Method for calculating the electronic structure of correlated materials from a truly first-principles LDA+U scheme

K. Karlsson,[1,2,4] F. Aryasetiawan,[3,4] and O. Jepsen[2,4]
[1]*Department of Life Sciences, Högskolan i Skövde, 54128 Skövde, Sweden*
[2]*Max Planck Institut für Festkörperforschung, D-705 06 Stuttgart, Germany*
[3]*Graduate School of Advanced Integration Science, Chiba University, Chiba 263-8522, Japan*
[4]*CREST, Japan Science and Technology Agency, Kawaguchi 332-0012, Japan*
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We present a method for calculating the electronic structure of correlated materials based on a truly *first-principles* local-density approximation (LDA)+U scheme. Recently we suggested how to calculate U from first principles, using a method which we named constrained random-phase approximation. The input is simply the Kohn-Sham eigenfunctions and eigenvalues obtained within the LDA. In our proposed self-consistent LDA+U scheme, we calculate the LDA+U eigenfunctions and eigenvalues and use these to extract U. The updated U is then used in the next iteration to obtain a new set of eigenfunctions and eigenvalues and the iteration is continued until convergence is achieved. The most significant result is that our numerical approach is indeed stable: it is possible to find the effective exchange and correlation interaction matrix in a *self-consistent* way, resulting in a significant improvement over the LDA results, regarding both the bandgap in NiO and the f-band exchange spin splitting in Gd but some discrepancies still remain.

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I. INTRODUCTION

The interest for a fundamental understanding of strongly correlated systems has led to the development of a number of electronic-structure methods. Among the most successful are the local-density approximation (LDA)+U approach proposed by Anisimov *et al.*[1] and the dynamical mean-field theory proposed by Georges *et al.*[2,3] Very recently a new scheme, dubbed the LDA+Gutzwiller method,[4] for treating strong electron correlations was introduced. In all these methods the strong Coulomb onsite correlations for electrons residing in the localized orbitals are explicitly taken care of via a set of Hubbard-type *parameters* or the Hubbard U. This is evidently unsatisfactory from the point of view of quantitative prediction of materials properties since optical and magnetic excitations are of vital importance in many technological applications such as solar cell design, optical memories, photoluminescent devices (semiconductor lasers and diodes), and photochemical reactions. Often it has been shown that by adjusting the Hubbard U one can get results in good agreement with experiment but not for a good reason. Hereby lies the importance of determining U entirely from first principles.

Over the last two decades a number of methods for calculating the Hubbard U from first principles have been proposed. The pioneering work may be traced back to the paper by Gunnarsson *et al.*[5] who proposed to calculate U using the constrained LDA (cLDA) scheme. A few years ago, a new method for calculating the Hubbard U, named the constrained random-phase approximation (cRPA) method in analogy to the cLDA method, was proposed.[6] The method allows for a systematic and precise determination of the Hubbard U entirely from first principles from the knowledge of the band structure alone. The method was based on the intuitive idea that the Hubbard U can be viewed as a Coulomb interaction screened by the polarization of the whole system excluding the polarization arising from a set of bands which are treated in the Hubbard model. In other words, the Hubbard U when further screened by the electrons in the Hubbard model yields the screened interaction of the full system. This intuitive idea was recently shown to be rigorously correct and the cRPA is just an approximate way of calculating the screened interaction U within the RPA.

By determining the Hubbard U from first principles the cRPA method offers the possibility of making methods based on the Hubbard U fully first-principles schemes. The purpose of the present work is to develop a scheme for calculating the electronic structure of correlated materials based on a truly *self-consistent first-principles* LDA+U scheme. In conventional LDA+U scheme as it was originally proposed,[1] the Hubbard U is taken as an adjustable parameter which is fixed for a given calculation. In our proposed self-consistent LDA+U scheme, we calculate the LDA+U eigenfunctions and eigenvalues and use these to calculate U using the cRPA method. The new U is then used in the next iteration to obtain a new set of eigenfunctions and eigenvalues and the iteration is continued until convergence is achieved. Thus, U is no longer an arbitrarily adjusted parameter like in the original LDA+U scheme but rather it is determined self-consistently within the theoretical scheme. Our first target will be to calculate the electronic structure of the transition-metal oxide series and as a test case we consider NiO, which is regarded as the epitome of Mott-Hubbard insulators. We are also aiming at obtaining a more satisfactory description of the electronic structure of the $4f$ electron series which is highly problematic for the LDA. The path is then opened for more complex materials, such as magnetic semiconductors, for which no realistic methods are in existent at present.

