

Combining the hybrid functional method with dynamical mean-field theory

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Abstract – We present a new method to compute the electronic structure of correlated materials combining the hybrid functional method with the dynamical mean-field theory. As a test example of the method we study cerium sesquioxide, a strongly correlated Mott band insulator. The hybrid functional part improves the magnitude of the *pd*-band gap which is underestimated in the standard approximations to density functional theory while the dynamical mean-field theory part splits the *4f*-electron spectra into a lower and an upper Hubbard band.

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Introduction. – Recently, there has been considerable progress in the realistic description of strongly correlated materials by combining the density functional theory [1] (DFT) with the dynamical mean-field theory (DMFT) [2–5]. In this DFT+DMFT approach [6,7], DFT is employed to obtain an effective mean-field description of the weakly correlated bands while the local correlations in the more strongly correlated bands (*i.e.* the *d*-bands of transition metals and the *f*-bands of lanthanides and actinides) are treated exactly. The DFT+DMFT method allows to predict spectra and energies of strongly correlated materials.

The DFT+DMFT method has been successfully applied to a variety of interesting materials that the conventional band structure theory is unable to deal with. For example, using the DFT+DMFT method the 25% of volume increase in the transition from the α - to the δ -phase of Pu could be explained by the presence of strong correlations in δ -Pu [8]. However, by construction the DFT+DMFT approach, does not work so well in situations where the one-electron spectra of the weakly correlated bands are not well approximated by the Kohn-Sham (KS) spectra of DFT. For example, the local density approximation (LDA) and the generalized gradient approximation (GGA) notoriously underestimate the magnitudes of band gaps of insulating materials. On the other hand, within the chemistry community, very accurate functionals called hybrid functionals [9], have been constructed by mixing LDA/GGA functionals with

Hartree-Fock. The hybrid functional (HYF) approach has been tremendously successful in providing very accurate energies for molecules. Moreover, one-electron spectra computed with HYFs give fairly accurate gaps for semiconducting materials [10].

In this work we propose a new method that combines the HYF approach with DMFT (HYF+DMFT) to yield a quantitatively *and* qualitatively correct description of combined band and Mott-Hubbard insulators. The HYF part improves the effective static mean-field description of the uncorrelated electrons while the DMFT part describes the dynamical local electronic correlations of the strongly localized electrons that can lead to Mott insulating behaviour. Although the HYF approach introduces a new parameter, α , that determines the amount of Hartree-Fock exchange, we show that this α can actually be linked to the Coulomb repulsion parameter U of the DMFT calculation.

An important example which illustrates the need for the HYF+DMFT method is provided by the rare-earth sesquioxides [11] series which are insulators. In addition to the Mott-Hubbard gap between the occupied and the unoccupied *4f*-bands, a band gap between the uncorrelated O *2p*- and *5d*-bands opens. One thus has to deal with the two-fold problem of finding an accurate description for the *pd*-band gap and the *4f* Hubbard bands in the same material.

DFT and related static mean-field methods fail to describe the splitting of the *4f* Hubbard band, without invoking some form of magnetic long-range order. For example, HYFs give the correct magnitude for the band

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gap of antiferromagnetic (AF) Ce_2O_3 [12,13]. However, the symmetry breaking is essential to obtain the correct insulating behaviour although it is clear that the magnetism should not be the driving mechanism behind the insulating behaviour since the Néel temperature is only 9 K and thus much smaller than the measured gap of about 2.5 eV. Similarly, symmetry breaking is crucial in order to capture the insulating behaviour of Ce_2O_3 and of Ce_2S_3 with the DFT + U method [14–17]. However, a satisfactory description of Ce_2O_3 should also yield the correct insulating behaviour in the paramagnetic phase.

Correlations on top of DFT, can be added within the DFT + DMFT method. Indeed recent studies of the rare-earth oxides have been carried out within this approach. The DFT + DMFT [18] approach, successfully describes the opening of the Hubbard band in the $4f$ -shell of these materials. However, they underestimate the pd -band gap. It is natural then to combine the virtues of the HYF and the DMFT method, in a HYF + DMFT approach, which is the subject of this paper.

