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AB-INITIO GUTZWILLER METHOD: FIRST APPLICATION TO PLUTONIUM

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Abstract. Using a density matrix approach to Gutzwiller method, we present a formalism to treat *ab-initio* multiband Tight-Binding Hamiltonians including local Coulomb interaction in a solid, like, for e.g., the degenerate Hubbard model. We first derive the main results of our method: starting from the density matrix of the non-interacting state, we build a multi-configurational variational wave function. The probabilities of atomic configurations are the variational parameters of the method. The kinetic energy contributions are renormalized whereas the interaction contributions are exactly calculated. A renormalization of effective on-site levels, in contrast to the usual one-band Gutzwiller approach, is derived. After minimization with respect to the variational parameters, the approximate ground state is obtained, providing the equilibrium properties of a material. Academic models will illustrate the key points of our approach. Finally, as this method is not restricted to parametrized Tight-Binding Hamiltonians, it can be performed from first principles level by the use of the so-called "Linearized Muffin Tin Orbitals" technique. To avoid double counting of the repulsion, one subtracts the average interaction, already taken into account in this density functional theory within local density approximation (DFT-LDA) based band structures method and one adds an interaction part "a la Hubbard". Our method can be seen as an improvement of the more popular LDA+U method as the density-density correlations are treated beyond a standard mean field approach. First application to Plutonium will be presented with peculiar attention to the equilibrium volume, and investigations for other densities will be discussed.

1. Introduction

Except for small molecules, it is impossible to solve many electrons systems without imposing severe approximations. If the configuration interaction approaches (CI) or Coupled Clusters techniques [1] are applicable for molecules, their generalization for solids is difficult. For materials with a kinetic energy greater than the Coulomb interaction, calculations based on the density functional theory (DFT), associated with the local density approximation (LDA) [2,3] give satisfying qualitative and quantitative results to describe ground state properties. These solids have weakly correlated electrons presenting extended states, like *sp* materials or covalent solids. The application of this approximation to systems where the wave functions are more localized (*d* or *f*-states) as transition metals oxides, heavy fermions, rare earths or actinides is more questionable and can even lead to unphysical results : for example, insulating FeO and CoO are predicted to be metalic by the DFT-LDA. On another hand, theoretical "many body" approaches like diagrammatic developments [4], slave bosons [5], decoupling of the equations of motion of Green functions by projection techniques [6], and more recently dynamical mean field theory (DMFT) in infinite dimension [7], treat in a much better way correlation effects than the DFT-LDA does. However the price to be paid is an oversimplification of the system, generally reducing the number of involved orbitals and using parameterized Hamiltonians (like Hubbard model) where the *ab-initio* aspect of the DFT-LDA is lost. Finally, these methods, contrary to the DFT-LDA, are scarcely variational. Recently several attemps have been proposed to couple these two points of view as in the LDA+U [8], or LDA+DMFT [9,10] approaches. In the same spirit, the approach we describe below, tries to keep advantages on both sides: it is a variational method which is multi-configurational, contrary to the DFT-LDA, but without loosing the "adjustable parameters free" advantages of the *ab-initio* side. The next section is devoted to the derivation of our formalism. It is then applied to known academic cases to prove the reliability of our approach. The insertion of this approach at the *ab-initio* level is presented in section 2.5. The nature of the electronic structure of Plutonium being still under discussion, the application of our method, in the last section, is in accordance with previous works and also gives some new insights for this material.

2. Method

2.1. GUTZWILLER APPROACH FOR THE ONE-BAND HUBBARD MODEL

Among numerous theoretical approaches, the Gutzwiller method [11, 12] provides a transparent physical interpretation in term of atomic configurations of a given site. Originally it was applied to the one-band Hubbard model Hamiltonian [13]:

$$H = H_{kin} + H_{int} \tag{1}$$

with

$$H_{kin} = \sum_{i \neq j, \sigma} t_{ij} c_{i\sigma}^{\dagger} c_{j\sigma} \tag{2}$$

and

$$H_{int} = U \sum_{i} n_{i\uparrow} n_{i\downarrow} \tag{3}$$

which contains a kinetic part H_{kin} with a hopping integral t_{ij} from site j to site i, and an interaction part with a local Coulomb repulsion U for electrons on the same site. $c_{i\sigma}^{\dagger}$ (respectively $c_{i\sigma}$) is the creation (respectively destruction) operator of an electron at site i with up or down spin σ. $n_{i\sigma} = c_{i\sigma}^{\dagger} c_{i\sigma}$ measures the number (0 or 1) of electron at site i with spin σ. This Hamiltonian contains the key ingredients for correlated up and down spin electrons on a lattice: the competition between delocalization of electrons by hoppings and their localization by the interaction. It is one of the most used models to study electronic correlations in solids (for a review see Ref. [14]).

In the absence of the interaction U, the ground state is that of uncorrelated electrons $|\Psi_0\rangle$ and has the form of a Slater determinant. As U is turned on, the weight of doubly occupied sites must be reduced because they cost an additional energy U per site. Accordingly, the trial Gutzwiller wave function (GWF) $|\Psi_G\rangle$ is built from the Hartree-like uncorraleted wave function (HWF) $|\Psi_0\rangle$,

$$|\Psi_G\rangle = g^D |\Psi_0\rangle \tag{4}$$

The role of g^D is to reduce the weight of configurations (i.e. a way of spreading N electrons over the lattice) with doubly occupied sites, where $D = \sum_i n_{i\uparrow} n_{i\downarrow}$ measures the number of double occupations and g (< 1) is a variational parameter. In fact, this method corrects the mean field (Hartree) approach for which up and down spin electrons are independent, and, some how, overestimates configurations with double occupied sites. Using the Rayleigh-Ritz principle, this parameter is determined by minimization of the energy in the Gutzwiller state $|\Psi_G\rangle$, giving an upper bound to the true unknown ground state energy of H. Note that to enable this calculation to be tractable, it is necessary to use the Gutzwiller's approximation which assumes that all configurations in the HWF have the same weight. Details of the derivation can be found in the article of Vollhardt [15].

Nozières [16] proposed an alternative way, showing that the Gutzwiller approach is equivalent to renormalize the density matrix in the GWF which can be reformulated as:

$$\rho_G = T^\dagger \rho_0 T \tag{5}$$

The density matrices $\rho_G = |\psi_G\rangle\langle\psi_G|$ and $\rho_0 = |\psi_0\rangle\langle\psi_0|$ are projectors on the GWF and HWF respectively. T is an operator, diagonal in the configuration basis, $T = \prod_i T_i$ and T_i is a diagonal operator acting on site i

$$T_i|L_i, L'\rangle = \sqrt{\frac{p(L_i)}{p_0(L_i)}}|L_i, L'\rangle \tag{6}$$

L_i is an atomic configuration of the site i, with probability $p(L_i)$ in the GWF and $p_0(L_i)$ in the HWF respectively, whereas L' is a configuration of the remaining sites of the lattice. Note that this prescription does not change the phase of the wave function as the eigenvalues of the operators T_i are real. The correlations are local, and the configuration probabilities for different sites are independent.

The expectation value of Hamiltonian (1) is given by

$$\langle H \rangle_G = Tr(\rho_G H) \tag{7}$$

The mean value of one-site operators (interaction U) is exactly calculated with the double occupancy probability $d_i = \langle n_{i\uparrow} n_{i\downarrow}\rangle_G$. d_i is the new variational parameter replacing g. From expressions (5) and (6), the two-sites operators contributions of the kinetic energy can be written as

$$\langle c_{i\sigma}^\dagger c_{j\sigma}\rangle_G = Tr(\rho_G c_{i\sigma}^\dagger c_{j\sigma}) = \langle c_{i\sigma}^\dagger c_{j\sigma}\rangle_0 \sum_{L_{-\sigma}} \sqrt{\frac{p(L'_\sigma, L_{-\sigma})}{p_0(L'_\sigma)}}\sqrt{\frac{p(L_\sigma, L_{-\sigma})}{p_0(L_\sigma)}} \tag{8}$$

where L'_σ and L_σ are the only two configurations of spin σ at sites i and j that give non-zero matrix element to the operator in the brackets as illustrated on Fig.1. The summation is performed over the configurations of opposite spin $L_{-\sigma}$. Their corresponding probabilities are pictured on Table 1 for an homogeneous state (for any site i, $\langle n_{i\sigma}\rangle = n$ and $\langle n_{i\uparrow} n_{i\downarrow}\rangle = d$). The probabilities p_0 in the HWF depend only on the number of electrons, whereas the p in the GWF also depend on d_i.