In the present paper we present some results for NiO and Gd, which we believe should provide us with a stringent test of the applicability of our method. The most important finding is that our numerical approach is indeed stable, i.e., it is possible to find U and J self-consistently. The band gap in NiO and the spin splitting of the f bands in Gd are found to compare well with experiment using our self-consistent determined values of the correlation parameters.

II. THEORY

A. Constrained RPA

We first give a short summary of the cRPA method presented in detail elsewhere.[6,7] The fully screened Coulomb interaction is given by

$$W = [1 - vP]^{-1} v, \quad (1)$$

where v is the bare Coulomb interaction and P is the noninteracting polarization given by

$$P(\mathbf{r},\mathbf{r}';\omega) = \sum_i^{occ} \sum_j^{unocc} \psi_i(\mathbf{r})\psi_i^*(\mathbf{r}')\psi_j^*(\mathbf{r})\psi_j(\mathbf{r}') \times \left\{ \frac{1}{\omega - \varepsilon_j + \varepsilon_i + i0^+} - \frac{1}{\omega + \varepsilon_j - \varepsilon_i - i0^+} \right\}, \quad (2)$$

where $\{\psi_i, \varepsilon_i\}$ are one-particle Bloch eigenfunctions and eigenvalues corresponding to the system's band structure. For systems with a narrow $3d$ or $4f$ band crossing the Fermi level, typical of strongly correlated materials, we may divide the polarization into $P = P_d + P_r$ in which P_d includes merely the transitions within the narrow band ($3d$-$3d$ *or* $4f$-$4f$ transitions) and P_r be the rest of the polarization, which includes transitions from the $3d$ band to the rest of the bands and vice versa. It was noticed that the following quantity can be interpreted as the effective interaction among electrons living in the narrow band (Hubbard U):

$$U(\omega) = [1 - vP_r(\omega)]^{-1} v, \quad (3)$$

where U can be related to the fully screened interaction W by the following *identity*:

$$W = [1 - UP_d]^{-1} U. \quad (4)$$

This identity explicitly shows that the interaction between the $3d$ or $4f$ electrons is given by a frequency-dependent interaction U. Thus the remaining screening channels in the Hubbard model associated with the localized d electrons, represented by the d-d polarization P_d, further screen U to give the fully screened interaction W. We refer the method of calculating the Hubbard U according to Eq. (3) as cRPA because we have constrained the polarization to exclude transitions within the narrow band (d-d transitions). Although the formula in Eq. (3) has been obtained within the RPA, the result is actually exact provided P_r is exact, as was shown recently.[8]

In the following, we retain only the local components of the effective interaction on the same atomic site by taking the following matrix element:

$$U_{L_1L_2,L_3L_4} = \int d^3r d^3r' \phi_{L_1}^*(\mathbf{r})\phi_{L_2}(\mathbf{r})U(\mathbf{r},\mathbf{r}')\phi_{L_3}^*(\mathbf{r}')\phi_{L_4}(\mathbf{r}'), \quad (5)$$

where ϕ_ζ is a ζ linear muffin-tin orbital (LMTO) (Ref. 9) orbital ($3d$ or $4f$) centered on an atomic site and the interaction $U(\mathbf{r},\mathbf{r}')$ is the static ($\omega=0$) value of Eq. (3). In calculating U we have approximated ϕ_ζ by the "head" of the LMTO, i.e., the solution to the Schrödinger equation inside the atomic sphere. This is expected to be a reasonable approximation because the ζ states are rather localized. LMTO is just one possible choice for the one-particle orbitals but other choices are perfectly legitimate. For example, the newly developed NMTO (where N is the number of energies chosen to span the region of interest)[10] and the recently proposed maximally localized Wannier orbitals[11] are possible choices. It is worth noting that the U entering the Hubbard model will inevitably depend on the choice of the one-particle basis ϕ_ζ defining the annihilation and creation operators, no matter what method we use to calculate $U(\mathbf{r},\mathbf{r}')$, which is independent of the basis functions used in the band-structure method.

