Hybrid Density-Functional Theory and the Insulating Gap of UO_2

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(Received 12 April 2002; published 9 December 2002)

We report the first calculations carried out with a periodic boundary condition code capable of examining *hybrid* density-functional theory (DFT) for f-element solids. We apply it to the electronic structure of the traditional Mott insulator UO_2, and find that it correctly yields an antiferromagnetic insulator as opposed to the ferromagnetic metal predicted by the local spin density and generalized gradient approximations. The gap, density of states, and optimum lattice constant are all in good agreement with experiment. We stress that this results from the functional and the variational principle alone. We compare our results with the more traditional approximations.

DOI: 10.1103/PhysRevLett.89.266402 PACS numbers: 71.20.–b, 71.15.Mb, 71.70.–d, 75.50.–y

The chemistry and physics of materials containing actinide species has proven to be an especially complex and interesting field of study [1–6]. There are a number of reasons for this, but one important consideration concerns the spatial extent of the $5f$ orbitals. Early members of the series (including uranium, $Z = 92$) possess a $5f$ orbital diffuse enough to be involved in molecular bonding [5] and to participate in forming metallic bands in the elemental solid [6,7]. In later actinides, the $5f$ orbital significantly contracts, and in fact by americium ($Z = 95$), electrons occupying the $5f$ orbitals are localized as evidenced by an abrupt increase in the atomic volume [8]. This tendency towards localized behavior in the heavier actinides is also apparent in their chemistry, which is much more lanthanidelike than the early members. It is this delicate balance between localization and delocalization which makes the electronic structure of these materials so interesting.

This competition between two extremes of chemical bonding challenges our conventional theories of electronic structure. The traditional workhorse of density-functional theory (DFT), the local-spin-density approximation, often gives qualitatively incorrect behavior in cases such as these where the overlaps are small, the bands narrow, and the electrons nearly localized [9]. One such system is UO_2. The local spin density approximation (LSDA) predicts it to be a ferromagnetic metal, while in reality it is an antiferromagnetic insulator with an optical gap of roughly 2 eV. Similar failures of the LSDA occur to varying degrees for other "Mott-Hubbard" transition metal oxides such as NiO and La_2CuO_4 [9]. A number of many-body alternatives, e.g., the LSDA + U [9] approximation and the self-interaction correction (SIC) LSDA [10], have been developed to address these problems, but the general applicability of these methods to systems with strong correlations still remains unclear.

In this work, we examine a more recently developed alternative, the hybrid DFT approximation [11–14] widely used in the molecular quantum chemistry community. These hybrid functionals combine the full nonlocal "exact" exchange interaction with the traditional exchange-correlation functionals of the LSDA or GGAs (generalized gradient approximations). The impetus for the development of hybrid functionals was to improve the tendency of the LSDA to overemphasize bond energies in molecules. This problem is related to an overestimate of delocalization [15–18] and, hence, the bandwidths [19–21] in solids, and it therefore seems natural to examine the performance of hybrid DFT for the problematic f element solids. As a step in this direction, we report in this Letter the first application of these methods to the electronic structure of bulk UO_2.

The calculations were carried out with the periodic boundary condition (PBC) algorithm of Kudin and Scuseria [22] implemented in the development version of the GAUSSIAN program [23]. GAUSSIAN has the capability to treat f orbitals and uses the relativistic effective core potential (RECP) approximation for heavy atoms. The RECPs are designed to have a screened Z_{eff}/R component and a short ranged repulsive component; the former can easily be absorbed into the nuclear attraction term and treated with the same techniques, while the latter is short ranged and therefore not particularly demanding in terms of summation over neighbor cells. The uranium atom was described with a "small core" RECP [24]; the $5s$, $5p$, $5d$, $6s$, $6p$, and $5f$ orbitals are all considered to be in the valence space. The associated $[11s10p9d7f]$ primitive Gaussian basis was employed, except that the two tightest functions in each angular momentum were found unnecessary in preliminary calculations and omitted for economy. In addition, the most diffuse s, p, and d functions in the original primitive set were deleted as they severely hinder the performance and are prone to cause linear dependence problems when used in dense solids. The final set was completely uncontracted $[8s8p6d5f]$. For the oxygen centers, the double-zeta 3-21G $[3s2p]$ basis set was employed. All calculations employed a doubled unit cell, U_2O_4, in order to study the antiferromagnetic state. In those cases where the exact exchange is required for the functional, first it was computed within a $3 \times 3 \times 3$ supercell (27 cells), and then the calculations were repeated within a 63 cell subset of a $5 \times 5 \times 5$ supercell. This two-step procedure allowed us to verify that the exact exchange was well converged with respect to the lattice summation. The reciprocal space integration used a mesh of $16 \times 16 \times 12$ k points with no symmetry. The PBE1PBE [13] hybrid functional is particularly simple; the exchange term is composed of 25% Fock exchange and 75% Perdew-Burke-Ernzerhof (PBE) exchange, and the PBE correlation functional is used as is [25]. This functional has been used quite successfully in molecular calculations [26].

