Calculations of Hubbard *U* from first-principles

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The Hubbard *U* of the 3*d* transition metal series as well as SrVO$_3$, YTiO$_3$, Ce, and Gd has been estimated using a recently proposed scheme based on the random-phase approximation. The values obtained are generally in good accord with the values often used in model calculations but for some cases the estimated values are somewhat smaller than those used in the literature. We have also calculated the frequency-dependent *U* for some of the materials. The strong frequency dependence of *U* in some of the cases considered in this paper suggests that the static value of *U* may not be the most appropriate one to use in model calculations. We have also made comparison with the constrained local density approximation (LDA) method and found some discrepancies in a number of cases. We emphasize that our scheme and the constrained local density approximation LDA method theoretically ought to give similar results and the discrepancies may be attributed to technical difficulties in performing calculations based on currently implemented constrained LDA schemes.

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I. INTRODUCTION

Many-electron problem in real materials is too complicated to be tackled directly from first principles. Direct conventional methods for calculating excited-state properties are available and one of the most successful among these is the GW approximation (GWA).[1,2] However, it has proven difficult to go beyond the GWA purely from first principles for a number of reasons. Seen from a diagrammatic point of view, the GWA is a sum of bubble diagrams corresponding to the random-phase approximation (RPA),[3] which can be more generally regarded as time-dependent Hartree approximation. First, it is far from obvious which classes of diagrams should be included beyond the RPA. Secondly when we do include another class of diagrams, the lowest order diagram, i.e., second order, is likely to be included twice. This is because there are only very few lower order diagrams so that different classes of diagrams will tend to have an overlap of the lowest-order diagrams. This double counting has to be taken into account. However, for an arbitrary frequency, the imaginary part of the second-order self-energy may be larger than, e.g., the imaginary part of the GW self-energy. When the second-order self-energy is subtracted for double counting this may lead to a wrong sign of the imaginary part of the self-energy with unphysical consequences such as a negative spectral function.

It is therefore worthwhile to consider an alternative approach of tackling the many-electron problem in real materials. We note that of the large number of degrees of freedom only a few are actually relevant for electron correlations. A typical problem that is difficult to treat with conventional methods corresponds to a system with localized orbitals embedded in extended states. Many so-called strongly correlated materials, such as perovskites, are of this type, consisting of localized 3*d* or 4*f* orbitals embedded in extended *s*-*p* states. Electrons living in the localized orbitals experience strong correlations among each other with a subtle coupling

to the extended states resulting in a complicated many-electron problem. The RPA is probably insufficient for treating correlations among electrons in localized orbitals. One may speculate that many classes of diagrams contribute with similar weight to correlations, making it very difficult to go beyond the RPA by including a few extra classes of diagrams.

The idea of isolating a few degrees of freedom relevant for correlation has been utilized for many years in the Hubbard model or the Anderson impurity model. Renormalized or screened Coulomb interaction (Hubbard *U*) is kept among electrons living in the localized orbitals. In the Anderson model some states coupled to the localized orbitals are also kept but without Coulomb interaction and the rest of the states are downfolded resulting in a renormalized Coulomb interaction. Although the physical picture seems clear it is not immediately evident how to calculate the Hubbard *U*. Indeed in practice it has usually been regarded as an adjustable parameter. Adjustable parameters are unsatisfactory since they limit the quantitative predictive power of the model and might lead to misleading conclusions. It is therefore highly desirable to find a systematic way of calculating the parameters in the Hubbard model, in particular the Hubbard *U*, from realistic electronic structure calculations.

The problem of determining the Hubbard *U* from first principles has been addressed by a number of authors. One of the earliest works is the constrained local density approximation (CLDA) approach[4–6] where the Hubbard *U* is calculated from the total energy variation with respect to the occupation number of the localized orbitals. A further improvement of this scheme was recently proposed.[7–9] A different approach based on the random-phase approximation (RPA) was later introduced,[10] which allows for the calculations of the matrix elements of the Hubbard *U* and its energy dependence. More recently, it was shown that it is possible to calculate the Hubbard *U* systematically from first principles.[11] It was soon realized that these two methods of calculating the Hubbard *U*, RPA, and CLDA, do not yield

the same results. This is very puzzling since the two approaches are supposed to give the effective interaction of the localized electrons and ought to give the same results. The purpose of the present work is to present results for the Hubbard U of the $3d$ series and a few other materials $(Ce, SrVO_3, YTiO_3)$ and to analyze the origin of the discrepancy between RPA and CLDA results.