B. LDA+*U*

In the spirit of the LDA+U approach,[1] we introduce an orbital-dependent exchange-correlation operator

$$\hat{V}_\sigma = \sum_{RL,R'L'} |\phi_{RL\sigma}\rangle V^\sigma_{RL,R'L'} \langle \phi_{R'L'\sigma}|,$$

acting among a localized set of electrons. The LMTO head is in general denoted by site index R, angular quantum number $L=(lm)$, and spin σ. In addition to the usual single-particle LDA Hamiltonian, we include appropriate matrix elements of $\hat{V}_\sigma$. In the TB representation[12] we get

$$\langle \chi^{\mathbf{k}}_{RL\sigma}|\hat{V}_\sigma|\chi^{\mathbf{k}}_{R'L'\sigma}\rangle = \sum_{R''L''} \langle \chi^{\mathbf{k}}_{RL\sigma}|\phi_{R''L''\sigma}\rangle V^\sigma_{R''L''} \langle \phi_{R''L''\sigma}|\chi^{\mathbf{k}}_{R'L'\sigma}\rangle$$

with

$$\langle \phi_{RL\sigma}|\chi^{\mathbf{k}}_{R'L'\sigma}\rangle = \delta_{RR'}\delta_{LL'} + o_{RL} h^{\mathbf{k}\sigma}_{RL,R'L'}.$$

We have used $V^\sigma_{RL,R'L'} = V^\sigma_{RL}\delta_{RR'}\delta_{LL'}$, an assumption which is confirmed numerically. Further, the diagonal overlap matrix o as well as the Hamiltonian matrix h are given in Ref. 12. Consider next V^σ_{RL}. Assuming a spin-independent Hubbard U and a diagonal spin-density matrix $n^\sigma_{RLL'} = n^\sigma_{RL}\delta_{LL'}$ (Ref. 13) we obtain

$$V^\sigma_{RL} = \sum_{L'\sigma'} U_{LL,L'L'} n^{\sigma'}_{RL'} - \sum_{L'} U_{LL',L'L} n^\sigma_{RL'} = \sum_{L'} U_{LL,L'L'} n^{-\sigma}_{RL'} + (U_{LL,L'L'} - U_{LL',L'L}) n^\sigma_{RL'}. \quad (6)$$

Now $U_{LL,L'L'}$ is substantial for all LL' in contrast to $U_{LL',L'L}$ which is rather small, except when $L=L'$. We shall use $U_{LL,L'L'} \equiv U$ independent of L,L' and $U_{LL',L'L} \equiv J$ for $L \neq L'$ which result in the simple form

$$V^{\sigma}_{RL} = (U - J)[1/2 - n^{\sigma}_{RL}],$$

where the double-counting term suggested in Ref. 1 has been added. For a fixed value of U and J, the matrix elements are evaluated and added to the LMTO Hamiltonian prior to diagonalization. The density matrix n^{σ}_{RL} is updated every iteration using the eigenvectors as well as the overlap matrix. The corresponding term, which has to be added to the total-energy functional, is given by

$$E^{U} - E_{dc} = \frac{(U-J)}{2}\left[N - \sum_{RL\sigma} n^{\sigma}_{RL} n^{\sigma}_{RL}\right],$$

where $N = \Sigma_{RL\sigma} n^{\sigma}_{RL}$. It should be noted that already the simple form of the nonlocal potential gives rise to upper and lower Hubbard bands with an energy separation given by $(U-J)$.

C. Self-consistent LDA+U

The cRPA method requires as input eigenfunctions and eigenvalues (fixed during the calculation) and delivers as output the Hubbard U matrix. On the other hand, the LDA+U method needs a U matrix (fixed during the calculation) as input and gives as output eigenfunctions and eigenvalues. The main point of the present work is to merge these two schemes in a self-consistent way.