Method. – The HYF + DMFT method follows the well-established DFT + DMFT methodology. We focus on the one-particle Green’s function:

$$\hat{G}(\mathbf{k}, \omega) = (\omega + \mu - \hat{H}(\mathbf{k}) - \hat{\Sigma}(\omega))^{-1} \quad (1)$$

which is expressed in terms of a one-body Hamiltonian $\hat{H}(\mathbf{k})$ and a local self-energy $\hat{\Sigma}(\omega)$. The self-energy describes the dynamic electron correlations of the strongly localized electrons and thus has non-zero elements only in the block of correlated bands. The correlations are captured by a Hubbard-like term which is added to the one-body Hamiltonian $\hat{H}(\mathbf{k})$ in the strongly correlated subspace:

$$\hat{H}_U = \frac{1}{2} \sum_{\substack{a_1, b_1, \sigma_1 \\ a_2, b_2, \sigma_2}} U_{a_1 a_2 b_1 b_2} \hat{c}_{a_1 \sigma_1}^\dagger \hat{c}_{a_2 \sigma_2}^\dagger \hat{c}_{b_2 \sigma_2} \hat{c}_{b_1 \sigma_1}, \quad (2)$$

where the indices a_1, a_2, b_1, b_2 denote orbitals of the correlated subspace in a local basis set.

Within DFT + DMFT the one-body Hamiltonian $\hat{H}(\mathbf{k})$ is given by the effective KS Hamiltonian $\hat{H}_{\text{ks}} = -\frac{\hbar^2}{2m} \nabla^2 + v_{\text{ext}}(\mathbf{r}) + v_{\text{h}}(\mathbf{r}) + v_{\text{xc}}(\mathbf{r})$. The KS Hamiltonian gives an effective one-body description of the electronic structure taking into account the Coulomb interaction on a mean-field level by the Hartree potential v_{h} and the exchange correlation (XC) potential v_{xc} .

One of the main shortcomings of the standard approximations to DFT like LDA and GGA is their difficulty to describe insulating materials. On the one hand, the insufficient cancellation of the self-interaction error by the approximate LDA and GGA XC functionals results in band gaps that are generally too small compared to the measured band gaps in semiconductors and insulators [10]. On the other hand, DFT is strictly speaking only a ground-state theory. Thus it does not necessarily

give a correct description of excited-state properties like the band gap of insulating materials.

The HYF method [9] improves on LDA/GGA by introducing a fraction α of exact Hartree-Fock exchange into the XC potential:

$$\hat{v}_{\text{xc}}^{\text{hyf}} = \alpha \hat{v}_{\text{x}}^{\text{hf}} + (1 - \alpha) \hat{v}_{\text{x}}^{\text{gga}} + \hat{v}_{\text{c}}^{\text{gga}}, \quad (3)$$

where $\hat{v}_{\text{x}}^{\text{gga}}$ is the LDA/GGA exchange potential and $\hat{v}_{\text{c}}^{\text{gga}}$ is the LDA/GGA correlation potential. $\hat{v}_{\text{x}}^{\text{hf}}$ is the Hartree-Fock exchange potential which is a non-local (*i.e.* non-diagonal in real space) effective one-body potential:

$$v_{\text{x}}^{\text{hf}}(\mathbf{r}, \mathbf{r}') = \langle \mathbf{r} | \hat{v}_{\text{x}}^{\text{hf}} | \mathbf{r}' \rangle = -\frac{1}{2} \rho(\mathbf{r}, \mathbf{r}') V_{\text{ee}}(\mathbf{r} - \mathbf{r}'), \quad (4)$$

where $\rho(\mathbf{r}, \mathbf{r}')$ is the density matrix and $V_{\text{ee}}(\mathbf{r} - \mathbf{r}') = \langle \mathbf{r}, \mathbf{r}' | \hat{V}_{\text{ee}} | \mathbf{r}, \mathbf{r}' \rangle = 1 / \|\mathbf{r} - \mathbf{r}'\|$ is the bare Coulomb interaction between two electrons.

