/2$ component has a strong peak, and as an analogous enhancement of the $j=5/2$ signal around 1 eV. Broadening of the spectral function maxima due to multiplet splitting is observed as well.

The final result for the spectral function of δ-Pu with the full Coulomb vertex at relatively low temperature of approximately 600 K is shown in Fig. 2. The position of the quasiparticle peak near the Fermi level as well as the spin-orbit splitting of the multiplet structure well reproduce the main features of the experimental photoemission spectra.[12,13] Note that a large contribution to the lower Hubbard bands (around -1.7 eV in the Fig. 2) comes from the high energy $j=7/2$ states.

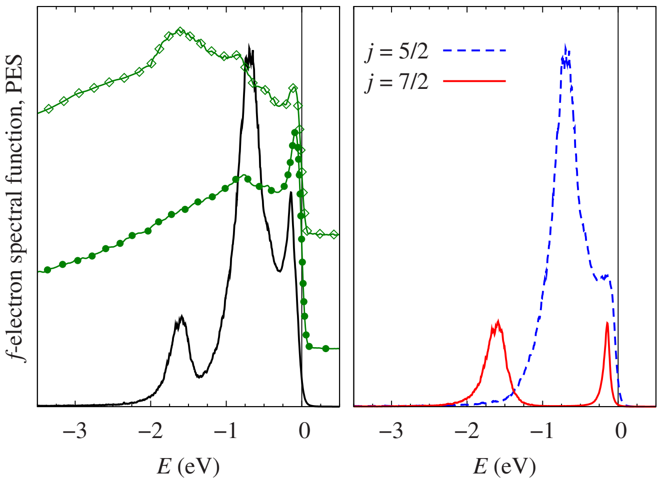

FIG. 2. (Color online) CT-QMC f-electron spectral function (black) in comparison with experimental photoemission spectra of bulk (green line decorated with circles) and surface (green line decorated with diamonds) of δ-Pu (Ref. 13). Right panel shows decomposition of the theoretical curve into orbital contributions.

Since the CT-QMC data presented here are limited to the first iteration toward the complete DMFT solution, it is illustrative to make a comparison with the results of charge-density self-consistent LDA+HIA calculations implemented in the full-potential LAPW basis.[31] This comparison indicates that the essential features of the final solution are captured already in the early stages of the DMFT cycle. For bulk δ-Pu (shown in Fig. 3) we find a reasonable semiquantitative agreement between full-Coulomb vertex calculations within CT-QMC and HIA. There are two $j=5/2$ peaks, one close to the Fermi edge and the other at approximately -1 eV in HIA, which are consistent with two $j=5/2$ peaks shown in Fig. 2. In addition, there is a peak around -0.7 eV of $j=7/2$ character in Fig. 3 that corresponds to the $j=7/2$ peak at -0.2 eV in CT-QMC. Furthermore, an extra $j=7/2$ satellite around -1.7 eV is seen in both the HIA and CT-QMC calculations. The $j=7/2$ structure centered at about 0.5 eV in

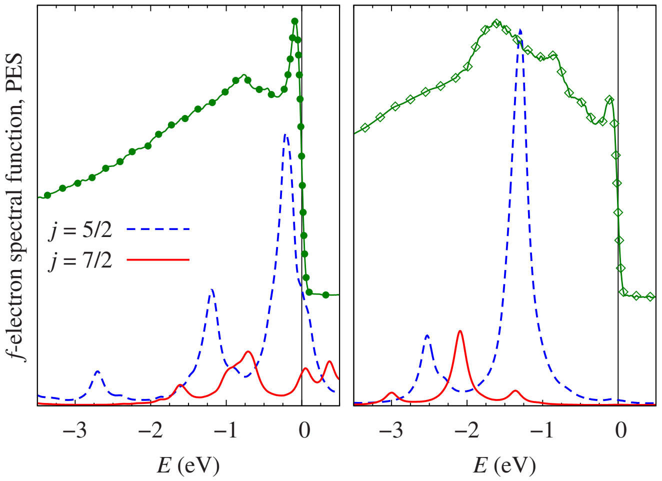

FIG. 3. (Color online) Orbital-resolved spectral function of bulk δ-Pu in the self-consistent Hubbard-I approximation (left panel). The full Coulomb interaction causes strong admixture of high-energy $j=7/2$ and low-energy $j=5/2$ states. Results of the same method applied to the Pu monolayer are shown in the right panel.