After some elementary algebra, one can show that the Gutzwiller mean value can be factorised:

$$\langle c_{i\sigma}^\dagger c_{j\sigma}\rangle_G = \sqrt{q_{i\sigma}}\langle c_{i\sigma}^\dagger c_{j\sigma}\rangle_0\sqrt{q_{j\sigma}} \tag{9}$$

where these renormalization factors $q_{i\sigma}$ are local and can be expressed as:

$$\sqrt{q_{i\sigma}} = \frac{\left(\sqrt{1 - n_{i\sigma} - n_{i-\sigma} + d_i} + \sqrt{d_i}\right)\sqrt{n_{i-\sigma} - d_i}}{\sqrt{n_{i\sigma}(1 - n_{i\sigma})}} \tag{10}$$
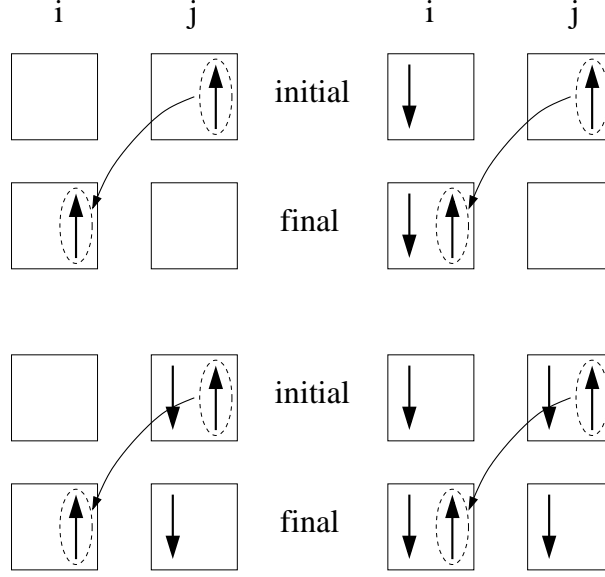
Figure 1. Initial and final configurations contributing to the mean value $\langle c^{\dagger}_{i\sigma} c_{j\sigma} \rangle_G$.

L_i	$p_0(L_i)$	$p(L_i)$
$\emptyset$	$(1-n)^2$	$1-2n+d$
$\uparrow$	$n(1-n)$	$n-d$
$\downarrow$	$n(1-n)$	$n-d$
$\uparrow\downarrow$	n^2	d

TABLE 1.   Different possible configurations of one site and the corresponding probabilities in the HWF (p_0) and GWF (p).

where $n_{i\sigma}$ is a shorthand for $\langle n_{i\sigma} \rangle$, the average number of electron on the considered "orbital-spin" in the HWF, which could be site and/or spin independent if the state is homogeneous and/or paramagnetic (it is the case we consider here for pedagogy, dropping indices $i\sigma$). The kinetic energy ϵ^0_{kin} of the non-interacting electrons state is renormalized by a factor q which is smaller than one in the correlated state, and equal to one in the HWF. Then, we minimize the variational energy

$$E(d) = \langle H \rangle_G = q\epsilon_{kin}^0 + Ud \tag{11}$$

with respect to d. In the case of half filling ($n = 1/2$), if the repulsion U exceeds a critical value $U_c = 8\epsilon_{kin}^0$, q is equal to zero, leading to an infinite quasiparticle mass with a Mott-Hubbard Metal-Insulator transition which is, in this context, often referred to as "the Brinkmann-Rice transition" [17], as these authors first applied the Gutzwiller approximation to the Metal-Insulator transition. Application of this "one orbital per site" formalism for inhomogeneous states is possible because all involved quantities are local. An example can be found in [18] for model CuO_2 planes, in connection with the electronic structure of High T_C superconductors.

2.2. INEQUIVALENT SITES: RENORMALIZATION OF LEVELS

When sites are inequivalent, or if orbitals belong to different symmetries as in a multiorbital *spdf* basis case of further sections, it is necessary to add to the Hamiltonian an on-site energy term

$$H_{on-site} = \sum_{i\sigma} \epsilon_{i\sigma}^0 n_{i\sigma} \tag{12}$$

Hence this enlarged Hubbard Hamiltonian can be written as

$$H = \sum_{i \neq j, \sigma} t_{ij} c_{i\sigma}^\dagger c_{j\sigma} + \sum_{i\sigma} \epsilon_{i\sigma}^0 n_{i\sigma} + U \sum_i n_{i\uparrow} n_{i\downarrow} \tag{13}$$

In that case, the starting HWF, directly obtained from the non-interacting part of the Hamiltonian, is not automatically the best choice, giving the optimal GWF, i.e. having the lowest energy. For example, if we look for the ground state of Hamiltonian (13) in the Hartree-Fock (HF) self-consistent field formalism, it is necessary to vary the orbital occupations. Practically, it can be achieved by replacing this Hamiltonian, by an effective Hamiltonian H_{eff} of independent particles with renormalized on-site energies $\epsilon_{i\sigma}$:

$$H_{eff} = \sum_{i \neq j, \sigma} t_{ij} c_{i\sigma}^\dagger c_{j\sigma} + \sum_{i\sigma} \epsilon_{i\sigma} n_{i\sigma} (+C) \tag{14}$$

The HWF we are looking for, is an *approximate* ground state of the *true* many-body Hamiltonian (13) and is the *exact* ground state of *effective* Hamiltonian (14). The additive constant C accounts for double counting energy reference, so that the ground state energies are the same for both Hamiltonians:

$$\langle H_{eff} \rangle = \langle H \rangle \tag{15}$$

The effective Hamiltonian depends on pararemeters $\epsilon_{i\sigma}$. The optimal choice can be obtained by minimizing the ground state energy of H_{eff} with respect

to these parameters. With the help of Hellmann-Feyman theorem, one can easily see that the derivative of the kinetic energy is

$$\frac{\partial \langle H_{kin} \rangle}{\partial \epsilon_{i\sigma}} = -\sum_{j \neq i, \sigma} \epsilon_{j\sigma} \frac{\partial \langle n_{j\sigma} \rangle}{\partial \epsilon_{i\sigma}} \tag{16}$$

On another hand, differentiation of equality (15) associated with expression (16) and the mean field approximation $\langle n_{i\uparrow} n_{i\downarrow} \rangle \approx \langle n_{i\uparrow} \rangle \langle n_{i\downarrow} \rangle$ enables to retrieve the well-known formula for the on-site energies

$$\epsilon_{i\sigma} = \epsilon_{i\sigma}^0 + U \langle n_{i-\sigma} \rangle \tag{17}$$

and the constant C is simply $-U \sum_i \langle n_{i\uparrow} \rangle \langle n_{i\downarrow} \rangle$.