One can think loosely of the HYF approach as a first-order correction of the KS Hamiltonian in a fraction α of the bare Coulomb interaction \hat{V}_{ee} . This $\alpha \hat{V}_{\text{ee}}$ can be interpreted as a “screened Coulomb interaction” in a similar way as the U -parameter in the LDA + U method [14,19]. But in contrast to the LDA + U method, HYFs make the correction in the screened Coulomb interaction on the *entire* LDA/GGA Hamiltonian and not only within a small subspace of atomic orbitals. Also note that the XC potential of the HYF method is non-local (*i.e.* dependent on both \mathbf{r} and \mathbf{r}' instead of \mathbf{r} alone) due to the contribution of exact Hartree-Fock exchange to the HYF. This shows that the HYF approach really falls outside the framework of conventional DFT where the XC potential is required to be local.

It turns out that the optimal amount α of Hartree-Fock exchange is almost universally of 20%–25% which has been rationalized by perturbation theory [20]. In the following we employ a functional similar to the popular B3LYP and B3PW functionals of quantum chemistry [21] that mix 20% of Hartree-Fock exchange with 80% of GGA exchange functionals but instead of GGA we employ plain LDA here and refer to this HYF as LDA20.

By adding the Hubbard term (2) to the KS band structure some of the Coulomb interaction within the correlated subspace is double-counted since it has already been taken into account on a static mean-field level by the KS Hamiltonian \hat{H}_{ks} . Thus, the KS Hamiltonian has to be corrected by a double-counting correction (DCC) term:

$$\hat{H}(\mathbf{k}) = \hat{H}_{\text{ks}}(\mathbf{k}) - \hat{h}_{\text{dc}}. \quad (5)$$

In the case of LDA/GGA an exact expression for this DCC term \hat{h}_{dc} is not known, and several forms of the DCC have been suggested [22]. In the case of HYFs, however, at least the DCC for the Hartree-Fock contribution to the HYF is known exactly: it is the Hartree potential \hat{v}_{h} plus the Hartree-Fock exchange potential $\hat{v}_{\text{x}}^{\text{hf}}$ projected onto the correlated subspace. Below we argue that this

is the only relevant contribution to the DCC term of the HYF + DMFT approach. However, we cannot prove this conjecture strictly so that ultimately it must be justified by its success in the application to different materials.

Our argument goes as follows: bearing in mind that the HYF approach corresponds to a first-order correction of the effective LDA Hamiltonian in a fraction α of the bare Coulomb interaction \hat{V}_{ee} , one first has to remove entirely this perturbation correction in $\alpha\hat{V}_{ee}$ in the correlated subspace since the DMFT calculation will treat the Coulomb interaction (locally) exact in that subspace. Thus if we take $\alpha V_{abcd} = \alpha \langle ab | \hat{V}_{ee} | cd \rangle$ as the screened Coulomb interaction U_{abcd} in the correlated subspace we obtain for the DCC of the HYF approach:

$$\langle a\sigma | \hat{h}_{dc}^{\text{hyf}} | b\sigma \rangle = \alpha \langle a\sigma | \hat{v}_h + \hat{v}_x^{\text{hf}} | b\sigma \rangle + \langle a\sigma | \hat{h}_{dc}^{\text{ldac}} | b\sigma \rangle, \quad (6)$$

where the last term $\langle a\sigma | \hat{h}_{dc}^{\text{ldac}} | b, \sigma \rangle$ corrects the double-counting in the LDA correlation potential \hat{v}_c^{lda} within the correlated subspace. This term is not known exactly since the contribution of a subspace to the total LDA correlation potential cannot be calculated exactly. However, the correlation potential is usually much smaller than the exchange potential, and we will thus neglect this contribution here.

Assuming that only the direct Coulomb interactions $U = U_{abab}$ and the exchange Coulomb interactions $J = U_{abba}$ are important, we find the following simplified term for the on-site HYF DCC which allows us to predict the positions of the strongly correlated orbitals for the DMFT calculation:

$$\langle a\sigma | \hat{h}_{dc}^{\text{hyf}} | a\sigma \rangle \approx U(N_f - n_a^\sigma) - J(N_f^\sigma - n_a^\sigma), \quad (7)$$

where N_f is the total number of correlated electrons per atom and n_a^σ is the number of electrons in atomic orbital a with spin σ . Equation (7) is different from the usual expression for the LDA DCC in that the HYF DCC term becomes now orbital dependent so that unoccupied orbitals experience a larger shift than occupied ones. Also note that since the Hartree-Fock potential is non-local (*i.e.* non-diagonal in real space) the DCC term is also non-local. But by construction the DCC term only acts on the correlated subspace.

