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Many-body electronic structure of metallic α-uranium

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We present results for the electronic structure of α-uranium using a recently developed quasiparticle self-consistent GW (QSGW) method. This is the first time that the f-orbital electron-electron interactions in an actinide have been treated by a first-principles method beyond the level of the generalized gradient approximation (GGA) or the local-density approximation (LDA) to the density-functional theory (DFT). We show that the QSGW approximation predicts an f-level shift upward of about 0.5 eV with respect to the other metallic $s-d$ states and that there is a significant f-band narrowing when compared to LDA band-structure results. We predict a considerable QSGW enhancement of the linear coefficient of specific heat. Nonetheless, because of the overall low f-electron occupation number in uranium, ground-state properties and the occupied band structure around the Fermi energy are not significantly affected. The correlations predominate in the unoccupied part of the f states. This provides the first formal justification for the success of LDA and GGA calculations in describing the ground-state properties of this material.

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It has long been recognized that $5f$ electron-electron correlations play an important role in the light actinides,[1,2] becoming increasingly significant as one moves across this series and the atomic number Z increases. This culminates in Pu, which has many extreme physical properties that are driven by these correlations,[3] such as the large volume expansion for the α to δ phase transformation.[4,5] What is less clear is the role of correlations for Z's less than Pu. Uranium stands at a kind of threshold in this regard. Experimentally, the pure material is weak to moderately correlated,[6] since specific-heat enhancements are moderate and no convincing satellites or Kondo photoemission peaks are observed, which is consistent with the success of band structure in predicting materials' properties.[7,8] At the same time, when the uranium atoms are pushed apart by other elements, they form many heavy fermion and other strongly correlated uranium compounds.[9] In this regard, uranium is an inviting target to study, since it should have interesting correlation effects beyond conventional metals like copper or aluminum, and yet these should be weak enough to have some hope of accurately calculating them. It is thus an important testing ground for correlation theory and how many-body effects correct conventional local-density approximation (LDA) band structures.

The most widely used electronic-structure method, the LDA, has been an immensely successful tool that reasonably predicts ground-state properties of weakly correlated systems. The LDA is much less successful at predicting optical properties of such systems, and its failures become more serious as correlations become stronger. Recent photoemission spectroscopy on high quality uranium single crystals has revealed additional information about the electronic structure of this material.[10,11] Comparison with LDA calculated electronic bands shows some disagreement between experiment and theory. Because of the poor treatment of electron correlations by LDA it is difficult to conclude whether the observed discrepancies between the predicted band structure and photoemission data are due to electronic correlations, even though perhaps weak, or to other effects such as surface states. For the same reason it is not clear how much of the mass enhancement observed in the specific heat[10,12] can be attributed to electron correlations and how much to electron-phonon coupling. To date all first-principles theoretical treatments of the uranium electronic structure have been based on LDA or the generalized gradient approximation (GGA) extension to LDA. Therefore, it is important to explore the electronic structure of uranium with methods that treat more accurately the electron-electron interactions and to understand how they affect the electronic properties of this material.

In Pu, it is now standard to use dynamical mean-field theory (DMFT) to treat the strong correlations that go well beyond conventional band structure.[13–15] However, this has the unsatisfactory aspect that a model Hamiltonian is grafted onto a band-structure approach in an *ad hoc* manner. Because of the much weaker correlations in uranium, it is possible in this material to instead use a more approximate treatment of correlation effects that is completely first principles and yet goes significantly beyond conventional band theory. Thus, in this Rapid Communication we apply for the first time for any actinide a rigorous *ab initio* self-consistent many-body theoretical approach, the GW approximation, and show how electronic correlation effects modify the electronic structure of uranium that is predicted by LDA band theory.

In this work we use the recently developed quasiparticle self-consistent GW (QSGW) version[16–18] of the GW method, which itself can be viewed as the first term in the expansion of the nonlocal energy dependent self-energy $\Sigma(\mathbf{r},\mathbf{r},\omega)$ in the screened Coulomb interaction W. From a more physical point of view the GW approximation can be interpreted as a dynamically screened Hartree-Fock approximation plus a Coulomb hole contribution.[19] Therefore, GW is a well-defined perturbation theory. In its usual implementation, sometimes called the "one-shot" approximation, it depends on one-electron Green's functions based on LDA eigenvalues and eigenfunctions, and the results can depend on this

choice. We have demonstrated[17] that as correlations become stronger serious practical and formal problems can arise in this approximation. In Ref. 16 a formal description is provided on how QSGW is a rigorous way to surmount this difficulty, based on using a self-consistent one-electron Green's function that is derived from the self-energy (the quasiparticle eigenvalues and eigenfunctions) instead of an LDA starting point. In the literature, it is has been demonstrated that the QSGW version of GW theory reliably describes a wide range of *spd* systems[18,20,21] and rare earths.[22] It should be noted that the energy eigenvalues of the QSGW method are the same as the quasiparticle spectra of the GW method (i.e., the peaks in the self-energy). This captures the many-body shifts in the quasiparticle energies. However, when presenting the quasiparticle density of states (DOS) this ignores the smearing by the imaginary part of the self-energy of the spectra due to quasiparticle lifetime effects, which should increase as one moves farther away from the Fermi energy.