A starting point for considering the electronic structure of UO_2 is in the ionic limit, where the U^{+4} ion is formally f^2. At room temperature, UO_2 crystallizes in the face centered cubic fluorite structure, in which each uranium is coordinated by eight oxygen atoms at the corners of a cube. In such a symmetry the f orbitals split into t_{1u}, t_{2u}, and a_{2u} symmetries, with the t_{1u} being most stable. In the strong crystal field limit, one would expect an orbitally degenerate t_{1u}^2 occupancy, leading to a high spin triply degenerate ground state ($^3T_{1g}$) according to Hund's rules. This simple picture is largely verified by experiment, with the caveat that the details are altered by the spin-orbit interaction (although the ground state remains triply degenerate). Inelastic neutron scattering shows that the triply degenerate ground state is split into three singlets due to a dynamical Jahn-Teller distortion of the oxygen cage which reduces the point symmetry at the uranium site [27,28]. Another complication is that UO_2 orders antiferromagnetically below the Neél temperature of 30.8 K [29]. The details of the magnetic ordering appear to be rather subtly associated with the structural distortion [30]. We do not consider these topics in this work, focusing instead on the undistorted cubic structure when comparing ferromagnetic and antiferromagnetic solutions of the unrestricted Kohn-Sham equations.

Our theoretical results for the total density of states (DOS) in the ferromagnetic state at the experimental lattice constant (5.47 Å) are presented in Fig. 1. Consistent with prior research [31–35], neither the LSDA nor the PBE GGA functional yield an insulator. Both give ferromagnetic conductors, where the Fermi level cuts a band constructed primarily from uranium f orbitals. Significantly, the PBE1PBE hybrid functional yields a gap of 2.6 eV, slightly larger than the gap of 2.1 eV observed in the optical spectrum [36,37]. In the hybrid solution, a fairly narrow band associated with the two orbitals occupied in the t_{1u}^2 configuration [38] splits off from the other components of the f-orbital band. This subband is ~1 eV wide at the Γ point and occupied by majority spin (α) electrons. Within the Mulliken approximation, we can break down the total DOS into atomic orbital components as shown for the PBE1PBE result in the upper panel of Fig. 2. The band at E_f is dominantly U $5f$, with a very small O $2p$ component at the leading edge. The total unpaired α spin population is U (2.06) with only slight β spin delocalized onto the oxygens (-0.03). This can be compared with 2.17 and 2.14 for the PBE and LSDA approximations, respectively. The O $2p$ band from -3 to -8 eV has some contribution from the U $5f$ orbitals in the lower binding energy (antibonding) region, and some U $6d$ character in the higher energy (bonding) range. The width, orbital character, and

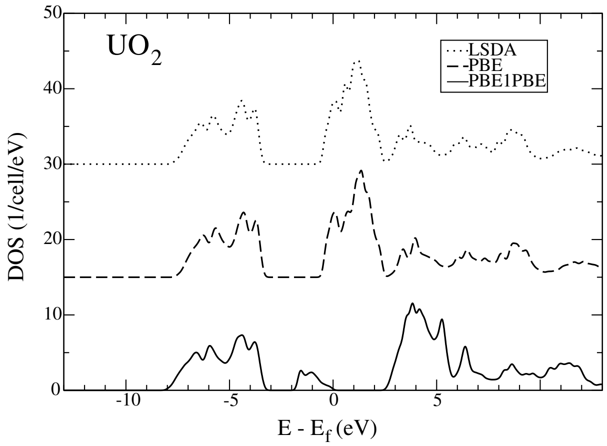

FIG. 1. The total DOS for UO_2 in the LSDA, the PBE GGA, and the PBE1PBE hybrid approximation for the ferromagnetic solution at the experimental lattice constant.

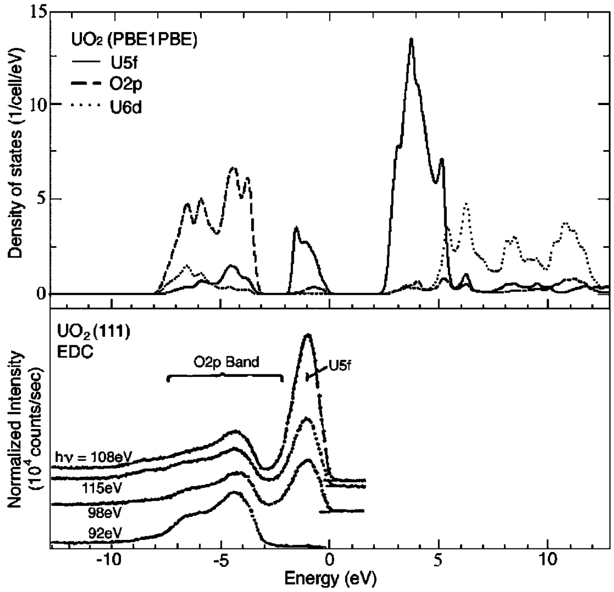

FIG. 2. The top panel displays the PBE1PBE partial DOS for UO_2. The peak near E_f is primarily U $5f$ with a very small O $2p$ contribution. The bottom panel reproduces the photoemission energy distribution curves taken by Cox *et al.* demonstrating the predominantly U $5f$ character of the feature near E_f. The incident photon energies correspond to the resonance (98 and 108 eV) and antiresonance (92 eV) in the U $5f$ cross section.

positions of all these features are in good agreement with the resonant photoemission data of Cox *et al.* [39] shown in the lower panel of Fig. 2. In particular, Cox *et al.* showed the feature near the Fermi energy is primarily U $5f$ by resonant photoemission.