Within DMFT the self-energy is determined self-consistently by mapping the original problem onto an Anderson impurity problem. To this end the local Green's function,

$$\hat{G}_{\text{loc}}(\omega) = \sum_{\mathbf{k}} (\omega + \mu - \hat{H}(\mathbf{k}) - \hat{\Sigma}(\omega))^{-1} \quad (8)$$

projected onto the correlated subspace is equated to the Green's function of the equivalent impurity problem:

$$\hat{G}_0(\omega) = (\omega + \mu - \hat{H}_0 - \hat{\Delta}(\omega) - \hat{\Sigma}_f(\omega))^{-1} \quad (9)$$

Here \hat{H}_0 is the (single-particle) Hamiltonian of the impurity site, $\hat{\Delta}(\omega)$ is the hybridization function with the

conduction bath electrons, and $\hat{\Sigma}_f = \hat{P}_f \hat{\Sigma} \hat{P}_f$ is the full self-energy projected onto the correlated subspace where \hat{P}_f is the projection operator for the correlated subspace. The mapping $\hat{G}_0(\omega) \equiv \hat{P}_f \hat{G}_{\text{loc}}(\omega) \hat{P}_f$ defines the so-called self-consistency condition which is central to the DMFT method. The mapping yields the hybridization function,

$$\hat{\Delta}(\omega) = \omega + \mu - \hat{H}_0 - \hat{\Sigma}_f(\omega) - (\hat{P}_f \hat{G}_{\text{loc}}(\omega) \hat{P}_f)^{-1} \quad (10)$$

with $\hat{H}_0 \equiv \sum_{\mathbf{k}} \hat{P}_f \hat{H}(\mathbf{k}) \hat{P}_f$. These are the relevant quantities for solving the impurity problem. By solving the impurity problem, one obtains in turn the self-energy $\hat{\Sigma}(\omega)$. Equations (8)–(10) define the self-consistent DMFT procedure for computing the self-energy $\hat{\Sigma}(\omega)$.

Solving the impurity problem given by (9) is the computationally most demanding step in most DMFT calculations. A variety of solvers—each suitable for a certain region of parameters—is available to deal with the impurity problem. An overview over the different techniques can be found in, *e.g.*, ref. [5]. Since we are interested in describing a Mott insulator a suitable method for solving the impurity problem is an expansion in the hybridization strength in the so-called non-crossing approximation (NCA) [23].

Results. – In order to show how the HYF method efficiently improves the gap of band insulators in comparison with conventional DFT methods we first perform LDA and HYF calculations of La_2O_3 which is similar to Ce_2O_3 but does not have the strongly correlated $4f$ -electrons. It is a typical band insulator with a reported band gap of about 5.5 eV between the O $2p$ valence band and the La $5d$ conduction band [11]. For the LDA and HYF calculations we employ here and in the following LDA + DMFT and HYF + DMFT calculations of Ce_2O_3 the CRYSTAL06 *ab initio* electronic structure program for crystalline solids [24] together with a Gaussian basis set and pseudo potential by Cundari and Stevens tailored for the rare-earth series elements [25]. The basis set retains the $4f$, $5s$, $5p$, $5d$, $6s$ and $6p$ shells for the electronic-structure calculations while the inner shells are described by an effective core pseudo potential. In the self-consistent LDA and HYF calculations the irreducible Brillouin zone is sampled by 193 k -points while in the DMFT calculations the entire Brillouin zone is sampled by 1000 k -points. The DMFT calculations are performed at a finite temperature of $k_B T = 0.2$ eV. The LDA + DMFT and HYF + DMFT calculations are not fully self-consistent in the charge density [18].