The QSGW method is currently implemented using a generalization of the full potential linear muffin-tin orbital (FP-LMTO) method,[23] so we make no approximations for the shape of crystal potential. The smoothed LMTO basis[17] includes orbitals with $l \leq l_{\max}=6$; both $7p$ and $6p$ as well as both $5f$ and $6f$ are included in the basis. $6f$ are added in the form of local orbitals,[17] that is an orbital strictly confined to the augmentation sphere, and has no envelope function at all. $7p$ are added as a kind of extended local orbitals the "head" of which is evaluated at an energy far above Fermi level,[17] instead of making the orbital vanish at the augmentation radius a smooth Hankel "tail" is attached to the orbital. A particularly important point is that core states are treated at the exchange-only level. We have demonstrated in some detail[17,24] that approximating the core by the LDA potential, i.e., computing Σ from the valence electrons only, sometimes leads to significant errors. Since QSGW gives the self-consistent solution at the scalar relativistic level, we add the spin-orbit operator $H_{\mathrm{SO}}=\mathbf{L}\cdot\mathbf{S}/2c^2$ as a perturbation (it is not included in the self-consistency cycle). For our calculations we use the equilibrium crystal structure of α-U, the orthorhombic *Cmcm*, with the uranium atoms located at the $4c$ positions: $(0,y,\frac{1}{4})$ and $(0,-y,\frac{3}{4})$ plus C centering; we use the experimental lattice parameters $a=2.858$ Å, $b=5.876$ Å, $c=4.955$ Å, and $y=0.105$.

In Fig. 1 we compare the calculated QSGW one-particle electronic structure of α-U with the LDA band-structure results. In both cases, the narrow bands located approximately between −1 and +3 eV are mainly due to the uranium $5f$ orbitals; the lowest dispersive bands seen on this plot have s character, and the bands above 3 eV are strongly hybridized. Both methods are roughly in agreement for the total DOS. However, the large DOS peak that is a little above the Fermi energy, E_F, is narrower in width and larger in magnitude for the QSGW calculation; also, the quasiparticle energies only agree well with the LDA band-structure results in the vicinity of E_F. As we move to higher or lower energies (away from E_F) the difference between QSGW and LDA quasiparticle energies gradually increase. Among the occupied states, the metallic $s-d$ bands at the lowest energies experience a significant downward shift relative to the f bands when compared to the LDA results (note that the main part of the p states are believed to lie above E_F, since they are repelled by the $6p$ semicore states that fall below and are well separated from the conduction band; hence only p hybridization tails appear in the occupied conduction-band region). For example, at the Γ point the shift is about 1 eV downward, but more generally, however, the energy shift is somewhat **k** dependent. The partial DOS presented in Fig. 2 shows that after integration over all **k** there is a downward energy shift of about 0.5 eV for the occupied $s-d$ bands.

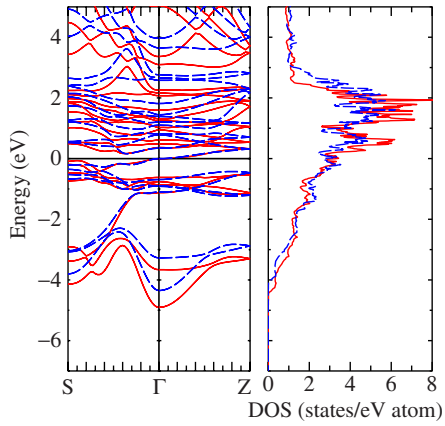

FIG. 1. (Color online) The energy bands (or quasiparticle energies) along two symmetry directions (left panel) and the total DOS (right panel); the QSGW results are represented by solid red/gray lines and the LDA band-structure results by dashed blue/dark gray lines.

