Slave Boson Theory of Orbital Differentiation with Crystal Field Effects: Application to UO_2

Nicola Lanatà,[1,*] Yongxin Yao,[2,†] Xiaoyu Deng,[3] Vladimir Dobrosavljević,[1] and Gabriel Kotliar[3,4]
[1]Department of Physics and National High Magnetic Field Laboratory, Florida State University, Tallahassee, Florida 32306, USA
[2]Ames Laboratory, U.S. DOE and Department of Physics and Astronomy, Iowa State University, Ames, Iowa 50011, USA
[3]Department of Physics and Astronomy, Rutgers University, Piscataway, New Jersey 08856-8019, USA
[4]Condensed Matter Physics and Materials Science Department, Brookhaven National Laboratories, Upton, New York 11973-5000, USA

(Received 13 July 2016; published 23 March 2017)

We derive an exact operatorial reformulation of the rotational invariant slave boson method, and we apply it to describe the orbital differentiation in strongly correlated electron systems starting from first principles. The approach enables us to treat strong electron correlations, spin-orbit coupling, and crystal field splittings on the same footing by exploiting the gauge invariance of the mean-field equations. We apply our theory to the archetypical nuclear fuel UO_2 and show that the ground state of this system displays a pronounced orbital differentiation within the $5f$ manifold, with Mott-localized Γ_8 and extended Γ_7 electrons.

DOI: 10.1103/PhysRevLett.118.126401

Orbital differentiation, where states with different orbital character exhibit different levels of correlation, is a pervasive phenomena in condensed matter systems [1–4], which gives rise to multiple functionalities in strongly correlated multiorbital systems. In all known Mott systems in nature, only a fraction of electrons form localized magnetic moments, while the other electronic states are extended (but away from the Fermi level). These systems are commonly called "selective Mott insulators," and the transition into these states is called the "orbitally selective Mott transition." Understanding the mechanism driving the selection process is a fundamental question in condensed matter. This issue is especially nontrivial to address in low-symmetry $5f$ electron systems, where the competition between inter- and intraorbital interactions, the crystal field splittings (CFSs), and the spin-orbit coupling (SOC) is very complicated, as none of these energy scales are negligible. Orbital differentiation is also a key issue in the presence of disorder [5,6] and/or charge ordering (Wigner-Mott transitions [7]), where only a fraction of the electrons Mott localize. Addressing these issues quantitatively and in an unbiased "*ab initio*" fashion is very challenging. In this Letter, we address the orbital differentiation problem from an *ab initio* perspective using the rotationally invariant slave boson (RISB) mean-field theory [8–10]. As we demonstrate, this method can be derived from an *exact* operatorial reformulation of the many-body problem, which reproduces the Gutzwiller approximation [11] at the mean-field level [12,13] and constitutes a starting point to calculate further corrections. By exploiting the gauge symmetry of the RISB theory, we build efficient systematic algorithms which enable us to solve the mean-field equations and elucidate the pattern of orbital differentiation even in low-symmetry $5f$ electron systems. We apply this method to UO_2 [14] (the most widely used nuclear fuel) and provide new insight into the role of the CFSs in the orbital differentiation and the nature of the chemical bonds in this material.

The multiband Hubbard model.—Let us consider a generic multiband Hubbard model:

$$\hat{H} = \sum_{k} \sum_{ij=1,\ldots,n_a} \sum_{\alpha=1,\ldots,M_i} \sum_{\beta=1,\ldots,M_j} \epsilon^{\alpha\beta}_{k,ij} c^{\dagger}_{ki\alpha} c_{kj\beta} + \hat{H}^{\mathrm{loc}}, \tag{1}$$

where k is the momentum conjugate to the unit-cell label R, the n_a atoms within the unit cell are labeled by i, j, and the spin orbitals are labeled by α, β. As in Refs. [9,15], the local interaction and the on-site energies are both included within the definition of

$$\hat{H}^{\mathrm{loc}} \equiv \sum_{Ri} \sum_{AB} [H^{\mathrm{loc}}_i]_{AB} |A, Ri\rangle\langle B, Ri|, \tag{2}$$

where $|A, Ri\rangle$ are local Fock states,

$$|A, Ri\rangle = [c^{\dagger}_{Ri1}]^{\nu_1(A)} \ldots [c^{\dagger}_{RiM_i}]^{\nu_{M_i}(A)} |0\rangle, \tag{3}$$

and $A = 1, \ldots, 2^{M_i}$ runs over all of the possible lists of occupation numbers $\{\nu_1(A), \ldots, \nu_{M_i}(A)\}$. In particular, in this work, we have used the Slater-Condon parametrization of the on-site interaction [16].