Figure 1 shows a comparison between the density of states (DOS) calculated with a pure LDA functional, on the one hand, and the LDA20 HYF, on the other hand. While in the LDA calculation the magnitude of the band gap is underestimated as expected by more than 1.5 eV, the HYF calculation does indeed give the experimental value of the band gap of about 5.5 eV.

We would like to stress here that changing the LDA or GGA functional part of the HYF does not alter the

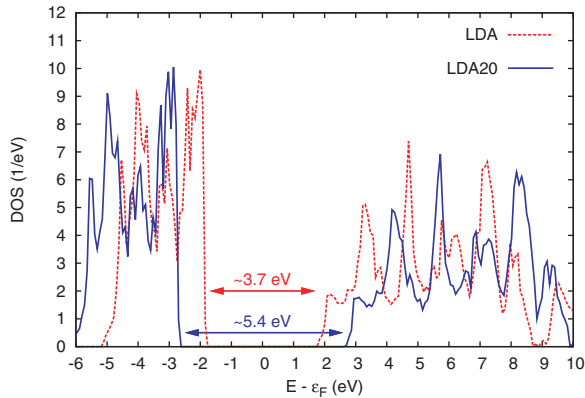


Fig. 1: (Color online) DOS of La_2O_3 calculated with an LDA functional (dashed red line) and with the LDA20 HYF (continuous blue line).

results significantly. In fact, we have obtained very similar results and the correct magnitude of the band gap also with the popular B3LYP or B3PW functionals. In contrast the results depend quite strongly on the exact amount of Hartree-Fock exchange. Thus increasing the amount of Hartree-Fock exchange to 25% already increases the magnitude of the band gap to about 6 eV.

To demonstrate the above-developed HYF + DMFT method we apply it now to the exemplary case of Ce_2O_3 . As before we employ the LDA20 HYF which reproduces correctly the band gap of La_2O_3 . The starting point is a HYF calculation of the paramagnetic phase of Ce_2O_3 which results in a metallic state with the Fermi level in the $4f$ -band. In order to prevent excessive symmetry breaking of the Ce $4f$ -orbitals prior to the DMFT calculations, the calculation is done at a finite temperature of $k_B T \approx 0.5$ eV.

In spite of the quite high temperature and although the crystal field splitting is actually quite weak (of order 0.1 eV), the *orbital* symmetry of the $4f$ -orbitals has been broken: the energy difference between the lowest and the highest $4f$ -orbital is about 1.2 eV. The reason for the symmetry breaking is the Hartree-Fock contribution to the HYF which tends to break symmetries to lower the energy of the system so that those $4f$ -orbitals that are slightly favored by the weak crystal field splitting become more occupied during the self-consistent solution of the KS equations while those unfavored by the crystal field splitting become less occupied. Therefore the splitting is strongly enhanced by the Hartree-Fock term. Since the Hartree-Fock term is the principal responsible for the symmetry breaking the energy difference between the lowest and the highest $4f$ -orbital is reduced to 0.4 eV when applying the HYF DCC scheme outlined above, partially restoring the symmetry. This can be understood by considering the orbital dependence of the HYF DCC (7) which shifts occupied orbitals less than unoccupied orbitals decreasing the symmetry breaking. At lower temperatures the symmetry breaking becomes