II. THEORY

A. Constrained RPA

The fully screened Coulomb interaction is given by

$$W = [1 - vP]^{-1}v, \tag{1}$$

where v is the bare Coulomb interaction and P is the non-interacting polarization given by

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

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 across the Fermi level, typical of strongly correlated materials, we may divide the polarization into $P = P_d + P_r$, in which P_d includes only $3d$ to $3d$ transitions [i.e., limiting the summations in Eq. (2) to $i,j \in \{\psi_d\}$], and P_r be the rest of the polarization. In a previous publication[11] it was shown that the following quantity can be interpreted as the effective interaction among electrons living in the narrow band (Hubbard U):

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

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

$$W = [1 - UP_d]^{-1}U. \tag{4}$$

This identity explicitly shows that the interaction between the $3d$ electrons is given by a frequency-dependent interaction U. Thus the remaining screening channels in the Hubbard model associated with the $3d$ electrons, represented by the $3d$-$3d$ polarization P_d, further screen U to give the fully screened interaction W. In analogy to the constrained LDA method, we refer the method of calculating the Hubbard U as in Eq. (3) as "constrained RPA" (CRPA) because we have constrained the polarization to exclude $3d$-$3d$ transitions. In contrast to Ref. 8, it is not necessary to subtract the contribution arising from rehybridization of the noninteracting Kohn-Sham band structure because the wave functions and eigenvalues appearing in Eq. (2) are fixed.

It is noteworthy that U in Eq. (3) is a function of positions $\mathbf{r}$ and $\mathbf{r}'$, independent of basis functions. This is because the polarization in Eq. (2) depends on the Bloch wave functions and eigenvalues, which can be calculated in any basis. Thus, our method is basis-independent. In the following, we retain

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

$$U = \int d^3r d^3r' |\phi_{3d}(\mathbf{r})|^2 U(\mathbf{r},\mathbf{r}') |\phi_{3d}(\mathbf{r}')|^2, \tag{5}$$

where ϕ_{3d} is a $3d$ LMTO (Ref. 12) orbital 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_{3d} 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 $3d$ states are rather localized. The lattice Hubbard model with a *static* interaction U is given by

$$
H = \sum_{Rn,R'n'} c_{Rn}^\dagger h_{Rn,R'n'} c_{R'n'}
$$
$$
+ \frac{1}{2} \sum_{R,nn',mm'} c_{Rn}^\dagger c_{Rn'} U_{nn',mm'} c_{Rm}^\dagger c_{Rm'}. \tag{6}
$$

$h_{Rn,R'n'}$ is the one particle part of the Hamiltonian consisting of hopping and the orbital energy. A model with a frequency-dependent U can be formulated within the action integral approach but cannot be formulated within the Hamiltonian approach.[11] It is clear that the U entering the Hubbard model will inevitably depend on the choice of the one-particle basis ϕ_{3d} defining the annihilation and creation operators, no matter what method we use to calculate $U(\mathbf{r},\mathbf{r}')$. 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)[13] and the recently proposed maximally localized Wannier orbitals[14] are possible choices.

B. Constrained LDA

The derivative of the total energy with respect to an occupation number n_i of a given state can be related to its Kohn-Sham eigenvalue as follows:[15]

$$\frac{\partial E}{\partial n_i} = \varepsilon_i. \tag{7}$$

From the Kohn-Sham equation[16] one can show that following relation holds:[10,17]

$$\frac{\partial \varepsilon_i}{\partial n_j} = \frac{\partial^2 E}{\partial n_i \partial n_j} = \langle ij|(v + f_{xc})\epsilon^{-1}|ij\rangle, \tag{8}$$

where

$$f_{xc}(\mathbf{r},\mathbf{r}') = \frac{\partial^2 E_{xc}}{\partial \rho(\mathbf{r})\partial \rho(\mathbf{r}')} = \frac{\partial v_{xc}(\mathbf{r})}{\partial \rho(\mathbf{r}')}$$

and ϵ^{-1} is the inverse dielectric function which can be expressed in terms of the linear density-density response function $R = \delta\rho / \delta v_{ext}$, i.e., the change in density ρ with respect to an external perturbation v_{ext}, as

$$\epsilon^{-1} = 1 + Rv.$$

The integral in Eq. (8) is defined as

$$\langle ij|F|ij \rangle = \int d^3r d^3r' |\phi_i(\mathbf{r})|^2 F(\mathbf{r},\mathbf{r}')|\phi_j(\mathbf{r}')|^2. \qquad (9)$$

Within the RPA, which is equivalent to time-dependent Hartree approximation, $f_{xc}=0$ implying that $(v+f_{xc})\epsilon^{-1}=v+vRv=W$, i.e., the change in the Kohn-Sham eigenvalue is directly related to the screened interaction. In fact in practice $f_{xc} \ll v$ so that to a good approximation we may assume that $\partial \varepsilon_i / \partial n_j = \langle ij|W|ij \rangle$.