In the Gutwiller approach, the same argument about the variation of orbital occupation, i.e. flexibility on the HWF $|\Psi_0\rangle$, is true. It is necessary to find a way to vary this Slater determinant from which the GWF $|\Psi_G\rangle$ is generated, so that the Gutzwiller ground-state energy is minimum. Clearly one has to find an equivalent of formula (17) in the Gutzwiller context, which has never been established, to our knowledge. The average value of Hamiltonian (13) on a GWF is given by:

$$\langle \Psi_G | H | \Psi_G \rangle = \sum_{ij\sigma} t_{ij} \sqrt{q_{i\sigma}} \langle c_{i\sigma}^\dagger c_{j\sigma} \rangle_0 \sqrt{q_{j\sigma}} + U \sum_i d_i + \sum_{i\alpha\sigma} \epsilon_{i\sigma}^0 \langle n_{i\sigma} \rangle_0 \tag{18}$$

Following the same footing of previous HF self-consistent field approach, one has to find an effective Hamiltonian H_{eff} of independent particles having $|\Psi_0\rangle$ as *exact* ground state. This state $|\Psi_0\rangle$ generates the GWF $|\Psi_G\rangle$ which is an *approximate* ground state of the true interacting Hamiltonian (13). In analogy with (15), the condition

$$\langle \Psi_0 | H_{eff} | \Psi_0 \rangle = \langle \Psi_G | H | \Psi_G \rangle \tag{19}$$

leads to the expression for the searched H_{eff}:

$$H_{eff} = \sum_{i \neq j, \sigma} \tilde{t_{ij}} c_{i\sigma}^\dagger c_{j\sigma} + \sum_{i\sigma} \epsilon_{i\sigma} n_{i\sigma} + C' \tag{20}$$

with effective but *fixed* renormalized hoppings $\tilde{t_{ij}} = \sqrt{q_{i\sigma}} t_{ij} \sqrt{q_{j\sigma}}$ and having effective on-site energies $\epsilon_{i\sigma}$ which have still to be determined. Hellmann-Feynman theorem applied to H_{eff} provides again an expression similar to (16), but with effective hoppings. Taking into account the dependence of the $q_{i\sigma}$'s through $n_{i\sigma}$ in differentiating (18) and (19) with respect to the parameters $\epsilon_{i\sigma}$, after some calculations, one obtains the equivalent expression of (17) in the Gutzwiller context:

$$\epsilon_{i\sigma} = \epsilon_{i\sigma}^0 + 2e_{i\sigma}\frac{\partial ln(\sqrt{q_{i\sigma}})}{\partial n_{i\sigma}} \tag{21}$$

Here $e_{i\sigma}$ is the partial kinetic energy of orbital-spin $i\sigma$, it is given by

$$e_{i\sigma} = \sum_{j\sigma} \tilde{t_{ij}}\langle c_{i\sigma}^\dagger c_{j\sigma}\rangle_0 = \int_{-\infty}^{E_F} E\tilde{N_{i\sigma}}(E)dE - \epsilon_{i\sigma}\langle n_{i\sigma}\rangle_0 \tag{22}$$

with $\tilde{N_{i\sigma}}$ the $i\sigma$-projected density of states (DOS) for Hamiltonian H_{eff}. The remaining constant C' that ensures (19) explicitly reads

$$C' = U\sum_i d_i - \sum_{i\sigma} 2e_{i\sigma}\frac{\partial ln(\sqrt{q_{i\sigma}})}{\partial n_{i\sigma}} \tag{23}$$

To solve the full problem of finding an approximate ground state to Hamiltonian (13), one is faced to a self-consistent loop which can be proceeded in two steps. First one can get the occupations $\langle n_{i\sigma}\rangle_0$ from a HWF, and a set of 'bare' $\epsilon_{i\sigma}^0$ levels. Then one obtains a set of configuration parameters, the probabilities of double occupation, d_i by minimizing (18) with respect to these probabilities. Afterwards the on-site levels are renormalized according to (21) and the next loop starts again for the new effective Hamiltonian H_{eff} till convergence is achieved.

As illustration of the importance of the renormalization of levels, we studied the case of an alternate Hubbard chain (often called Ionic Hubbard model). This model contains two kinds of alternating atoms A and B on an infinite chain, having on-site energies ϵ_A^0 and ϵ_B^0 respectively, coupled by a hopping integral t. The same local Coulomb repulsion U acts on each site. For a given total number of electrons, one can fix a repartition of electrons among sites A and B, and compute the energy of the ground state: first within the HF mean field approximation, and secondly, within the Gutzwiller approach. Browsing the electronic occupation of A-site, by adjunction of Lagrange multiplier to fix it to a given value, one looks for the lowest energy state. The corresponding ground state energies as function of the A-filling are presented on Fig. 2. First of all, the lowest Hartree state could be more efficiently directly found, after some self-consistent loops, via the on-site renormalization of levels of equation (17) in the HF context, as explained in precedent paragraph. By inspection of the curve, it is also obvious that this lowest Hartree does not generate the lowest Gutzwiller state. It is necessary to browse among different A-fillings to find the best Gutzwiller ground state. If this browsing procedure is still tractable for simple models, as we did in Ref. [18], its generalization to multiorbitals cases would be practically impossible. It is the main advantage of formula (21) to avoid this cumbersome search for optimized levels and to provide a systematic way of finding them, similar to (17), leading to the best (i.e. lowest) Gutzwiller ground state.
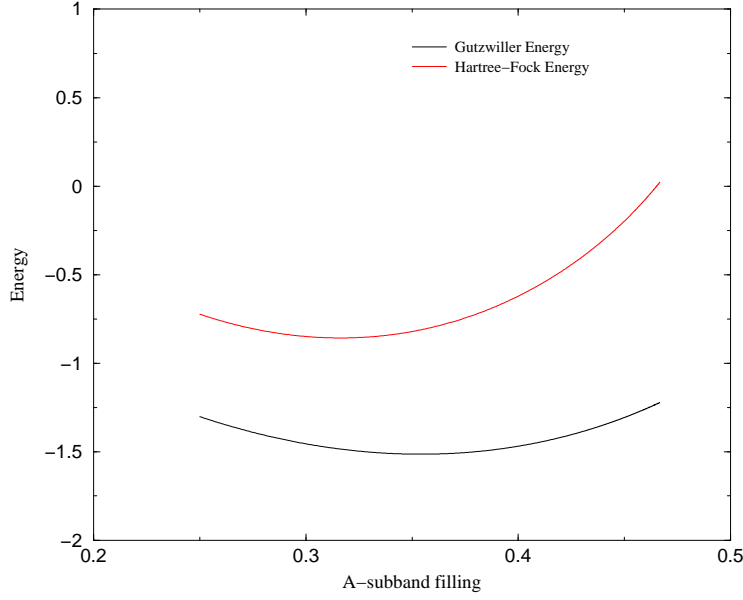
Figure 2. Total energy of the alternate chain versus A-subband filling. Upper curve: Hartree-Fock result, Lower curve: Gutzwiller result. The 2 minima are clearly different

2.3. GENERALIZATION TO THE DEGENERATE HUBBARD HAMILTONIAN

Now we generalize this density matrix formalism [19,20] for the degenerate Hubbard Hamiltonian which, with usual notations, reads:

$$H = \sum_{i \neq j \alpha \beta \sigma} t_{i\alpha, j\beta} c_{i\alpha\sigma}^\dagger c_{j\beta\sigma} + H_{\text{int}} \tag{24}$$

with the model interaction

$$H_{\text{int}} = \frac{1}{2} \sum_{i, \alpha\sigma \neq \beta\sigma'} U_{\alpha\sigma\beta\sigma'} n_{i\alpha\sigma} n_{i\beta\sigma'} \tag{25}$$

where α, β and σ, σ' are orbitals and spins index respectively, necessary to account for orbital degeneracy. The case $\alpha\sigma = \beta\sigma'$ is excluded from the interaction because of Pauli principle. We neglect any spin flip term in the interaction for simplicity. They could be in principle taken into account in our approach, as it is done in a different work by Bünemann et al [21]. However this procedure would involve a diagonalization of atomic part of Hamiltonian, that complicates the presentation of our approach without bringing any new physical ingredients.