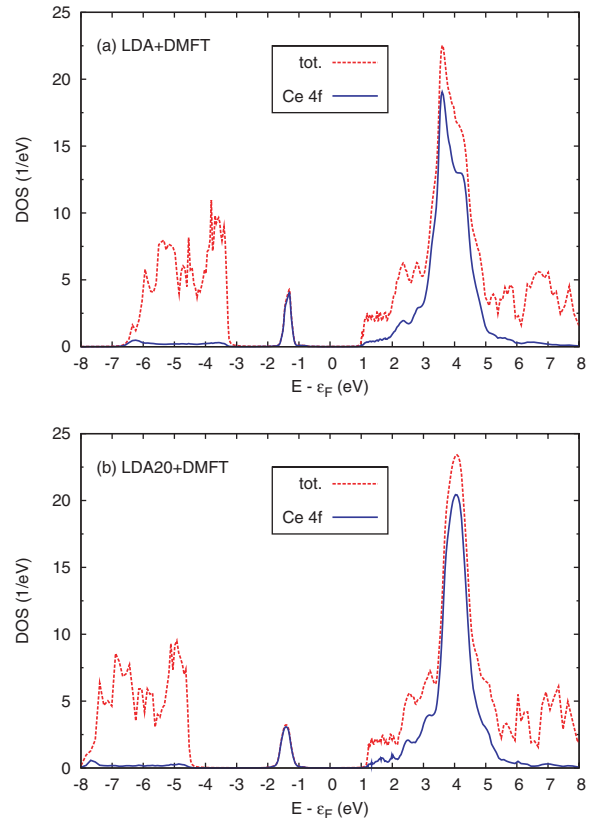


Fig. 2: (Color online) Total DOS (dashed red line) and partial Ce $4f$ DOS (continuous blue line) of Ce_2O_3 calculated with LDA + DMFT (a) and compared to the HYF + DMFT approach (b) as explained in the text. The on-site Coulomb repulsion for the DMFT calculation is $U = 5$ eV and $J = 0.2$ eV in both cases.

even stronger: *e.g.* for $k_B T \approx 0.2$ eV the splitting of the $4f$ -orbitals is still of about 2.3 eV *after* applying the DCC.

We note that the on-site Coulomb repulsion αV_{aaaa} corresponding to the Hartree-Fock contribution is about 5 eV. This value is only slightly smaller than the U usually employed for the Ce $4f$ -orbitals in actual LDA + U and DMFT calculations [15,16,18] which is between 5.5 eV and 6.5 eV. This again points to the correctness of the interpretation of αV_{aaaa} as a screened Coulomb interaction similar to the U of the LDA + U method [14].

In fig. 2 we compare DMFT calculations (a) on top of the plain LDA calculation and (b) on top of the LDA20 HYF calculations. In both cases the $4f$ -band splits into a lower Hubbard band filled with one electron per Ce atom and an upper unoccupied Hubbard band. We take $\alpha V_{aaaa} = 5$ eV as an estimate for U and similarly $\alpha V_{abba} = 0.2$ eV as an estimate for J . The resulting band gap between the occupied $4f$ Hubbard band and the empty $5d$ conduction band is about 2.3 eV in both cases, which is in very good agreement with the measured band gap of 2.5 eV [11]. The agreement can be improved by slightly increasing U to about 5.5 eV. Most importantly, the *pd*-gap between the occupied O $2p$ -bands and the unoccupied Ce $5d$ -bands is 5.5 eV in

the HYF + DMFT calculation and is thus exactly the experimentally measured pd -gap of about 5.5 eV. This is a considerable improvement over the LDA + DMFT where the pd -gap is only of about 4 eV. The occupancy N_f of the Ce $4f$ -shell is very similar in both methods: we find $N_f = 1.00$ for the LDA + DMFT, and $N_f = 0.98$ for the HYF + DMFT calculation. Finally, we mention that we have also obtained satisfactory results (not shown) for the Nd_2O_3 compound using the same methodology.

Conclusions. – In conclusion, we have proposed a new method that combines the HYF approach with DMFT. We have shown that this HYF + DMFT method gives a qualitatively *and* quantitatively correct description of the electronic structure of Ce_2O_3 as a prototypical example of the strongly correlated insulating rare-earth compounds. While the HYF part fixes the magnitude of the pd -band gap which is underestimated in the LDA + DMFT approach, the DMFT part takes care of the strongly localized $4f$ -electrons which are not properly taken into account within conventional KS band theory. It thus predicts correctly the opening of the Mott-Hubbard gap in the Ce $4f$ -band in addition to the band gap between the O $2p$ valence band and the Ce $5d$ conduction band. While the HYF is computationally slightly more expensive than the LDA, its cost is either comparable or less than that of the DMFT calculation. It is also computationally considerably less demanding than the GW approximation which gives an accurate description of the quasi-particle spectra of weakly correlated materials [26,27] and can be combined with DMFT in a natural way [28]. Hence, the HYF + DMFT approach is an attractive avenue for improving the overall accuracy of spectra in materials containing both correlated and uncorrelated electrons at reasonable computational cost.

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