In Fig. 2(b) we present the partial DOS for the f bands. One of the important effects of electronic correlation is to narrow the width of a band. This shows up as a narrower f-band width in the QSGW calculation. In addition, since the area under the curve is proportional to the number of f states, which remains constant, the amplitude of the quasiparticle peak is also higher. The narrowing of the f band together

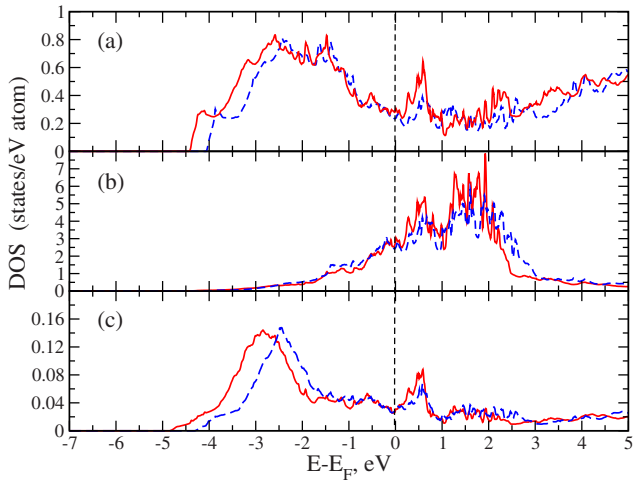

FIG. 2. (Color online) (a) The d partial DOS. (b) The f partial DOS. (c) The s partial DOS. In all cases the QSGW results are the solid red/gray lines, and the LDA results are the dashed blue/dark gray lines.

with its energy shift results in a slight change in the electron occupation. Comparison of the partial DOS shows that the f band shifts up, relatively to s and d bands, toward unoccupied states. The f occupation is equal to 3.19 in the QSGW and 3.57 in the LDA calculation, hence in QSGW about $0.4f$ electron is lost to the $s-d$ interstitial charge. The overall f occupation in uranium is relatively low so that the position of the Fermi level remains in the lower part of the f peak, where the difference between QSGW and LDA calculation is negligible. For this reason, even though the $5f$ electron states in uranium appear to be correlated, the physical properties that are related only to occupied electron states should be predicted well by the LDA approximation. It is mainly in the excited-state spectra of the f states above the Fermi energy where the correlation effects are strongly apparent. Consistent with the weak to moderate strength of the correlations, we find that the first iteration of the QSGW method, which is sometimes called the "one-shot GW," is very similar to the fully self-consistent QSGW results.

The electron DOS at the Fermi level in QSGW is 3.35 states/eV atom while the LDA result is 2.75 states/eV atom. We have found that the DOS has a lot of variation around the Fermi level and requires a very large number of k points to converge (we used 82^3). This explains deviations of our DOS with earlier results (e.g., Ref. 11 and references therein). Our LDA LMTO results using a Barth-Hedin exchange-correlation potential were found to be in excellent agreement with GGA (gradient-corrected) LAPW calculations using a Perdew-Burke-Ernzerhof (PBE) exchange-correlation potential that we calculated with the WIEN2K code;[25] e.g., we found insignificant differences in the total LDA and GGA DOS.

It was shown by Luttinger[26] that the linear coefficient of specific heat for a system of interacting electrons is given by the quasiparticle DOS, i.e., $\gamma \sim \Sigma_{\mathbf{k}} \delta[E_F - E(\mathbf{k})]$. This can be compared to the one-electron coefficient, which is given by $\gamma^0 \sim \Sigma_{\mathbf{k}} \delta[E_F^0 - \epsilon(\mathbf{k})]$. Here, E_F and $E(\mathbf{k})$ are the Fermi and quasiparticle energies of the interacting electron gas (in the QSGW approximation), while E_F^0 and $\epsilon(\mathbf{k})$ are the Fermi energy and band-structure eigenvalues. Hence only the quasiparticle shifts are needed for calculating the specific heat, which are included by construction in the QSGW energy eigenvalues and DOS. Therefore, the specific heat of the interacting QSGW electron gas is proportional to the QSGW DOS at the Fermi level $N(E_F)$, and there is no need to include an additional renormalization factor $(1 - d\Sigma/d\omega)$, which in model calculations converts the band-structure DOS to the quasiparticle DOS. We find that the linear coefficient of specific heat in QSGW is $\gamma = 7.89$ mJ mol^{-1} K^{-2} while in LDA is $\gamma = 6.48$ mJ mol^{-1} K^{-2}, giving a QSGW enhancement factor of $N^{\mathrm{QSGW}}(E_F)/N^{\mathrm{LDA}}(E_F) = \gamma^{\mathrm{QSGW}}/\gamma^{\mathrm{LDA}} = 1.22$. A recently measured value,[12] $\gamma_{\mathrm{exp}} = 9.15$ mJ mol^{-1} K^{-2}, is larger than the QSGW result by a factor of $\gamma_{\mathrm{exp}}/\gamma_{\mathrm{QSGW}} = 1.16$ and larger than the LDA result by a factor of $\gamma_{\mathrm{exp}}/\gamma_{\mathrm{LDA}} = 1.41$. The relatively small remaining enhancement that is not accounted for by QSGW must almost certainly be the electron-phonon enhancements that are present in all metals and that are typically at least this big.