Slave boson reformulation.—Here we derive the RISB gauge theory and show that it constitutes an exact reformulation of the generic Hubbard system defined above. As in Ref. [9], we introduce a new set of fermionic modes

$\{f_{Ria}|a=1,\ldots,M_i\}$ that we call quasiparticle operators. Furthermore, we introduce a bosonic mode Φ_{RiAn} for each couple of fermionic local multiplets $(|A,Ri\rangle,|n,Ri\rangle)$ having equal number of electrons, i.e., $N_A \equiv \sum_{a=1}^{M_i}\nu_a(A)=N_n\equiv\sum_{a=1}^{M_i}\nu_a(n)$. Applying the algebra generated by $\{\Phi^\dagger_{RiAn}\}$ and $\{f^\dagger_{Ria}\}$ to the vacuum $|0\rangle$ generates a new Fock space $\mathcal{H}_{\rm SB}$. We define the "physical Hilbert space" $h_{\rm SB}$ as the subspace of $\mathcal{H}_{\rm SB}$ satisfying the following equations (Gutzwiller constraints):

$$K^0_{Ri}\equiv\sum_{An}\Phi^\dagger_{RiAn}\Phi_{RiAn}-\hat{I}=0, \tag{4}$$

$$K_{Riab}\equiv f^\dagger_{Ria}f_{Rib}-\sum_{Anm}[F^\dagger_{ia}F_{ib}]_{mn}\Phi^\dagger_{RiAn}\Phi_{RiAm}=0, \tag{5}$$

where $\hat{I}$ is the identity, $[F_{ia}]_{nm}\equiv\langle n,Ri|f_{Ria}|m,Ri\rangle$, and $|n,Ri\rangle$ and $|m,Ri\rangle$ are Fock states constructed as in Eq. (3) but using the quasiparticle operators f_{Ria}.

In Ref. [15] it was shown that the following Hamiltonian is an exact representation of $\hat{H}$ within $h_{\rm SB}$:

$$\underline{\hat{H}}=\sum_{kij\alpha\beta}\epsilon^{\alpha\beta}_{k,ij}\underline{c}^\dagger_{ki\alpha}\underline{c}_{kj\beta}+\sum_{RiAB}[H^{\rm loc}_i]_{AB}\sum_n\Phi^\dagger_{RiAn}\Phi_{RiBn}, \tag{6}$$

where $\underline{c}^\dagger_{Ri\alpha}\equiv\sum_a\hat{\mathcal{R}}_{Ria\alpha}f^\dagger_{Ria}$, and the operators

$$\hat{\mathcal{R}}_{Ria\alpha}=\sum_{AB}\sum_{nm}\frac{[F^\dagger_{i\alpha}]_{AB}[F^\dagger_{ia}]_{nm}}{\sqrt{N_A(M_i-N_B)}}\Phi^\dagger_{RiAn}\Phi_{RiBm} \tag{7}$$

are such that $\underline{c}^\dagger_{Ri\alpha}$ are a representation in $h_{\rm SB}$ of $c^\dagger_{Ri\alpha}$. A remarkable property of $\underline{\hat{H}}$ is that it is invariant with respect to the gauge Lie group generated by the Gutzwiller constraint operators K_{Riab} [see Eq. (5)]:

$$e^{i\sum_{Riab}\theta_{ab}K_{Riab}}\underline{\hat{H}}e^{-i\sum_{Riab}\theta_{ab}K_{Riab}}=\underline{\hat{H}}\quad\forall\ \theta=\theta^\dagger. \tag{8}$$

In fact, Eq. (8) does not hold only within the subspace $h_{\rm SB}$ [which would be a trivial consequence of Eq. (5)] but in the entire RISB Fock space $\mathcal{H}_{\rm SB}$ [17–23].

Operatorial formulation of RISB theory.—The operators $\hat{\mathcal{R}}_{Ria\alpha}$ defined above are constructed in such a way that $\underline{c}^\dagger_{Ri\alpha}$ are a representation in the physical RISB subspace of the corresponding original fermionic operators $c^\dagger_{Ri\alpha}$. However, this construction is *not* unique. In particular, Eq. (7) can be modified as follows:

$$\hat{\mathcal{R}}_{Ria\alpha}=:\sum_{AB}\sum_{nm}\frac{[F^\dagger_{i\alpha}]_{AB}[F^\dagger_{ia}]_{nm}}{\sqrt{N_A(M_i-N_B)}}\Phi^\dagger_{RiAn}[\hat{1}+\hat{X}_{AB}]\Phi_{RiBm}: \tag{9}$$

where ":" indicates the normal ordering [24], and $\hat{X}_{AB}$ is any normally ordered algebraic combination of bosonic ladder operators such that each term contains at least two modes. In fact, since $\hat{X}_{AB}$ is normally ordered and the physical RISB states contain only one boson by construction [see Eq. (4)], the matrix elements of Eqs. (7) and (9) are independent of $\hat{X}_{AB}$ within $h_{\rm SB}$.