As in the one-band case, we define a Gutzwiller renormalized density matrix with the operator T given by eqs (5) and (6). The main difference being the greater number of atomic configurations, equal to 2^{2N}, with N the orbital degeneracy. For a given site we have now probabilities for double, triple, etc... multiple occupancy, which are the new variational parameters generalizing the role of d. Of course, the number of independent variational probabilities is smaller than the number of configurations, as different configurations could have the same probabilities for symmetries reasons. For example, in a paramagnetic case, a configuration and its spin reverse are equivalent leading to the same probability. Moreover, the probabilities are not independent of each other as the sum over all probabilities have to be equal to 1, and we have also to conserve the average electronic occupation of given orbital-spin $\langle n_{i\alpha\sigma} \rangle$. These constraints could be either directly included in the expressions of empty and single occupied configurations probabilities, or treated by adjunction of Lagrange multipliers as in the slaves bosons approach [5]. This last formulation has the advantage of giving more symmetric expressions. Using the expression (6) of T_i operators, we can directly obtained the factorized form of the kinetic energy terms:

$$\langle c_{i\alpha\sigma}^{\dagger} c_{j\beta\sigma} \rangle_G = \sqrt{q_{i\alpha\sigma}} \langle c_{i\alpha\sigma}^{\dagger} c_{j\beta\sigma} \rangle_0 \sqrt{q_{j\beta\sigma}} \qquad (26)$$

where the q-factors reduce the kinetic energy and are expressed as functions of the variational parameters and the number of electrons according to:

$$\sqrt{q_{i\alpha\sigma}} = \frac{1}{\sqrt{n_{i\alpha\sigma}(1 - n_{i\alpha\sigma})}} \sum_{L_i'} \sqrt{p(i\alpha\sigma : unocc, L_i')p(i\alpha\sigma : occ, L_i')} \qquad (27)$$

Here $p(i\alpha\sigma : occ, L_i')$ (respectively $p(i\alpha\sigma : unocc, L_i')$) represents the probability of the atomic configuration of site i, where the orbital α with spin σ is occupied (resp. unoccupied) and where L_i' is a configuration of the remaining orbitals of this site. This result is similar to the expression obtained by Bünemann et $al.$ [22], but it is obtained more directly by the density matrix renormalization (5). To obtain the expression of the $q_{i\alpha\sigma}$ factors, an additional approximation to the density matrix of the uncorrelated state was necessary. This approximation can be viewed as the multiband generalization of the Gutzwiller approximation, exact in infinite dimension [23]

$$\langle LL''|\rho_0|L'L'' \rangle \approx p_0(L'') \sum_{L''} \langle LL''|\rho_0|L'L'' \rangle \qquad (28)$$

Where we have replaced an off-diagonal element of the density by its average value over the configurations L''. L and L' are configurations of one or two sites, involved in the calculation of interaction or kinetic term and L'' is the configuration of remaining sites. This approximation allows to perform calculations, and however preserves sum rules of the density matrix.

Similarly, the interaction between an electron at site i on orbital α with spin σ and an electron on orbital β with spin σ' involves a term

$$\langle n_{i\alpha\sigma} n_{i\beta\sigma'} \rangle = \sum_{L_i'} p(i\alpha\sigma : occ, i\beta\sigma' : occ, L_i') \qquad (29)$$

where L_i' is a configuration of the remaining spin-orbitals of this site, other than $\alpha\sigma$ and $\beta\sigma'$.

As illustration, we studied the academic case of paramagnetic state for doubly degenerate bands like, for instance, e_g-symmetry d-orbitals in cubic or octahedral environment. Hybridization among these degenerate orbitals is supposed to produce a kinetic energy ϵ_{kin}^0 in the uncorrelated state. We take a model interaction where the general expression (25) reduces to:

$$H_{\text{int}} = U \sum_{i\alpha\sigma} n_{i\alpha\sigma} n_{i\alpha-\sigma} + U' \sum_{i\alpha\neq\beta\sigma} n_{i\alpha\sigma} n_{i\beta-\sigma}$$
$$+ (U' - J) \sum_{i\alpha\neq\beta\sigma} n_{i\alpha\sigma} n_{i\beta\sigma} \qquad (30)$$

with two independent parameters U and U' as the relation $U - U' = 2J$ stands [24]. The interaction between electrons of same spin is reduced by the exchange integral J, which is essential to reproduce first Hund's law of maximum spin. The application of the above prescription directly leads to the variational energy:

$$E_G = 2q\epsilon_{kin}^0 + 2Ud_0 + 2U'd_1 + 2(U' - J)d_2 + 2(U + 2U' - J)(2t + f) \quad (31)$$

f and t are the quadruple and triple occupancy respectively, whereas there are three possibilities of double occupancies : d_0 (same orbital, different spin), d_1 (different orbital, different spin)and d_2 (different orbital, same spin). Some of the corresponding configurations with multiple occupancy are pictured on Table 2, followed by their probability and their interaction energy. This expression is identical to the result obtained by different authors using Gutzwiller-type wave function [25, 26], or multiband slave-boson approach [27] which is a multiorbital generalization of Ref. [5]. It is to be stressed the very physical "transparent" approach with the density matrix formalism, leading to simple expressions. Also, there is no approximation about less favorable configurations, discarded from the beginning as in Ref. [28]. For a given electronic filling, we use a Newton-Raphson procedure to minimize E_G with respect to d_0, d_1, d_2, t and f. We again choose a half filled case, and we scale all contributions in term of the kinetic energy.

On Fig. 3 we plot the probabilities of different configurations versus the direct Coulomb interaction U. It can be seen that the system undergoes a metal-insulator transition for a sufficiently high value of U, close to 9. It is easy to perform the same kind of calculation in the case of triply degenerate

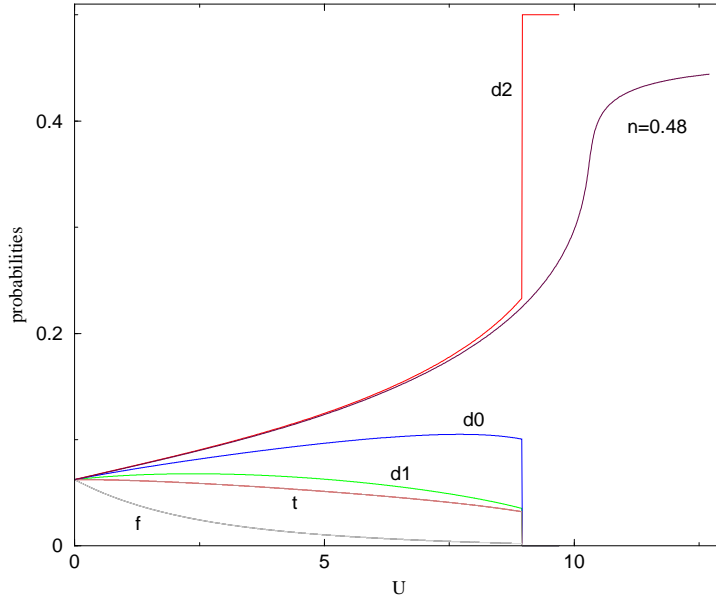|		
$\boxed{\uparrow\downarrow\ \ \big|\ \ \ }$	d_0	U
$\boxed{\uparrow\ \ \big|\ \downarrow\ }$	d_1	U'
$\boxed{\uparrow\ \ \big|\ \uparrow\ }$	d_2	$U' - J$
$\boxed{\uparrow\downarrow\ \big|\ \downarrow\ }$	t	$U + 2U' - J$
$\boxed{\uparrow\downarrow\ \big|\ \uparrow\downarrow\ }$	f	$2U + 2(2U' - J)$

TABLE 2.

Figure 3.   For the half filling case all the probabilities are equal for $U = 0$. For $U_c \sim 9$ we have a transition from the metallic to the insulator state which is of first order at half filling and second order for other concentration as seen for $n = 0.48$.

orbitals relevant for d-orbitals with the symmetry t_{2g}, (for instance Ti t_{2g} in LaTiO$_3$), f-orbitals with the symmetry T_1 or T_2 in cubic or octahedral environment (rare-earth element or actinides) or p-orbitals like in fullerene C$_{60}$.