The bremsstrahlung isochromat spectroscopy (BIS) of

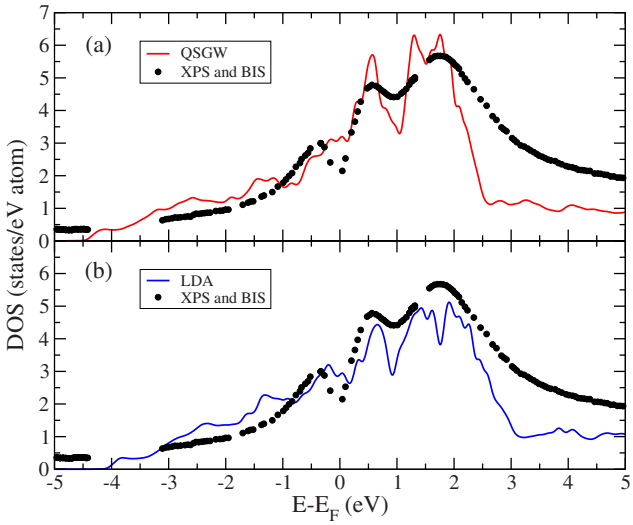

FIG. 3. (Color online) (a) Comparison of photoemission data with the calculated QSGW DOS. (b) Comparison of photoemission data with the calculated LDA DOS. In both cases, the DOS has a Gaussian broadening of 0.05 eV.

α-uranium exhibits a double peak structure within the interval of 1–2 eV above E_F (Ref. 27); as one can see in Fig. 3, this feature is reproduced by both calculations. However, further comparison of the two methods with photoemission data is difficult because the photoemission peaks are too broad compared to the bandwidth narrowing and quasiparticle shifts observed with the help of QSGW method. Recent angle-resolved photoemission (ARPES)[11] and ultraviolet photoemission spectroscopy (UPS)[10] were found to be in good agreement with GGA band-structure calculations. However, a low-energy UPS peak and several APRES local maxima were not predicted by GGA band structure. Since the QSGW energy bands along $\Gamma \rightarrow Z$ direction in the energy window −2–0 eV are very similar to those obtained with LDA the agreement with the valence band (UPS) is of the same level with LDA. The unexplained APRES local maxima are located in the vicinity of Γ point with energies around −5 eV and −2 eV.[10] Even though the QSGW bands along $\Gamma \rightarrow S$ direction agree less with LDA than they do along $\Gamma \rightarrow Z$ direction, the differences are not significant

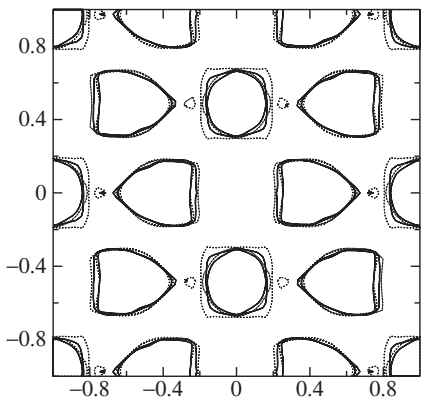

FIG. 4. The Fermi-surface cross section cut by the [100]-[010] plane at $h = 0.288$; QSGW—solid lines, LDA—dotted lines.

enough to explain the aforementioned ARPES data. We suspect that the presence of uranium surface states as was suggested in Ref. 11 or final-state effects are a more likely explanation for these features.

The [100]-[010] cross section of the Fermi surface is presented in Fig. 4. It shows that there are only slight changes in QSGW compared to the LDA calculations. This is representative of several cross sections that were plotted, showing that overall the electron correlations have no significant effect on the shape and size of the Fermi surface.

In conclusion, we have used the QSGW method to show that moderate f-electron correlation effects are present in α-U, and that it is because of the low occupation of f electrons that these effects do not show up more strongly in Fermi surface and other ground-state properties of this material. Most of the correlation effects only appear in the excited-state spectra in the unoccupied f states. As is commonly suspected, LDA or GGA band-structure methods somewhat misplace narrow bands, such as d and f bands, with respect to the remaining metallic bands. For uranium the error is about 0.5 eV.

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