Of course, any choice of $\hat{X}_{AB}$ in Eq. (9) would be equivalent if we were able to solve $\underline{\hat{H}}$ exactly. However, this choice affects the RISB mean-field approximation (that we are going to introduce below). Interestingly, it is possible to construct $\hat{X}_{AB}$ in such a way that (i) the RISB mean-field theory is exact for any uncorrelated Hubbard Hamiltonian, and (ii) the invariance property [Eq. (8)] of $\underline{\hat{H}}$ with respect to the gauge group remains valid. To the best of our knowledge, this operatorial construction, which is derived in the Supplemental Material of this Letter [17], was not provided in any previous work.

RISB mean-field theory.—At zero temperature, the RISB mean-field theory consists in minimizing the expectation value of $\underline{\hat{H}}$ with respect to $|\Psi_{\rm MF}\rangle=|\Psi_0\rangle\otimes|\phi\rangle$, where $|\Psi_0\rangle$ is a Slater determinant constructed with the quasiparticle operators f_{Ria}, $|\phi\rangle$ is a bosonic coherent state, and the Gutzwiller constraints [see Eqs (4) and (5)] are enforced only in average.

It can be verified that taking the expectation value of Eqs. (4) and (5) with respect to $|\Psi_{\rm MF}\rangle$ gives

$$\mathrm{Tr}[\phi^\dagger_i\phi_i]=1\quad\forall\, i, \tag{10}$$

$$[\Delta_{pi}]_{ab}\equiv\mathrm{Tr}[\phi^\dagger_i\phi_iF^\dagger_{ia}F_{ib}]=\langle\Psi_0|f^\dagger_{Ria}f_{Rib}|\Psi_0\rangle\quad\forall\, i, \tag{11}$$

where the matrix elements $[\phi_i]_{An}$, which we call "slave boson amplitudes," are the eigenvalues of the annihilation operators Φ_{RiAn} with respect to $|\phi\rangle$. Similarly, it can be verified that the expectation value of $\underline{\hat{H}}$ with respect to $|\Psi_{\rm MF}\rangle$ (normalized to the number of k points $\mathcal{N}$) is given by

$$\mathcal{E}\equiv\frac{1}{\mathcal{N}}\langle\Psi_{\rm MF}|\underline{\hat{H}}|\Psi_{\rm MF}\rangle=\sum_i\mathrm{Tr}[\phi_i\phi^\dagger_iH^{\rm loc}_i]+\frac{1}{\mathcal{N}}\sum_{kij}\sum_{ab}[\mathcal{R}_i\epsilon_{k,ij}\mathcal{R}^\dagger_j]_{ab}\langle\Psi_0|f^\dagger_{kia}f_{kjb}|\Psi_0\rangle, \tag{12}$$

where $[\mathcal{R}_i]_{a\alpha}\equiv\langle\phi|\hat{\mathcal{R}}_{Ria\alpha}|\phi\rangle$ is given by

$$[\mathcal{R}_i]_{a\alpha}=\mathrm{Tr}[\phi^\dagger_iF^\dagger_{i\alpha}\phi_iF_{ib}][\Delta_{pi}(1-[\Delta_{pi}])]^{-\frac{1}{2}}_{ba}, \tag{13}$$

where 1 is the identity matrix, and $\hat{\mathcal{R}}_{Ria\alpha}$ are the renormalization operators represented in Eq. (9) and constructed explicitly in the Supplemental Material [17]. The RISB mean-field theory amounts to minimize Eq. (12) with respect to $|\Psi_{\rm MF}\rangle$ while fulfilling Eqs. (10) and (11).

Advantages of the gauge invariant formulation.—As shown in the Supplemental Material [17], the above-constrained minimization problem can be conveniently

cast analogously to Dynamical Mean Field Theory [25–27] as a root problem for the variables $(\mathcal{R}_i, \lambda_i)$, where $\mathcal{R}_i$ were defined in Eq. (13), and λ_i are matrices of Lagrange multipliers introduced in order to enforce the Gutzwiller constraints [Eq. (11)]. These variables encode the so-called "Gutzwiller self-energy" of each inequivalent atom, which is defined as

$$\Sigma_i(\omega) \equiv (I - \mathcal{R}_i^\dagger \mathcal{R}_i)(\mathcal{R}_i^\dagger \mathcal{R}_i)^{-1}\omega + (\mathcal{R}_i^{-1}\lambda_i \mathcal{R}_i^{\dagger -1}), \quad (14)$$