2.4. DIFFERENT ORBITAL SYMMETRIES: FULLY HYBRIDIZED HAMILTONIAN

As our aim is to describe realistic materials from the *ab-initio* level, it is necessary to have a full set of *spd* and possibly f (for actinides or rare earths) basis. The system can be described by the following Hamiltonian which is the sum of a kinetic term, local Coulomb repulsions and an on-site contribution accounting of difference of site (and/or symmetries)

$$
\begin{aligned}
H = & \sum_{i \neq j \alpha \beta \sigma} t_{i\alpha, j\beta} c_{i\alpha\sigma}^{\dagger} c_{j\beta\sigma} \\
& + \tfrac{1}{2} \sum_{i, \alpha\sigma \neq \beta\sigma'} U_{\alpha\sigma\beta\sigma'} n_{i\alpha\sigma} n_{i\beta\sigma'} \\
& + \sum_{i\alpha\sigma} \epsilon_{i\alpha\sigma}^{0} n_{i\alpha\sigma}
\end{aligned}
\tag{32}
$$

The kinetic term is responsible of the hybridization of orbitals with different ℓ-symmetries on neignboring sites among each others. Moreover,we assume that the interaction part of the Hamiltonian H_{int} only concerns one subset of correlated orbitals (say f). All atomic configurations Γ of this subset on each site i will be considered. Note that H can be seen as a multiband hybrid between the Hubbard Hamiltonian and the periodic Anderson Hamiltonian. It contains hybridization of localized interacting f orbitals among each others (Hubbard) but also with extended *spd* states (Anderson). Using the results of previous sections, the variational energy in the Gutzwiller state reads

$$
\begin{aligned}
E_G = & \sum_{i \neq j \alpha \beta \sigma} \sqrt{q_{i\alpha\sigma}} t_{i\alpha, j\beta} \langle c_{i\alpha\sigma}^{\dagger} c_{j\beta\sigma} \rangle_0 \sqrt{q_{j\beta\sigma}} \\
& + \sum_{i, \Gamma} U_{\Gamma} p_i(\Gamma) + \sum_{i\alpha\sigma} \epsilon_{i\alpha\sigma}^{0} \langle n_{i\alpha\sigma} \rangle_0
\end{aligned}
\tag{33}
$$

In this expression the q-factors of site i are functions, through (27), of the probabilities $p_i(\Gamma)$ of the atomic configurations Γ of f-orbitals at the same site. They are equal to 1 if orbital α or β does not belong to this subset, i.e. for extended states. U_{Γ} is a proper combination of Coulomb direct and exchange contributions $U_{\alpha\sigma\beta\sigma'}$, accounting for the interaction energy which arises as prefactors of expressions (29), and which can be seen for e.g. on simplified case of (31). As in our previous simpler models, the probabilities $p_i(\Gamma)$ are the variational parameters and one has to minimize E_G with respect to each of them (and at each inequivalent site) according to

$$
\begin{aligned}
0 = \frac{\partial E_G}{\partial p_i(\Gamma)} = & \sum_{\alpha j \beta \sigma} \frac{\partial \sqrt{q_{i\alpha\sigma}}}{\partial p_i(\Gamma)} t_{i\alpha, j\beta} \langle c_{i\alpha\sigma}^{\dagger} c_{j\beta\sigma} \rangle_0 \sqrt{q_{j\beta\sigma}} \\
& + \sum_{j \beta \sigma} \sqrt{q_{j\beta\sigma}} t_{j\beta, i\alpha} \langle c_{j\beta\sigma}^{\dagger} c_{i\alpha\sigma} \rangle_0 \frac{\partial \sqrt{q_{i\alpha\sigma}}}{\partial p_i(\Gamma)} + U_{\Gamma}
\end{aligned}
\tag{34}
$$

To avoid the cumbersome calculations of all $\langle c_{i\alpha\sigma}^{\dagger} c_{j\beta\sigma} \rangle_0$ cross-terms which are present in a fully hybridized case, we propose a recursive procedure for the minimization of E_G, i.e. the search for the optimal set of probabilities. In spirit close to the impurity model of the DMFT approach, we first consider that there is only one correlated site, say $i = 0$. This site is supposed to be embedded in a reference fixed medium where all q's other than the considered site '0', are equal to 1 at beginning or to their previous values in the self-consistent process that has to be performed afterwards. Then the set of equations (34) for all configurations Γ_0 of site 0 can be rewritten as

$$\frac{\partial E_G}{\partial p_0(\Gamma)} = \sum_{\alpha\sigma} 2e_{i=0\alpha\sigma} \frac{\partial ln(\sqrt{q_{0\alpha\sigma}})}{\partial p_0(\Gamma)} + U_{\Gamma} \tag{35}$$

The partial kinetic energies $e_{i=0\alpha\sigma}$ of orbital $\alpha\sigma$ at site $i = 0$, generalizing (22), are obtained from partial projected DOS, available from any electronic structure code, and computed with site $i = 0$ embedded in the reference medium. To ensure numerical stability when solving system of eqs. (35) and according to the spirit of Landau theory of Fermi liquids, the interactions are progressively switched on from zero to their final values starting from the probabilities of uncorrelated case. After solution, the probabilities $p_0(\Gamma)$ are used to compute the local q-factors of site 0. If all sites are equivalent, one would get the same results on other sites. Accordingly, the q-factors of other sites are all set equal to the '0'-th ones (one would have to repeat this impurity-like calculation if there are inequivalent sites, i.e. crystal structures with more than one atom per cell or disordered systems). Changing the q-factors affects the partial kinetic energies $e_{i=0\alpha\sigma}$ and also the occupation of orbitals, as the reference medium now has new effective hoppings. Process must be iterated till convergence. The advantage of this way of solving iteratively eqs. (34) is that the only required ingredients to get the solutions are partial (local) kinetic energies and occupations of orbitals at site 0 directly obtained from partial DOS's. The price to be paid is a greater number of electronic structure paths. It can be easily implemented in existing codes, without searching to get cross-terms, reducing the numerical effort to adapt our method in these codes.

Finally, as in the one-band case, it is necessary to find the best Slater determinant leading to optimized effective levels. One can easily show that expression (21) can be generalized for orbital degeneracy:

$$\epsilon_{i\alpha\sigma} = \epsilon_{i\alpha\sigma}^0 + 2e_{i\alpha\sigma} \frac{\partial ln(\sqrt{q_{i\alpha\sigma}})}{\partial n_{i\alpha\sigma}} \tag{36}$$

Again, as in the one-band case, it is necessary to perform self-consistent calculations (for a given previously converged $\{p_0(\Gamma)\}$ set) till the overall convergence is reached i.e. the on-site effective levels as well as the hoppings are converged. Once achieved, the effective Hamiltonian H_{eff} can be used

to a quasiparticles description of the system as proposed by Vollhardt [15]. In fact, he has shown that the Gutzwiller method is a natural frame to obtain the parameters of the phenomenological Landau theory of Fermi liquids. One can also expect finite temperature extension of our method in analogy with [47] and references therein.

2.5. AB-INITIO APPROACH: ALTERNATIVE TO THE LDA+U METHOD

We present now how to implement such an approach in an *ab-initio* calculation of solids. The linearized muffin-tin orbital in the atomic sphere approximation (LMTO-ASA) is widely used and peculiarly suited for our purpose as the basis set has a local representation. Other *ab-initio* approaches could be used, and if they have not this local property, one could transform the basis into a Wannier representation. The LMTO method is well described elsewhere [29, 30] and we would like to remind here only the main results which are usefull for this paper. In the frame of DFT-LDA band structure calculations, the LMTO method is based on some approximations. The space is divided in atomic spheres where the potential is spherically symmetric and interstitial region where it is flat ("Muffin Tin" potential). In the Atomic Sphere Approximation (A.S.A.), the spheres radii are chosen so that the total volume of the spheres equals that of the solid. One makes a further approximation by supposing that the kinetic energy in the interstitial region is zero (without this non-essential assumption, Laplace equation, as used below, should be replaced by Helmoltz equation). In this region, the Schrödinger equation reduces to Laplace equation having regular and irregular solutions: $Y_L(\hat{r})r^\ell$ and $Y_L(\hat{r})r^{-\ell-1}$ respectively. Here $L = (\ell, m)$ represents the angular momentum index and $Y_L(\hat{r})$ the spherical harmonics in direction $\hat{r} = (\theta, \phi)$. For the sphere centered at site R and in the momentum index ℓ ($\ell = 0, 1, 2, 3$), one finds the solution $\varphi_{R\ell\nu}$ of the radial Schroedinger equation for a given energy E_ν, usually taken at the center of gravity of the occupied part of the ℓ-band and the energy derivative of $\varphi_{R\ell\nu}$ noted $\dot{\varphi}_{R\ell\nu}$. It can be shown that the corresponding orbitals $\varphi_{R\ell\nu}$ and $\dot{\varphi}_{R\ell\nu}$ are orthogonal to each other and nearly orthogonal to the core levels. It is thus possible to build a basis set of orbitals χ_{RL} centered at sphere of site R in the following way. Outside the sphere, in the interstitial region χ_{RL} is proportional to the irregular solution $Y_L(\hat{r})r^{-\ell-1}$ of Laplace equation and it is augmented (i.e. substituted according to Slater terminology) in its own sphere by a linear combination of $\varphi_{R\ell\nu}$ and $\dot{\varphi}_{R\ell\nu}$ having logarithmic derivative $-\ell - 1$ at the radius s_R of the sphere so that the orbital is continuous and derivable at the sphere boundary. In any other sphere R', the irregular solution of Laplace equation can be expanded in term of regular solutions in that sphere:

$$Y_L(\hat{r}_R)(\frac{r_R}{a})^{-\ell-1} = -\sum_{L'} \frac{1}{2(2\ell'+1)} S^0_{R'L',RL} Y_{L'}(\hat{r}_{R'})(\frac{r_{R'}}{a})^{\ell'} \qquad (37)$$

and the orbital χ_{RL} should be augmented in sphere R' with the same expansion of linear combination of $\varphi_{R'\ell'\nu}$ and $\dot{\varphi}_{R'\ell'\nu}$ having the logarithmic derivative ℓ' at the radius $s_{R'}$ of sphere R'. In (37), a is a scale factor and $S^0_{R'L',RL}$ are the so-called "structure constants" which depend only on the crystallographic structure of the material. In this basis set of the orbitals χ_{RL} both Hamiltonian and Overlap matrices can be expressed in terms of $S^0_{R'L',RL}$, and the potential parameters $\varphi_{R\ell\nu}(s_R)$, $\dot{\varphi}_{R\ell\nu}(s_R)$ and their logarithmic derivatives $D_{R\ell\nu}$ and $\dot{D}_{R\ell\nu}$ at sphere boundary. Since the structure constants $S^0_{R'L',RL}$, decreasing as $r^{-\ell-\ell'-1}$ with distance, are very long ranged for s and p orbitals, it can be more convenient to change the basis set so that the Hamiltonian can have the Tight-Binding (TB) form or any desired properties (like the orthogonality of overlap). It can be achieved by adding to the regular solution of Laplace equation an amount of the irregular solution for a given angular momentum. It is possible to choose this amount $\bar{Q}_\ell$ so that the transformed structure constants S can be screened with a short-range dependence with the distance or so that the orbitals of the transformed basis set are orthogonal (the so-called TB or most localized and orthogonal representations, respectively). With appropriate choice for $\bar{Q}_\ell$, the transformed structure constant matrix obeys to the following equation:

$$S = S^0(1 - \bar{Q}_\ell S^0)^{-1} \qquad (38)$$

Matrix elements fo the Hamiltonian can be written as:

$$H_{RL,R'L'} = C_{RL}\delta_{RL,R'L'} + \Delta^{1/2}_{RL} S_{RL,R'L'} \Delta^{1/2}_{R'L'} \qquad (39)$$

which is limited to first order in $(E-E_\nu)$ in the TB representation, whereas it is valid up to second order in the orthogonal representation (and it is even possible to add third order correction). C_{RL} determines the middle of the band "RL" and Δ_{RL} its width and the strength of hybridization. These parameters are expressed in terms of the 4 potential parameters: $\varphi_{R\ell\nu}(s_R)$, $\dot{\varphi}_{R\ell\nu}(s_R)$, $D_{R\ell\nu}$ and $\dot{D}_{R\ell\nu}$. It should be stressed that hybridization between bands of different angular moments is due to the matrix elements $S_{RL,R'L'}$ which couples RL-states to $R'L'$ ones. When these matrix elements are set equal to zero for $\ell \neq \ell'$, one obtains bands having pure ℓ character. This approximation was suggested in the standard (unscreened) representation and the resulting bands were called "canonical" bands. In that case it would be quite easy to apply single band Gutzwiller method (one equation per ℓ symmetry) without the need of the previous fully hybridized generalization. However, as we want to treat realistic bands, we do not use the canonical

bands in this paper. We use a scalar relativistic LMTO-ASA code neglecting spin-orbit coupling, with the so-called "combined corrections" which correct the ASA. The density functional formalism, before the Gutzwiller correction explained below, was treated within the LDA with the exchange and correlation potential of von Barth and Hedin [31].

The Hamiltonian of valence electrons (39), in the so-called orthogonal representation (or in the most localized representation, neglecting orbital overlap) can be mapped on a tight-binding form Hamiltonian

$$H_{LMTO} = \sum_{i \neq j \alpha \beta \sigma} t_{i\alpha,j\beta} c_{i\alpha\sigma}^{\dagger} c_{j\beta\sigma} + \sum_{i\alpha\sigma} \epsilon_{i\alpha\sigma} n_{i\alpha\sigma} \qquad (40)$$

The hoppings and on-site energies are directly outputs of the *ab-initio* calculation, as explained in Ref. [30] and by identification of expression (40) with (39), making the correspondance: $R \rightarrow i$, $L \rightarrow \alpha$. This opens the possibility of treating our approach from first principle level, without any adjustable parameters, except the interactions U. They could be however also computed from constrained LDA calculations but in the following we rather treat them as free parameters. As in (32), (40) describes a full *spd* (and possibly f as in application of this method to Plutonium, see next section) basis. The terms $\epsilon_{i\alpha\sigma}$ account for different on-site energies for orbitals with different angular momentum or lying on inequivalent sites with possible crystal field splitting between orbitals of same angular momentum, but belonging to different irreducible group representations: it is due to the on-site contribution of $S_{RL,RL}$ that arises in the TB or in the nearly orthogonal representation.

In the spirit of the Anderson model, we separate electrons into two subsystems: delocalized electrons for which the LDA is assumed to give reasonable results and localized electrons for which it is well known that the LDA can lead to unphysical results. To treat these states in a better way, and to avoid double counting, we exclude the interaction between localized electrons (f or d) already taken into account in an average way in the LDA-on-site energy

$$\epsilon_{i\alpha\sigma}^0 = \epsilon_{i\alpha\sigma}^{\text{LDA}} - U(n_f - \frac{1}{2}) \qquad (41)$$

where U is a proper combination of direct and exchange Coulomb integral giving a true one-electron Hamiltonian H_0. n_f is the average number of f (or d) electrons given by the LDA calculation. We then re-add an interaction part H_{int} " a la Hubbard" for the localized electrons and the full Hamiltonian $H' = H_0 + H_{\text{int}}$ is treated within the previously described multiband Gutzwiller approach. In fact this starting Hamiltonian H' is the same one used in the so-called "LDA+U" method [8], the difference being in the way the interaction part is treated. In the LDA+U method, it is treated

in a mean field Hartree-Fock like approach, which can be questionable in case of strong correlations. It is however a suitable way of introducing an orbital-dependent potential which is absent in DFT formalism. In our approach the correlation is treated exactly, within the approximation of the Gutzwiller ansatz. Note that our method also contains an orbital-depend potential through the renormalization of levels (36). A detailed study of the involved derivative indeed reveals an orbital filing dependence when rewriting this formula:

$$\epsilon_{i\alpha\sigma} = \epsilon_{i\alpha\sigma}^0 - \frac{2e_{i\alpha\sigma}}{n_{i\alpha\sigma}(1 - n_{i\alpha\sigma})}(\frac{1}{2} - n_{i\alpha\sigma})$$
$$+\frac{\partial}{\partial n_{i\alpha\sigma}} ln(\sum_{L_i'} \sqrt{p(i\alpha\sigma : unocc, L_i')p(i\alpha\sigma : uocc, L_i')}) \qquad (42)$$

Similarly to what happens in the LDA+U method, one sees the tendency of lowering for levels with occupation greater than one half, and a rising upwards for the less than half filled ones (the partial kinetic energy $e_{i\alpha\sigma}$ is always negative, it would be zero for a filled band). The difference with LDA+U method is the partial kinetic energy prefactor (instead of U) and other terms that come from the derivative of the empty and single occupied configurations.