The idea in a constrained LDA calculation (CLDA) is to perform a self-consistent (supercell) total energy calculation with a constrained $3d$ occupancy on the so called impurity atom. Furthermore, the coupling between the impurity ($3d$ level) and the rest of the system, which is explicitly included in the model Hamiltonian, is removed in order to avoid double counting. According to Eq. (8) the Hubbard U is then given by the change in the $3d$ level when the number of localized $3d$ electrons are varied and the hopping for the localized $3d$ electrons is suppressed:

$$U = \frac{\partial C_{3d}}{\partial n_{3d}}, \qquad (10)$$

where C_{3d} is the center of the $3d$ band. By suppressing the hopping of the $3d$ electrons, the screened interaction so obtained corresponds to an effective interaction without the participation of screening from the $3d$ electrons, which is what we mean by the Hubbard U. However, by cutting off the hopping of the $3d$ electrons, we do not only eliminate hopping to $3d$ bands but also hopping to bands other than $3d$. We will elucidate later that the neglect of the latter hopping is the main origin of the discrepancy between CLDA and CRPA.

Within the LMTO atomic sphere approximation (ASA) scheme, the $3d$ level, or in fact the band-center C_{3d}, is obtained by solving the radial Schrödinger equation for the impurity atom using fix boundary condition (BC) at the muffin-tin (MT) sphere.[12] The BC are arbitrarily chosen so the radial wavefunction in the sphere ϕ_{3d}, matches smoothly to r^{-l-1} at the MT sphere, which corresponds to a logarithmic derivative for the $3d$ states of $D_l=-l-1=-3$. We note that in the above definition ϕ_{3d} is allowed to relax (self-consistently) upon a change in the $3d$ charge. A decrease in the number of $3d$ electrons will make the potential more attractive and consequently the wave function will contract. This effect is compensated due to remaining electrons located outside the impurity sphere, which tend to screen. In addition we have performed so called modified U calculations using a fixed wave function, obtained in an ordinary bulk calculation, in order to make sure that the wave function ϕ_{3d} coincides with the one used in the cRPA approach. Then the definition of U has to be slightly modified [denoted cLDA (modified) in Fig. 7], and defined as the change in the expectation value of the impurity potential related to changes in $3d$ occupancy:

$$U = \frac{\partial \langle \phi_{3d}|V|\phi_{3d} \rangle}{\partial n_{3d}} = \frac{\partial}{\partial n_{3d}} \int d^3r \phi_{3d}^2(r)V(r). \qquad (11)$$

The above formula is obtained by observing that to first order in the perturbing potential the change in ε_{3d} or C_{3d} is given by $\langle \phi_{3d}|V|\phi_{3d} \rangle$. In order to validate such a procedure for evaluating U, we have also adopted a scheme where firstly the supercell calculation is done until self-consistency using the fixed bulk wave functions, i.e., we perform a constrained calculation as usual but with fixed wave functions. Secondly the resulting self-consistent potential is used only once (BC $D_l=-3$) to obtain the C_{3d} level by solving the radial Schrödinger equation. Our results confirm that the value of U obtained from Eq. (10) using this one-shot iteration for the C_{3d} level is in fact the same as the value obtained from the modified definition in Eq. (11).

We must have in mind that in the LMTO-ASA method,[12] any polarization of the screening charge is neglected. However, the screening charge inside the atomic sphere (on-site screening) is taken care of with good accuracy, but the nonlocal screening from other spheres is merely due to point charges located at the sphere centers (Madelung screening). In reality, this charge is expected to be located somewhat closer to the impurity sphere, thus reducing the value of the calculated U. As a consequence systems with almost all screening charge inside the impurity sphere are expected to be well described.

The beauty of the LMTO method is that the basis used in the band structure calculation is the same as the one-particle basis defining the annihilation and creation operator of the Hubbard model. Thus by constraining the occupation number of the orbital one directly obtains the corresponding U from the change in the orbital energy with respect to the occupation number as in Eq. (8) or (10). This is in contrast to methods not based on localized orbitals,[8,9] where projection to some localized orbitals defining to the one-particle basis of the model Hamiltonian is necessary.