where $Z_i \equiv \mathcal{R}_i^\dagger \mathcal{R}_i$ are *matrices* of quasiparticle weights. Let us represent formally the above-mentioned root problem as follows:

$$\mathcal{F}[(\mathcal{R}_1, \lambda_1), \ldots, (\mathcal{R}_{n_a}, \lambda_{n_a})] = 0, \quad (15)$$

where n_a is the number of inequivalent atoms within the unit cell. As shown in the Supplemental Material [17], each evaluation of $\mathcal{F}$ requires us to solve n_a impurity models, where the bath has the same dimension of the impurity for each inequivalent atom [15]. An important advantage of the present formulation with respect to Ref. [15] is that by virtue of Eq. (8), Eq. (15) has a manifold of physically equivalent solutions, which are mapped one into the other by the following group of gauge transformations: $\mathcal{R}_i \to u_i^\dagger(\theta_i)\mathcal{R}_i$, $\lambda_i \to u_i^\dagger(\theta_i)\lambda_i u_i(\theta_i)$, where $u_i(\theta_i) \equiv e^{i\theta_i}$ are generic unitary matrices. This property effectively reduces the dimension of the root problem, which makes the code more stable and speeds up the convergence by reducing substantially the number of evaluations of $\mathcal{F}$ necessary to solve Eq. (15). Remarkably, we found that exploiting the gauge freedom mentioned above is essential in order to study strongly correlated materials where the SOC and the CFSs are equally important, which generally makes the structure of $\Sigma_i(\omega)$ particularly complex [28]. Further technical details are discussed in the Supplemental Material [17].

Calculations of UO_2.—UO_2 is widely used as a nuclear fuel. At ambient pressure, it is a Mott insulator and crystallizes in a cubic fluorite structure. Given the importance of this material, its electronic structure and energetics have been extensively investigated both experimentally and theoretically, e.g., with Density Functional Theory plus U (DFT + U) [30–32] and other single-particle approaches [33,34]. However, within these techniques it is not possible to address the properties of the paramagnetic state of this material, which is stable above the Néel temperature $T_N \simeq$ 30.8 K [35]. Because of this reason, several Dynamical Mean Field Theory studies of paramagnetic UO_2 have been recently performed [14,36–38]. A particularly important statement concerning the orbital differentiation of the U-5f electrons was made in Refs. [14,36], where it was observed that the $5f_{5/2}$ states are Mott localized, while the $5f_{7/2}$ states are extended (but gapped). However, these studies did not investigate how this conclusion is influenced by the crystal field effects, which is the main goal of this Letter. For this purpose, we perform charge self-consistent DFT + RISB simulations of paramagnetic UO_2 taking fully into account the CFSs. As in Ref. [15], we utilize the DFT [39] code WIEN2K [40] and employ the Local Density Approximation (LDA) and the standard "fully localized limit" form for the double-counting functional [16]. These calculations would have been prohibitive without the algorithms derived in this work [17].

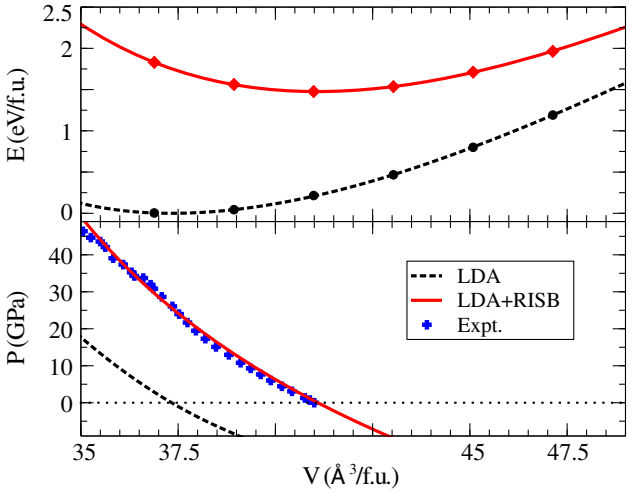

FIG. 1. Zero-temperature LDA and LDA + RISB total energies (upper panel) and corresponding pressure-volume phase diagrams compared with the room-temperature experiments of Ref. [41] (lower panel).