The starting Hamiltonian H' has been also used to make a link between $ab\text{-}initio$ LMTO band structure calculation and a DMFT treatment of correlations for the studies of LaTiO$_3$ [9] and Plutonium [10]. This last approach, assuming infinite dimension, goes beyond our approach. We only expect to be able to describe the coherent part of the spectrum, whereas the incoherent part leading to lower and upper Hubbard subbands are not accessible in our model, however as already stressed, variationally based.

The practical scheme we proposed to perform our $ab\text{-}initio$ Gutzwiller approach is the following one. First, we perform a LDA $ab\text{-}initio$ LMTO-ASA calculation of the solid in a given crystal structure. This calculation provides the core and the valence (band) electrons contribution total energy, as well as occupations and partial kinetic energies for valence orbitals. From these ingredients, and for a given model interaction Hamiltonian, it is possible to evaluate the variational Gutzwiller energy, which will be minimized, providing an optimized set of variational configurational probabilities. Then the on-site levels are varied according to the prescription renormalization of levels (36) as well as the adjunction of q-factors (27) which modified hoppings. New partial kinetic energies and occupations are recalculated from the modified Hamiltonian H', until self-consistency is achieved. At the end of procedure, the total energy, sum of the core and band energies, is calculated, leading to the properties of the ground state. One can then change, for example, the volume and redo the whole loop to obtained the

equilibrium properties and the most favorable atomic configurations in the solid. Close to the Fermi level we can also obtain an approximate *ab-initio* description of quasiparticles spectrum which enables comparison with spectroscopy experiments for moderately correlated electron systems. That way, one has an *ab-initio* method which is multi-configurational and variational.

In this first application, we made a slight simplification, with respect to the general process described in last paragraph, for the band calculation part: starting from converged LMTO potential parameters, we build up a first order Hamiltonian in TB representation with neglect of overlap matrix (i.e. equal to unity) as explained in [32] and references therein. As our scheme only reorganizes valence (band) electrons, we make a frequently used frozen core approximation assuming that the core energy remains unaffected by this reorganization and we will now concentrate on the band energies. It is well-known that this first order Hamiltonian is accurate close to E_ν, i.e. close to the center of gravity of the occupied part of the bands. Far from it, it has the effect of a slight reduction of the bandwidth, but we have verified that it has a negligible effect on integrated quantities: for example, before the Gutzwiller process is switched on, we have checked that the band energies calculated from the third order Hamiltonian and from the first order one with the recursion process described below, are in excellent agreement. We used a full *spdf* basis set with hoppings up to second nearest neighbors. For all 7 inequivalent orbitals, in cubic environment from the overall 16 orbitals, we performed a real space recursion procedure [33] to get the partial projected densities of states (DOS) from which all needed quantities, like occupancies or band energies, can be calculated. These partial DOS are obtained from the imaginary part of diagonal elements of a Green function, which are developed in a continued fraction expansion up to a given level. This level is chosen so that a convergence criterium is reached, i.e. adding one more level does not affect the result. Practically we took 40 steps of recursion. Various terminators (the well-known square root terminator, or more elaborated ones in presence of gaps [34]) are then used to close the continued fraction expansion. A full self-consistent approach within the Gutzwiller loop, using third order Hamiltonians and including spin-orbit coupling, is still in preparation, and some intermediary results will be given in next section.

3. Application to Plutonium

We now give a simple application of the present method to Plutonium which is a good test case. Pu lies between light actinides with itinerant $5f$ electrons and heavy actinides with localized $5f$ electrons. The competition between these two electronic regimes in Pu is responsible for a lot of unusual properties as large values of the linear term in the specific heat coefficient and of the electrical resistivity or a very complex phase diagram.

The ground state α phase (monoclinic with 16 atoms by cell) is known to be well described by *ab-initio* DFT-LDA calculations, whereas for the high temperature δ phase (fcc), the calculated equilibrium volume is of the order of 30 percent smaller than the experimental one. It is very important to reproduce the properties of Pu to take into account the delicate balance between the itinerancy of the f electrons and the large intra atomic Coulomb interaction. This requires a much more complicated theory for the electrons than the LDA which is like a mean-field treatment of the correlations [35]. Recently several attempts to go beyond LDA have given a new understanding of the α-δ transition. In the LDA+U method [36] an orbital-dependent correction, treated in the mean-field approximation is added to the LDA functional. These calculations have showed how the equilibrium volume is improved in comparison to previous results using LDA, and how an augmentation of the orbital moment is observed following Hund's rules, reducing the total magnetic moment in agreement with experiments. Going a step beyond the LDA+U, Savrasov *et al* [37] have used an implementation of DMFT. The LDA+U can be viewed as the static approximation of the DMFT. With this dynamical treatment of the f-electrons they have recovered the experimental equilibrium volume of δ-Pu, the photoemission peak at the Fermi level and given an understanding picture of the transition between α and δ phases. Different approaches, using the spin-polarized generalized gradient approximation (GGA) and antiferromagnetic configurations [38–40] have well reproduced the ground state properties of δ-Pu. All these works show how a spin/orbital polarization is crucial to describe the δ-phase. In the Gutzwiller method, the correlations, via the q-factors, are supposed to reduce the hoppings, and so to weaken the covalency character of the bonding, and consequently the attraction between atoms. Thus we expect to increase the interatomic distance, leading to a greater equilibrium volume. Of course, the same approach has to be performed for α and δ phase.

An extra difficulty arises from the Atomic Sphere Approximation (ASA) of the LMTO method: the atomic potential, inside an atomic "muffin-tin" sphere, is spherized, or equivalently, the true "full" potential is approximated by its first $\ell = 0$ component. This approximation greatly simplifies the calculation, as the wave function basis in a sphere, used to build the LMTO set, can be factorized in a product of a radial wave function and a spherical harmonics as explained above. It presents however the shortcomings that, it is not a "full potential" approach and forbids to change the symmetry when making comparison between structures. We overcome this difficulty here by performing the calculation in a fcc structure browsing different volume: it is correct for the δ phase, but the α phase will be replaced by a "pseudo"-α phase, in a fcc structure, having however the same density than the experimental one.

The valence states taken into account in the LMTO part were the $7s$, $6p$,

$6d$, $5f$ of Pu with 16 fully hybridized orbitals per site, the remaining orbitals being treated as core states. In this first approach, as we concentrate more on the correlation effects, we neglect, however important for this heavy element, the spin-orbit coupling. The crystal field splitting on f orbitals (and other ones), is directly accounted by the LMTO method, lifting the f degeneracy in the 6-fold (including spin) T_1, the 6-fold T_2 and 2-fold A_2 symmetries. Finally, the interaction H_{int}, added to H_0, is simply given by the same local term between electrons on different f-orbitals

$$H_{\text{int}} = \frac{U}{2} \sum_{i,\alpha\sigma \neq \beta\sigma'} n_{i\alpha\sigma} n_{i\beta\sigma'} \qquad (43)$$

neglecting any exchange term as done in [36,37]. In this simplified paramagnetic version, the number of inequivalent atomic configurations, necessary to perform the Gutzwiller part, reduces to 14 because all atomic configurations having the same electronic occupancy are equivalent in this model. Similarly, we took an average occupation per f orbital in the expression of q-factors, leading to a single q for all f orbitals, regardless to crystal field splitting. It was, however, included for the on-site levels renormalization, since the partial kinetic energy and occupations are not exactly equal for different symmetries. We have nevertheless checked this assumption by performing a much heavy calculation, including 3 different q's, one per crystal symmetry with 7x7x3 = 147 variational parameters: the final result was not sensitive to this detail. It reflects the small f-crystal field splitting in Plutonium, producing very similar occupations and partial kinetic energies.