We summarize the iterative steps: (1) first we do a normal cRPA calculation[7] in order to achieve the initial Hubbard U matrix (iteration one; matrix U_1) to be used in the LDA+U calculation. (2) After the LDA+U calculation has converged we save the output LDA+U eigenfunctions and eigenvalues and use these to calculate U within cRPA [Eqs. (2), (3), and (5)], in order to find the updated U matrix for the next LDA+U calculation (iteration two; matrix U_2). (3) The procedure is continued until the U matrix is stable, i.e., after n iterations we have $U_{n+1} \approx U_n$. The size of the U matrix is rather large, however many elements are related by symmetry.

III. RESULTS AND DISCUSSION

All the results presented in this paper used the simple form of the nonlocal potential because a substantial number of tests have shown that more elaborate forms of the potential do not influence the final results. The most important finding in the present work is indeed the possibility to converge the U matrix within the defined self-consistency cycle. In all cases studied convergency is reached within a reasonable number of iterations.

To illustrate the applicability of the present scheme to real materials we have applied the scheme to NiO, which is an epitome of the charge-transfer insulators, and Gd. These two systems have been extensively studied both experimentally and theoretically. The NiO LDA band gap is known to be too small and likewise the LDA exchange splitting in 4f Gd is too small. These provide a motivation for improving upon the LDA.

A summary of some results for our prototype systems: for NiO, the self-consistent determined values $U = 6.6$ eV and $J = 0.9$ eV, improves the band gap (2.5 eV), compared with conventional LDA, though too small in comparison with experiment (4 eV). The exchange spin splitting of the f bands in Gd is found to compare rather well with experiment ($\sim 12-13$ eV) using our self-consistent determined values of $U = 12.4$ eV and $J = 1.0$ eV. We have also calculated the Gd (NiO) magnetic moment to be $\mu = 7.8(1.5)$, which is comparable to the experimental value $\mu = 7.6\mu_B$ (Ref. 14) $(1.6-1.9\mu_B)$ and an improvement compared to LDA.

We first discuss Gd, where the LDA+U band structure corresponding to the self-consistent values of U and J are displayed in Figs. 1 and 2. The majority (spin-up) f bands are centered around -11 eV and the minority ones around 3 eV. The occupied spin-up bands are very narrow due to shielding by the 5s and 5p electrons, due to the hybridization with other bands the unoccupied minority bands display some dispersion, making it difficult to extract the exchange splitting. However, we estimate that our calculated exchange splitting at convergency is somewhat too large by about $\sim 1-2$ eV.

We note that our parameters differ significantly from those previously used in literature. Harmon *et al.*[15] found $U = 6.7$ eV and $J = 0.7$ eV using a supercell approach. The experimental gap (splitting between the photoemission spectroscopy and bremsstrahlung isochromat spectroscopy main

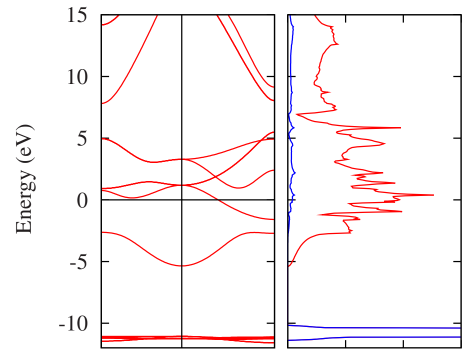

FIG. 1. (Color online) Gadolinium spin-up bands using the self-consistent determined parameters: $U = 12.4$ eV and $J = 1.0$ eV. Fermi energy at 0 eV and the directions displayed are $1/2(1,1,1) \rightarrow \Gamma \rightarrow (1,0,0)$. The corresponding total density of states (DOS) and f partial DOS are also displayed.