As in Ref. [36], here we assume that the Hund's coupling constant is $J = 0.6$ eV. In the upper panel of Fig. 1 are shown the LDA and LDA + RISB total energies $E(V)$ obtained at zero temperature for $U = 10$ eV [17]. The corresponding pressure (P-V) curves obtained from $P(V) = -dE/dV$ are shown in the lower panel in comparison with the experimental data of Ref. [41] (which were obtained at room temperature). The RISB P-V curve and, in particular, the experimental equilibrium volume $V_{\mathrm{eq}} \simeq 41$ Å^3/f.u. compare remarkably well with the experiments. This favorable comparison with the experiments gives us confidence that our theoretical approach is able to describe the ground-state properties of this material. As shown in the Supplemental Material [17], the P-V curve (and, in particular, the equilibrium volume) is essentially identical for $U = 8$ eV, which is the value assumed in Ref. [36]. Furthermore, reducing U from 10 to 8 eV does not influence appreciably the electronic structure of UO_2 at V_{eq} [42].

In order to describe the orbital differentiation in UO_2 taking into account the CFSs, it is necessary to decompose the U-5f single-particle space in irreducible representations of the double O point symmetry group [29,44] of the U atoms. It can be shown that this repartition consists in: $1\Gamma_6(2)$ doublet, $2\Gamma_7(2)$ doublets, and $2\Gamma_8(4)$ quartets [45]. These irreducible representations are generated by the following states:

$$
\begin{aligned}
|\Gamma_6,7/2,\pm\rangle &= \sqrt{5/12}|7/2,\pm 7/2\rangle + \sqrt{7/12}|7/2,\mp 1/2\rangle,\\
|\Gamma_7,7/2,\pm\rangle &= \mp\sqrt{3/4}|7/2,\pm 5/2\rangle \pm \sqrt{1/4}|7/2,\mp 3/2\rangle,\\
|\Gamma_8^{(1)},7/2,\pm\rangle &= \pm\sqrt{7/12}|7/2,\pm 7/2\rangle \mp \sqrt{5/12}|7/2,\mp 1/2\rangle,\\
|\Gamma_8^{(2)},7/2,\pm\rangle &= \mp\sqrt{1/4}|7/2,\pm 5/2\rangle \mp \sqrt{3/4}|7/2,\mp 3/2\rangle,\\
|\Gamma_7,5/2,\pm\rangle &= \sqrt{5/6}|5/2,\pm 3/2\rangle - \sqrt{1/6}|5/2,\mp 5/2\rangle,\\
|\Gamma_8^{(1)},5/2,\pm\rangle &= \sqrt{1/6}|5/2,\pm 3/2\rangle + \sqrt{5/6}|5/2,\mp 5/2\rangle,\\
|\Gamma_8^{(2)},5/2,\pm\rangle &= |5/2,\pm 1/2\rangle,
\end{aligned}
\tag{16}
$$

which are expressed in terms of the conventional basis of eigenstates of the total angular momentum (JJ basis). By virtue of the Schur lemma [29], the entries of the U-5f self-energy $\Sigma(\omega)$ coupling states belonging to inequivalent irreducible representations are equal to 0. However, the total angular momentum J^2 is not a good quantum number, as the matrix elements of $\Sigma(\omega)$ coupling the following states are allowed: $|\Gamma_7,5/2,\pm\rangle$ with $|\Gamma_7,7/2,\mp\rangle$ $|\Gamma_8^{(1)},5/2,\pm\rangle$ with $|\Gamma_8^{(2)},7/2,\mp\rangle$ and $|\Gamma_8^{(2)},5/2,\pm\rangle$ with $|\Gamma_8^{(2)},7/2,\pm\rangle$. Furthermore, the $5/2$ and $7/2$ states are not degenerate [17]. Note that these CFSs are present because of the crystal structure and would not exist if the environment of the U atom was isotropic.

The main goals of this work are (1) to show that the CFSs affect substantially the electronic structure of UO_2 and (2) to describe and explain the pattern of orbital differentiation of the U-5f electrons in this material.

In Table I are shown the eigenvalues of the 5f quasiparticle matrix $Z = \mathcal{R}^\dagger\mathcal{R}$ obtained by taking into account the CFSs and the corresponding orbital occupations. The approximate results calculated by averaging over the CFSs are also shown. The details of the averaging procedure are described in the Supplemental Material [17]. We observe that when the CFSs are taken into account, the selective Mott localization occurs only within the Γ_8 sector, while the eigenvalues of Z of the other 5f degrees of freedom are relatively large. More precisely, Z has four null eigenvalues with Γ_8 character. On the other hand, when the CFSs are neglected [14,36], the Mott localization can only occur within the entire $5/2$ sector, which is 6-fold degenerate. It is important also to observe that when the CFSs are taken into account, the Mott-localized Γ_8 states do not have a well-defined total angular momentum J^2. In fact, we found that the eigenstates of Z with null eigenvalues are the following:

$$
\begin{aligned}
|1\rangle &\simeq 0.939|\Gamma_8^{(1)},5/2,+\rangle + 0.343|\Gamma_8^{(2)},7/2,-\rangle,\\
|2\rangle &\simeq 0.939|\Gamma_8^{(1)},5/2,-\rangle + 0.343|\Gamma_8^{(2)},7/2,+\rangle,\\
|3\rangle &\simeq 0.939|\Gamma_8^{(2)},5/2,+\rangle + 0.343|\Gamma_8^{(1)},7/2,-\rangle,\\
|4\rangle &\simeq 0.939|\Gamma_8^{(2)},5/2,-\rangle + 0.343|\Gamma_8^{(1)},7/2,+\rangle,
\end{aligned}
\tag{17}
$$

which have considerably mixed J^2 character. A further indication of the importance of the CFSs in UO_2 is given by the orbital occupations of the U-5f electrons. In fact, the occupation corresponding to the Mott-localized 5f electrons is 1.92, while the remaining 0.32 5f electrons are extended (but gapped). Instead, when the CFSs are neglected, the total number of Mott-localized 5f electrons is 1.98, while the occupation of the extended 5f degrees of freedom is only 0.16. The fact that the overall occupancy of the 5f levels deviates considerably from an integer value confirms the importance of covalency effects in UO_2, which has been pointed out also in previous experimental and theoretical studies [46–49]. Note also that the Mott-localized Γ_8 degrees of freedom have occupancy close to integer, which is a factor that is known to promote localization [3].

Let us now address the question of what is the physical origin of the strong CFSs orbital differentiation in UO_2. The first important observation is that the importance of the CFSs splittings in UO_2 is not related with the U-5f crystal fields (on-site energy splittings) [2–4], which are very small in this material (∼7 meV). In fact, a direct calculation shows that neglecting the CFSs contributions to the on-site energy splittings [17] does not affect sensibly any of the results considered above (data not shown). Furthermore, we find that the total energy of the approximate solution obtained by averaging over the crystal fields is about 0.59 eV/f.u. higher with respect to the solution where the CFSs are taken into account, which is a much larger energy scale with respect to the above-mentioned on-site energy splittings. These observations and the data in Table I indicate that the main physical reason why it is essential to take into account the CFSs concerns the above-mentioned covalent nature of the bonds in UO_2, i.e., the hybridization between the U-5f and the uncorrelated electrons (in particular, the O-2p states). In particular, we note that neglecting the CFSs implies (by construction) that the $|\Gamma_7,5/2,\pm\rangle$ electrons are Mott localized, which leads to an underestimation of the contributions to the energy arising from the hybridization of these electrons with the O-2p bands. On the other hand, taking into account the CFSs enables us to capture the fact that the

TABLE I. Eigenvalues of the 5f quasiparticle matrix Z and corresponding orbital occupations for LDA + RISB calculations at $U = 10$ eV. Theoretical results obtained by taking into account the crystal field splittings and by neglecting them.

With CFSs	$\Gamma_8(4)$	$\Gamma_7(2)$	$\Gamma_8(4)$	$\Gamma_7(2)$	$\Gamma_6(2)$
Z	0	0.92	0.92	0.95	0.95
n	1.92	0.14	0.08	0.06	0.04

Without CFSs	$5/2$	$7/2$
Z	0	0.96
n	1.98	0.16

hybridization of the Γ_7 electrons is larger with respect to the Γ_8 localized states [37].

More details about the electronic structure of UO_2 are reported in the Supplemental Material [17].

In summary, we have derived an exact RISB reformulation of the multiband Hubbard model, which establishes the foundation of the mean-field approximation and constitutes a starting point for calculations beyond mean-field. The gauge invariance of our theory has resulted also in substantial algorithmic advancements, which make it possible to study from first principles the energetics and the electronic structure of strongly correlated materials taking into account simultaneously electron correlations, SOC and CFSs. By utilizing our theoretical approach, we have performed first principles calculations of the orbital-selective Mott insulator UO_2, finding good agreement with available experimental data. Furthermore, we have demonstrated that taking into account the CFSs is essential in order to capture the correct pattern of orbital differentiation between the U-5f states and that the main physical reason underlying the CFSs orbital differentiation in UO_2 is not the contribution of the crystal field on-site energies (which is essentially negligible), but concerns the hybridization between the U-5f and the O-2p electrons [37], which originates covalent bonds in this material [46–49]. The strong orbital differentiation between the Γ_8 and the Γ_7 electrons could be directly detected experimentally, e.g., by means of angle-resolved photoemission techniques [50,51], which would enable us to discriminate between the spectral contributions of the different states based on their symmetry properties. In particular, based on the orbital occupations of Table I and the Friedel sum rule, we predict that the 5f spectral weight [52,53] below the Fermi level has mostly Γ_8 character—while it would have also a substantial Γ_7 contribution if the CFSs orbital differentiation was a negligible effect. The analysis presented here is very general and could be applied also to other f electron systems, e.g., to materials displaying strong magnetic anisotropy or more general forms of multipolar order [54].