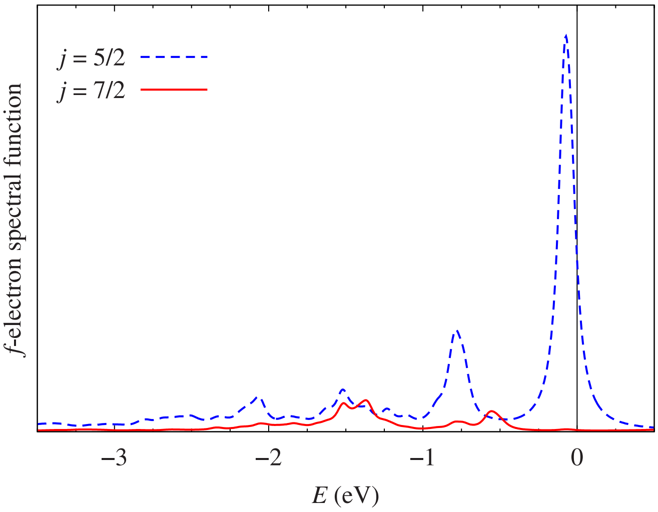

FIG. 4. (Color online) Ground-state ($T=0$ K) spectral function of a plutonium f shell coupled to 12 spinorbitals representing the hybridization function.

the HIA originates from $f^5 \rightarrow f^6$ transitions and lies completely above the Fermi edge with a tail slightly extending to negative energies only due to our use of a 0.06 eV full width at half maximum broadening function. The Hubbard-I spectral function above the Fermi level (not shown) continues to exhibit significant mixing of $j=5/2$ and $j=7/2$ states analogous to Fig. 1 obtained with the CT-QMC method.

One may wonder if the $j=7/2$ satellite at -1.7 eV is related to the experimental peak visible at about the same energy in the photoemission spectrum recorded for a thin film of δ-Pu.[13] To clarify the comparison between the theory and experiment we performed LDA+HIA calculations for a freestanding δ-Pu monolayer. The resulting j-resolved spectral function is shown in Fig. 3. The f-states localization is clearly visible in the monolayer as the f spectral weight is shifted away from the Fermi level. In particular, the main $j=5/2$ peak is now located at -1.6 eV. These calculations therefore suggest that the feature found around -1.6 eV in the experimental photoemission spectrum of a single monolayer has $j=5/2$ and not $j=7/2$ character.

In spite of quite reasonable agreement between CT-QMC and HIA, which supports the atomiclike origin of the observed three peak structure in the photoemission spectrum, one needs to keep in mind that the hybridization between f and conduction electrons is not accounted for very accurately in the Hubbard-I procedure. To examine possible effects of the hybridization more thoroughly, we studied a model consisting of a correlated f shell explicitly coupled to several bath spinorbitals that mimic the hybridization with conduction electrons. We used band-Lanczos algorithm[32] to find the ground state as well as to calculate the one-particle spectral function shown in Fig. 4. We were able to include up to 12 bath spinorbitals in addition to the 14 that represent the f shell, at which point the corresponding many-body Hilbert spaces reached dimensions on the order of 10^7. Arguably, such sparse discretization represents only a rather crude approximation of the actual environment the plutonium f shell experiences in the real solid. Nevertheless, the solution of this model possesses several important properties.

The ground state of the cluster (f shell+bath) is a singlet that explains the absence of local magnetic moments in plutonium.[7] The corresponding f-shell occupation is fractional (approximately 5.4) and even configurations with four and seven f electrons have appreciable weights. We think that the absence of magnetic moment in δ-Pu is a manifestation of a mixed-valence state.[16,21] It is known from the mixed-valence rare-earth systems (Sm and Yb compounds) that if one of the involved atomic configurations is nonmagnetic the whole system is nonmagnetic as well.[33,34] The situation is paradoxical. Despite the fact that the average occupation of the f shell is closer to 5 then to 6, the spectral features near the Fermi threshold (Fig. 4) are dominated by the atomic $f^6 \rightarrow f^5$ transitions. This observation further justifies the interpretation of the photoemission spectral features located near the Fermi edge as atomiclike multiplet transitions.

To conclude we emphasize that the present calculations, employing the *full rotationally invariant* Coulomb interaction, have been able to reproduce the spectral properties of the δ phase of plutonium in agreement with recent photoemission experiments. The large peak of f character in the density of states near the Fermi level as well as the multiplet-like structure with spin-orbital splitting is obtained. The success of the continuous-time quantum Monte Carlo method for a "simple" elemental metal further opens a way for its application to a host of fascinating compounds that challenge condensed-matter theorists.

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