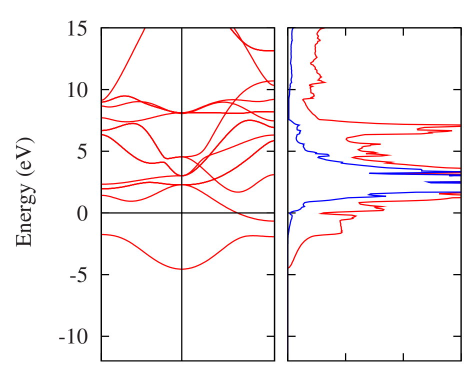

FIG. 2. (Color online) Gadolinium spin-down bands using the self-consistent determined parameters: $U = 12.4$ eV and $J = 1.0$ eV. Fermi energy at 0 eV and the directions displayed are $1/2(1,1,1) \rightarrow \Gamma \rightarrow (1,0,0)$. The corresponding total DOS and f partial DOS are also displayed.

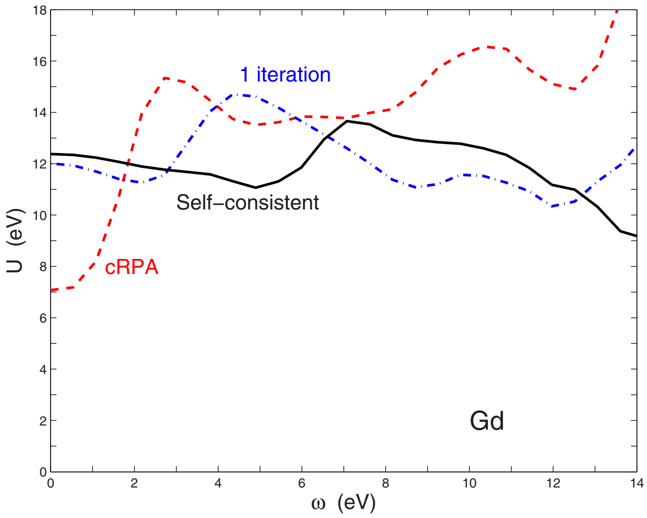

FIG. 3. (Color online) Frequency-dependent U of gadolinium.

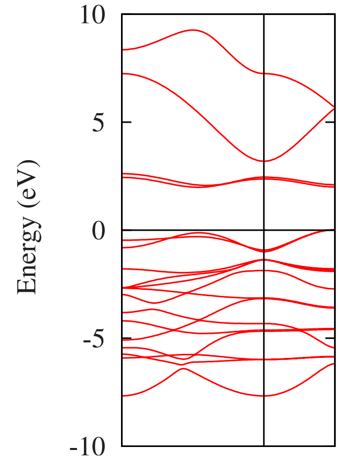

FIG. 4. (Color online) NiO bands using the self-consistent determined parameters: $U=6.6$ eV and $J=0.9$ eV. Fermi energy at 0 eV and the directions displayed are $1/2(1,1,-1)\rightarrow\Gamma \rightarrow 1/4(1,1,1)$.

peaks) is given by $E_g=E_{N+1}+E_{N-1}-2E_{GS}$, which from purely atomic considerations is predicted to be $U+6J$, using $N=7$ spin-up electrons in the ground state (GS). With the parameters of Harmon *et al.*,[15] an underestimation is obtained, resulting in a splitting of 11 eV. As can be seen in Fig. 2, the 4f states no longer form a narrow atomiclike band but hybridized with other states in the same energy range. Thus, the atomic picture used to estimate the exchange splitting may not be valid anymore.

The frequency-dependent U (Ref. 16) from the normal cRPA calculation, i.e., from calculation starting from the LDA band structure, is shown in Fig. 3. We note the dramatic change in U for small energies, shooting up to the self-consistent value of U already within 2 eV. In fact, the frequency dependence would have become even stronger if we had not used a lifetime broadening when calculating the response function. Using a tetrahedral method for the Brillouin-zone integration without a lifetime broadening would probably result in a decrease in U from its zero-energy value before it shoots up to a large value at around 1.5 eV. This behavior is in contrast to the transition metals studied earlier.[7] Toward self-consistency we noticed a significant change in U already in the second cRPA calculation (1 iteration); U is in fact enhanced for small energies giving rise to a quite smooth curve with weak dependency on frequency. As seen in Fig. 3, the frequency dependence of U is indeed much weaker after self-consistency, with a relatively constant value of $U=12$ eV in the frequency range around 5 eV. The weakening of the energy dependence of U for small energies may be explained by the increase in the exchange splitting of the up and down 4f states. As the occupied 4f states are pushed down the excitation energies from the occupied 4f states to unoccupied states increase. Similarly, as the unoccupied 4f states are pushed up, the excitation energies from occupied states to the unoccupied 4f states increase. Thus, the peak structure in the imaginary part of the screened interaction arising from these excitations is shifted to higher energy. Through the Kramers-Kronig relation this results in much smoother behavior of U at low energy. This result is very encouraging since it gives justification for using a static value of U.