We thank Cai-Zhuang Wang, Kai-Ming Ho, and Tsung-Han Lee for useful discussions. This research was supported by the U.S. Department of Energy, Office of Science, Basic Energy Sciences, as a part of the Computational Materials Science Program. V. D. and N. L. were partially supported by the National Science Foundation Grant No. DMR-1410132 and the National High Magnetic Field Laboratory. N. L. and Y. Y. equally contributed to this work. N. L. contributed mostly to the formal and algorithmic aspects of the theory, and Y. Y. contributed mostly to the numerical implementation. X. D. performed part of the calculations of UO_2. All the authors contributed to writing the manuscript. G. K. supervised the project.

*Corresponding author.
lanata@magnet.fsu.edu
†Corresponding author.
ykent@iastate.edu

[1] A. Koga, N. Kawakami, T. M. Rice, and M. Sigrist, Phys. Rev. Lett. **92**, 216402 (2004).
[2] V. Anisimov, I. Nekrasov, D. Kondakov, T. M. Rice, and M. Sigrist, Eur. Phys. J. B **25**, 191 (2002).
[3] L. de' Medici, S. R. Hassan, M. Capone, and X. Dai, Phys. Rev. Lett. **102**, 126401 (2009).
[4] N. Lanatà, H. U. R. Strand, G. Giovannetti, B. Hellsing, L. de' Medici, and M. Capone, Phys. Rev. B **87**, 045122 (2013).
[5] V. Dobrosavljević, N. Trivedi, and J. M. Valles, Jr., *Conductor Insulator Quantum Phase Transitions* (Oxford University Press, Oxford, 2012).
[6] C. A. Marianetti, G. Kotliar, and G. Ceder, Nat. Mater. **3**, 627 (2004).
[7] A. Camjayi, K. Haule, V. Dobrosavljević, and G. Kotliar, Nat. Phys. **4**, 932 (2008).
[8] G. Kotliar and A. E. Ruckenstein, Phys. Rev. Lett. **57**, 1362 (1986).
[9] F. Lechermann, A. Georges, G. Kotliar, and O. Parcollet, Phys. Rev. B **76**, 155102 (2007).
[10] T. Li, P. Wölfle, and P. J. Hirschfeld, Phys. Rev. B **40**, 6817 (1989).
[11] M. C. Gutzwiller, Phys. Rev. **137**, A1726 (1965).
[12] J. Bünemann and F. Gebhard, Phys. Rev. B **76**, 193104 (2007).
[13] N. Lanatà, P. Barone, and M. Fabrizio, Phys. Rev. B **78**, 155127 (2008).
[14] Q. Yin, A. Kutepov, K. Haule, G. Kotliar, S. Y. Savrasov, and W. E. Pickett, Phys. Rev. B **84**, 195111 (2011).
[15] N. Lanatà, Y. X. Yao, C.-Z. Wang, K.-M. Ho, and G. Kotliar, Phys. Rev. X **5**, 011008 (2015).
[16] V. I. Anisimov, F. Aryasetiawan, and A. I. Lichtenstein, J. Phys. Condens. Matter **9**, 767 (1997).
[17] See the Supplemental Material at http://link.aps.org/supplemental/10.1103/PhysRevLett.118.126401, which includes Refs. [18–23], for operatorial construction RISB, algorithms, parametrization of the local interaction in terms of U and J, and details of the electronic structure of UO_2.
[18] N. Lanatà, H. U. R. Strand, X. Dai, and B. Hellsing, Phys. Rev. B **85**, 035133 (2012).
[19] R. Bhatia, *Positive Definite Matrices* (Princeton University Press, Princeton, NJ, 2007).
[20] F. Zhou and V. Ozoliņš, Phys. Rev. B **83**, 085106 (2011).
[21] M.-T. Suzuki, N. Magnani, and P. M. Oppeneer, Phys. Rev. B **88**, 195146 (2013).
[22] G. Amoretti, A. Blaise, R. Caciuffo, J. M. Fournier, M. T. Hutchings, R. Osborn, and A. D. Taylor, Phys. Rev. B **40**, 1856 (1989).
[23] H. Nakotte, R. Rajaram, S. Kern, R. J. McQueeney, G. H. Lander, and R. A. Robinson, J. Phys. Conf. Ser. **251**, 012002 (2010).
[24] K. Schönhammer, Phys. Rev. B **42**, 2591 (1990).
[25] A. Georges, G. Kotliar, W. Krauth, and M. J. Rozenberg, Rev. Mod. Phys. **68**, 13 (1996).
[26] V. I. Anisimov, A. I. Oteryaev, M. A. Korotin, A. O. Anokhin, and G. Kotliar, J. Phys. Condens. Matter **9**, 7359 (1997).