The Coulomb interaction U could be also provided by constrained LDA calculations. In that sense, it would not be an adjustable parameter. However, we did not recalculate its value and took it from literature, close to 0.3Ry, as in the LDA+DMFT calculation of Savrasov et al. [10], or as in the LDA+U calculation of Bouchet et al. [36]. An improved version of calculation, including exchange interaction, as in the degenerate Hubbard model, with one q-factor per symmetry, will be used in a forthcoming paper, in which we will investigate also ferromagnetic and antiferromagnetic ground states. In this work we just want to appreciate the effect of our method and of the Gutzwiller approximation on a simple case,where there exists known results with other methods.

The total energy versus volume for fcc-Pu and different values of the interaction U is presented in Fig. 4. The curve $U = 0$ corresponds to a LDA calculation. As previously found in several works the minimum of this curve is very low ($\sim$ 7.70 ua) compared to the experimental value of the δ phase (8.60 ua) and closer to the α phase value (8.0 ua). In fact there is no sign of the correlated δ phase in the $U = 0$ calculation. As we turn on the correlations, a new feature appears in the curves, almost instantly. We observe a new energy minimum close to the experimental volume of the δ

phase. Moreover the first minimum increases to approach the value of the experimental α volume, showing that correlations are already important to reproduce the properties of this phase. For a value of U close to 0.3 Ry, the two minimums correspond to the experimental values of α and δ-Pu. This double-well feature of the total energy curve of Pu was previously discovered by Savrasov *et al* [10], using a DMFT approach. In our calculations the first minimum is the lower one, since the α phase is the ground state for Pu, and we haven't added any temperature effect in our calculations. As U increases we see a tendency of the two minimums to be closer. In fact the energies of the two phases are very similar and a small perturbation, for example the temperature, can be sufficient for the phase transition. Of course the model studied in this work is still very simple and we don't want to conclude too far but we think that it already contains the key ingredients (competition between localization and delocalization, atom-like or bands-like descriptions) to reproduce the main characteristics of Plutonium phase diagram. Due to the roughness of our first approach, the (rather) good agreement for the equilibrium properties, may be incidental or due to some compensation effect, and the disagreement with other aspects (like bulk modulus, see below) is not surprising. Indeed, it is well known the the spin-orbit coupling is a key ingredient for this element: the splitting between 5/2 and 7/2 states could give significant differences in occupation and kinetic energies. One may expect then a difference between $q_{5/2}$ and $q_{7/2}$, and obtain localized and less localized behaviors as suggested by Pénicaud [41] who proposed to split f states between localized and more delocalized ones to explain the properties of Plutonium. The freezing of f-states to similar occupation in our present calculation could be responsible for the high value of the bulk modulus (637 GPa) we get, in contrast with the experimental value of 30 GPa [42]. Primary result with an improved version involving third order LMTO Hamiltonian full self-consistent computation, neglecting yet spin-orbit coupling, reduces this value to 196 GPa, which is slightly better than the LDA result of 214 GPa [43].

This *ab-initio* Gutzwiller approach is able to handle correctly the correlation aspects without loosing the *ab-initio* adjustable parameters free aspect of the more familiar DFT-LDA, and that way, corrects the deficiency of this method. It gives similar results to the methods that account for many-body effects like the LDA+DMFT of Ref. [10] from the *ab-initio* levels or that can have an orbital dependent potential like in the LDA+U calculation of Ref. [36], which is impossible to DFT-LDA approach. On another hand, we stress again that our approach is clearly variational, and is able to provide an approximate ground state in contrast with those of Refs. [10] and [36].

The effective optimized Hamiltonian H', was used to compute quasiparticles density of states, in the vicinity of Fermi energy. The result, shown on Fig. 5, is restricted to an energy window of 2eV on both sides of Fermi
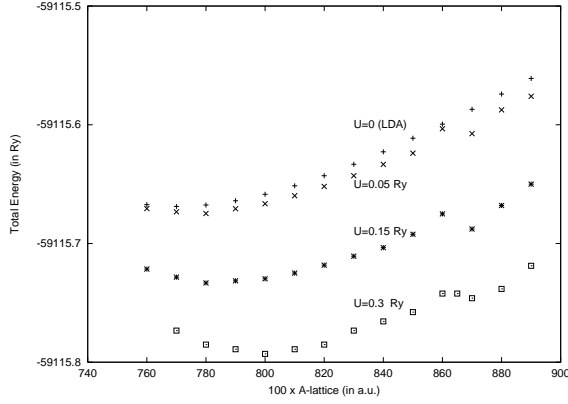
Figure 4. Total energy of fcc-Pu versus volume for different values of the interaction U. $U = 0$ corresponds to a LDA calculation.
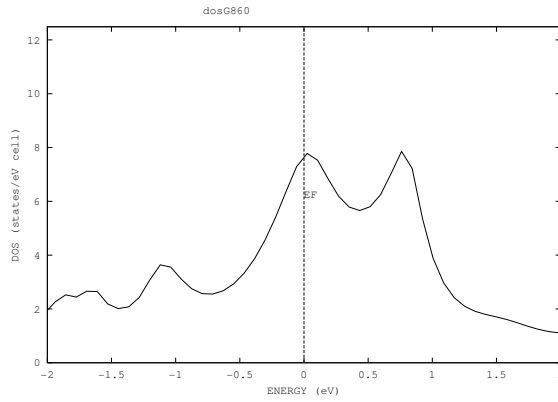

Figure 5. Quasiparticles density of states obtained from Gutzwiller method for Plutonium in δ phase.

level: further, the spectrum would be in the region of the Hubbard sub-bands, which are beyond the scope of our approach (it should be necessary to include fluctuations to get the incoherent part of the spectrum). It is to be stressed that our result compares well, in the presented region, with the more elaborated LDA+DMFT result of Ref. [10]. Both results are also in good agreement with the photoemission experiments of Arko et al. [44]. The peak at the Fermi level, which results mainly from the reduction of hoppings due to q-factors, associated with a small shift of Fermi level due to the renormalization of levels (36), has the consequence of a significant improvement of the electronic specific heat contribution, multiplied by a factor of 2 with respect to the LDA value. Our result, of the order of 13 mJ K^{-2} mol^{-1}is however yet far from the experimental value of 64 mJ K^{-2}

mol^{-1} found by Lashley *et al* [45]. The q-factor, responsible for this increase of the DOS at the Fermi level, is of the order of 0.8 in the equilibrium δ phase. This moderate renormalization is due to hybridization of the f states with the low lying p-states which lead to a significant partial f kinetic energy, greater than what it would be considering only the narrow group of predominant f-character states. With a naive single f-band argument, if we had used for example canonical (i.e. unhybridized) bands, one obtains a much reduced q-factor close to .3 [46]. It can be shown that the q-factor is the spectral weight of the quasiparticles. A moderate value, as obtained by our realistic calculation (i.e. fully hybridized bands), means a rather high weight: for independent particles it would be equal to one. It validates a quasiparticles picture description, allowing *a posteriori* comparison we did with spectroscopy experiments. At the volume of the "pseudo" α phase, this q factor reduces to .9, indicating that the electrons are less correlated in this phase, which can explain the relative success of its description by LDA calculation.

4. Conclusion

To conclude, we have generalized the density matrix approach to Gutzwiller method for the degenerate Hubbard Hamiltonian. We have shown that we can express the total energy in the Gutzwiller state in terms of the different probabilities of configurations. Moreover to apply the method to cases of physical interest we have developed this method for inequivalent sites and for different orbital symmetries. In this way we have given the expression of the different q factors which renormalize the hopping terms and an expression to renormalize the on-site energies in the Gutzwiller context. This method is limited to ground state properties but can extend to finite temperature and low-frequency excitations in analogy with the work of Gebhard [47]. Of course, as a quasiparticle approach, this method is limited to cases where the Fermi-liquid theory is valid, i.e. close to Fermi energy. Thereafter we have have described a simple implementation of our method in a *ab-initio* calculation as the LMTO method. To give an example, we have applied this technique to the particular case of Pu in fcc structure. In despite of the simplicity of our model, we were able to extract interesting results such as the double-well feature in the energy-volume curve and more generally improve the LDA results. Our results compare well with previous works.

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