The unoccupied DOS appears consistent with the optical spectrum of Schoenes [36,37], although our assignment differs. He associated the gap with $5f \rightarrow 6d$ transitions with localized $5f \rightarrow 5f$ transitions lying in the gap. We find the levels at the onset of the conduction band to be composed of unoccupied t_{1u}, t_{2u}, and a_{2u} f states. These show significant dispersion, spanning a range from 2.5–6 eV. This width arises from a combination of the crystal field splitting and true f-f interactions. For example, at the Γ point the lowest virtual level is the bonding combination of an f_{xyz} (a_{2u}) orbital with another on the neighboring uranium. The corresponding antibonding combination occurs $\sim$1 eV higher. Significant $6d$ character in the unoccupied states begins at about 5 eV in our PBE1PBE spectrum, and we suggest that the stronger absorption observed experimentally at $\sim$5–6 eV be assigned to the optically allowed $5f \rightarrow 6d$ transitions. Note also that the O $2p \rightarrow 5f$ charge transfer transitions are predicted to occur in this vicinity. A rather broad band of empty f levels is also in accord with the bremsstrahlung isochromat spectrum [40] and x-ray absorption near-edge structure [41]. These techniques essentially measure the levels of the N + 1 electron system, and both find evidence for $5f^3$ final states extending from 2–8 eV above the Fermi energy. Although this is wider than the 4 eV we find for the unoccupied f band, final state effects (and our neglect of the spin-orbit interaction) complicate a detailed comparison of the one-electron DOS with experiment. The overall picture which emerges from the hybrid functional appears to be in satisfactory agreement with experiment.

We have made an initial foray into studying the magnetic properties of UO_2, by examining the solution generated from coupling the two local triplets antiferromagnetically. If the lattice is constrained to cubic symmetry, the optimum PBE1PBE lattice constant for the ferromagnetic state is 5.42 Å, in good agreement with the experimental lattice constant of 5.47 Å. This is in contrast to the significantly shorter distances predicted in this work by the LSDA (5.28 Å) and PBE (5.38 Å) approximations, again suggesting the hybrid solution is less covalent than the metallic solutions. In contrast to all the previous studies, with PBE1PBE the antiferromagnetic broken symmetry solution at this geometry lies slightly lower in energy than the ferromagnet (2.2 meV per UO_2). This difference, while small, is well within the precision of our numerical procedures (≤ 0.1 meV), and implies a Heisenberg J of $-25\,^\circ$K [16]; not an unreasonable number given the Neél temperature of 30.8 K.

It is interesting to note that the difference in the hybrid functional relative to the PBE GGA is not directly concerned with the Coulomb repulsion U central to the LSDA + U models [33,34]; it is instead a simple modification of the exchange interaction to include an (orbital dependent) Hartree-Fock component. This interaction is attractive between like spins and stabilizes a ${}^3T_{1g}$ multiplet separating it from the remainder of the f band. Other occupancies may lead to stable multiplets as well and appear as levels "localized" in the gap. An indirect effect on the Coulomb repulsion is that inclusion of Hartree-Fock exchange negates some, but not all, of the self-interaction correction, and modifies the shape of the exchange hole.

In conclusion, we have reported the first hybrid DFT calculation on an f element solid with periodic boundary conditions and Gaussian orbitals. The approach appears very promising, yielding a reasonable gap for the problematic insulator UO_2. The ground state consists of a pair of triplet coupled f electrons at each metal site which then couple antiferromagnetically between neighbors. The hybrid approach also significantly improves the prediction of the lattice constant. The picture emerging from the hybrid calculations is not simply a set of localized f levels, as is imposed in many calculations which artificially zero matrix elements between uranium neighbors in order to localize the f manifold. We find a significant width ($\sim$ 1 eV) for the band at E_f which is dispersive in origin. An angle resolved photoemission experiment could discriminate the present picture from the traditional completely localized atomic multiplets model. It is especially encouraging that the variational principle and the hybrid functional alone leads to semiquantitative agreement with several experiments.

This work was sponsored by the Division of Chemical Sciences, U.S. Department of Energy, through Grant No. DE-FGO301ER15137, Contract No. W-7405-ENG-36, and the LDRD program at Los Alamos. We thank Dr. P. J. Hay and Dr. J. C. Boettger for their help and useful discussions, and Mrs. E. P. Vigil for help with the figures.

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