[27] A. I. Lichtenstein and M. I. Katsnelson, Phys. Rev. B **62**, R9283 (2000).
[28] The interplay between SOC and CFSs can generate multiple equivalent representations of the point symmetry group in the local single-particle space so that $\Sigma(\omega)$ is not made automatically diagonal by selection rules [29].
[29] E. P. Wigner, *Group Theory and Its Application to the Quantum Mechanics of Atomic Spectra* (Academic Press, New York, 1959).
[30] H. Y. Geng, Y. Chen, Y. Kaneta, and M. Kinoshita, Phys. Rev. B **75**, 054111 (2007).
[31] B.-T. Wang, P. Zhang, R. Lizárraga, I. Di Marco, and O. Eriksson, Phys. Rev. B **88**, 104107 (2013).
[32] R. Laskowski, G. K. H. Madsen, P. Blaha, and K. Schwarz, Phys. Rev. B **69**, 140408 (2004).
[33] K. N. Kudin, G. E. Scuseria, and R. L. Martin, Phys. Rev. Lett. **89**, 266402 (2002).
[34] I. D. Prodan, G. E. Scuseria, and R. L. Martin, Phys. Rev. B **73**, 045104 (2006).
[35] B. C. Frazer, G. Shirane, D. E. Cox, and C. E. Olsen, Phys. Rev. **140**, A1448 (1965).
[36] L. Huang, Y. Wang, and P. Werner, arXiv:1506.06548.
[37] Q. Yin and S. Y. Savrasov, Phys. Rev. Lett. **100**, 225504 (2008).
[38] J. Kolorenc, A. B. Shick, and A. I. Lichtenstein, Phys. Rev. B **92**, 085125 (2015).
[39] P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964).
[40] P. Blaha, K. Schwarz, G. K. H. Madsen, D. Kvasnicka, and J. Luitz, *WIEN2k: An Augmented Plane Wave Plus Local Orbitals Program for Calculating Crystal Properties*, edited by K. Schwarz Vienna University of Technology, Austria, 2001.
[41] M. Idiri, T. Le Bihan, S. Heathman, and J. Rebizant, Phys. Rev. B **70**, 014113 (2004).
[42] Smaller values of U have not been considered because, within our LDA + RISB functional, the system would result metallic for $U < 6$ eV (which is the value of the screened Hubbard interaction parameter previously computed in Ref. [43]), and, at the same time, the agreement with the experimental P-V curve would worsen.
[43] B. Amadon, T. Applencourt, and F. Bruneval, Phys. Rev. B **89**, 125110 (2014).
[44] M. S. Dresselhaus, G. Dresselhaus, and A. Jorio, *Group Theory, Application to the Physics of Condensed Matter* (Springer, New York, 2007).
[45] In this work, we adopted the so-called Koster notation.
[46] J. G. Tobin, S.-W. Yu, R. Qiao, W. L. Yang, C. H. Booth, D. K. Shuh, A. M. Duffin, D. Sokaras, D. Nordlund, and T.-C. Weng, Phys. Rev. B **92**, 045130 (2015).
[47] K. T. Moore, G. van der Laan, R. G. Haire, M. A. Wall, and A. J. Schwartz, Phys. Rev. B **73**, 033109 (2006).
[48] I. D. Prodan, G. E. Scuseria, and R. L. Martin, Phys. Rev. B **76**, 033101 (2007).
[49] C. H. Booth, S. A. Medling, J. G. Tobin, R. E. Baumbach, E. D. Bauer, D. Sokaras, D. Nordlund, and T.-C. Weng, Phys. Rev. B **94**, 045121 (2016).
[50] P. Puschnig, S. Berkebile, A. Fleming, G. Koller, K. Emtsev, T. Seyller, J. Riley, C. Ambrosch-Draxl, F. Netzer, and M. Ramsey, Science **326**, 702 (2009).
[51] J. Ziroff, F. Forster, A. Schöll, P. Puschnig, and F. Reinert, Phys. Rev. Lett. **104**, 233004 (2010).
[52] Y. Baer and J. Schoenes, Solid State Commun. **33**, 885 (1980).
[53] J. G. Tobin and S.-W. Yu, Phys. Rev. Lett. **107**, 167406 (2011).
[54] P. Santini, S. Carretta, G. Amoretti, R. Caciuffo, N. Magnani, and G. H. Lander, Rev. Mod. Phys. **81**, 807 (2009).