Finally we consider NiO, where the LDA+U band structure corresponding to the self-consistent values of U and J are shown in Fig. 4. For this system cLDA calculations yields $U=8$ eV and $J=1$ eV,[1] which is comparable to our self-consistent values of $U=6.6$ eV and $J=0.9$ eV. The gap obtained using the cLDA parameters is 3 eV,[1] compared to the experimental gap of 4 eV.[17] The difference between our and the cLDA U (1.4 eV) is reflected in our decreased band gap of 2.5 eV (Table I).

As in the case of Gd, the Hubbard U as a function of frequency undergoes a significant change as self-consistency is achieved. Starting from the LDA band structure, the resulting U calculated using the cRPA method exhibits a strong energy dependence at low energy. As the band gap increases, the energy dependence of U at low energy becomes smoother. The explanation of this behavior is similar to the case of Gd, namely, as the gap increases the peak structure in the imaginary part of the screened interaction is shifted to higher energy and through the Kramers-Kronig relation, it results in a smooth behavior of U at low energy.

In Gd the separation between the occupied and unoccupied 4f states, or the exchange splitting, is in reasonably

TABLE I. A summary of results for U and J, obtained with the present method in comparison with other methods (in brackets). We compare also the magnetic moments with experimental findings (in brackets).

	U (eV)	J (eV)	Magnetic moment (μ_B)
NiO	6.6 (8.0[a])	0.9 (1.0[a])	1.5 (1.6–1.9[b,c])
Gd	12.4 (6.7[d])	1.0 (0.7[d])	7.8 (7.6[e])

[a]Reference 1.
[b]Reference 18.
[c]Reference 19.
[d]Reference 15.
[e]Reference 14.

good agreement with experiment. However, the positions of the 4f states significantly deviate from experiment. This deficiency may be related to the double-counting problem in the LDA+U scheme. This problem becomes apparent when the relative position of the correlated bands with respect to other bands is important. This relative position is rather sensitive to the double-counting formula used in the scheme, which essentially shifts the correlated bands with respect to the uncorrelated bands. We believe this double-counting problem is responsible for the incorrect positioning of the 4f bands in Gd. If a different double-counting formula shifted the 4f bands up by about 2 eV, the peak positions would be in rather good agreement with photoemission experiment. A similar problem seems to occur also in NiO. While the separation between the unoccupied e_g and occupied t_{2g} bands of nickel is reasonably well reproduced, the relative position of these 3d bands with respect to the oxygen 2p bands is incorrect, which results in a too small band gap since the gap is formed between the top of the valence band of oxygen 2p character and the bottom of the conduction band of Ni e_g character. The too small band gap in NiO calculated within the LDA+U scheme has also been found in other works.[20]

IV. CONCLUSION

We have developed a new self-consistent LDA+U scheme in which the important parameter U is determined self-consistency using the cRPA method. As test cases we have considered NiO and Gd and it is shown that the scheme does yield converged results. The exchange splitting in Gd has been found to be too large by 1–2 eV whereas the band gap in NiO has been found to be too small, 2.5 eV compared with the experimental value of about 4.0 eV. An interesting finding is that the energy dependence of U at low energy is found to be much smoother after self-consistency compared with the result obtained from the LDA band structure. This provides justification for using a static value of U. Our results indicate some shortcomings of the LDA+U scheme, in particular, the incorrect positioning of the 4f states in Gd and the 3d states in NiO points to a need for a more elaborate form of the double-counting term. Investigating different forms of the double-counting term within the newly developed self-consistent LDA+U scheme could be a fruitful direction to pursue in the future.

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