III. RESULTS AND DISCUSSIONS

A. SrVO₃

SrVO₃ is an ideal case because across the Fermi level there is a narrow band of mainly t_{2g} character originating from V $3d$, well separated from other bands. This allows for an unambiguous application of Eq. (3). To aid in visualizing the various transitions between occupied and unoccupied states the partial density of states of SrVO₃ are displayed in Fig. 1. The effects of various possible screening channels on the value of the screened interaction are calculated systematically and shown in Fig. 2. From the figure we can read the value of U for the t_{2g} band, namely, $U=3.5$ eV. As can be seen from the figure, eliminating transitions from t_{2g} band to e_g band has hardly any effect on U. This implies that the Hubbard U for a model with only t_{2g} orbitals (case 1) is approximately the same as the one for a model with both t_{2g} and e_g orbitals (case 2). In fact, eliminating all transitions from the t_{2g} band (case 3) has little effect on U. This is because the small number of $3d$ electrons (~ 1) contribute little to the polarization other than $3d$-$3d$ polarization. From
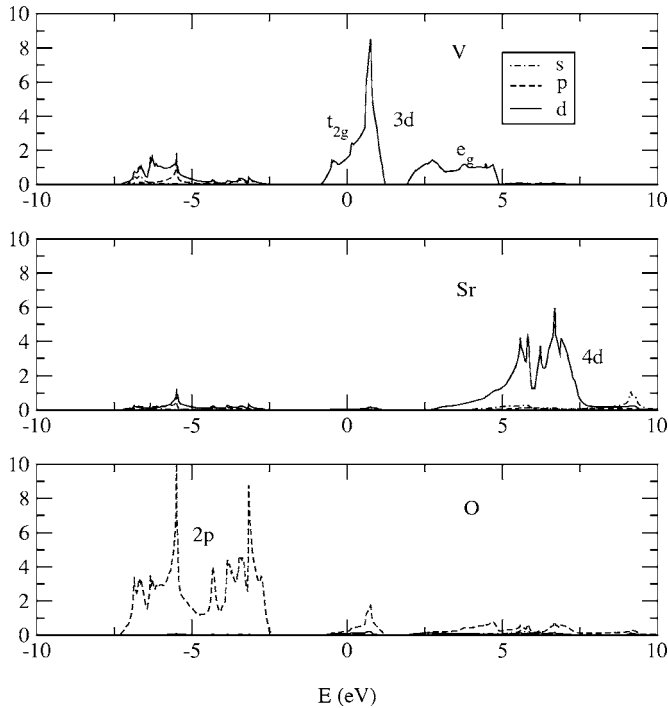
FIG. 1. Partial density of states of $SrVO_3$.

cases 4, 5, and 6 it becomes evident that screening from the oxygen $2p$ electrons is very important. In particular, the transitions from oxygen $2p$ to t_{2g} and e_g bands are most significant (see also a recent work of Solovyev and Imada[7]). However, cases 9 and 10 are surprising: when all transitions from the oxygen $2p$ are eliminated, the resulting screened interaction is almost the same as the fully screened interaction W (case 11). This means that the t_{2g} electrons alone are very efficient in performing the screening so that after the t_{2g} electrons have performed the screening there is little left for the oxygen $2p$ electrons to screen. In retrospect, it is a reason-
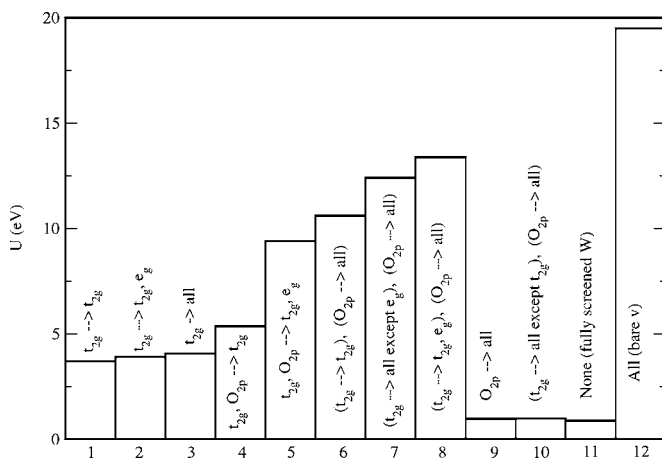

FIG. 2. The Hubbard U of $SrVO_3$ obtained by eliminating various transitions as indicated in the picture. For example, case 5 corresponds to eliminating transitions $t_{2g} \rightarrow t_{2g}$, $t_{2g} \rightarrow e_g$, $O_{2p} \rightarrow t_{2g}$, and $O_{2p} \rightarrow e_g$ and case 6 corresponds to eliminating $t_{2g} \rightarrow t_{2g}$ transition and all transitions from O_{2p}. Discussion of the result is described in the text.
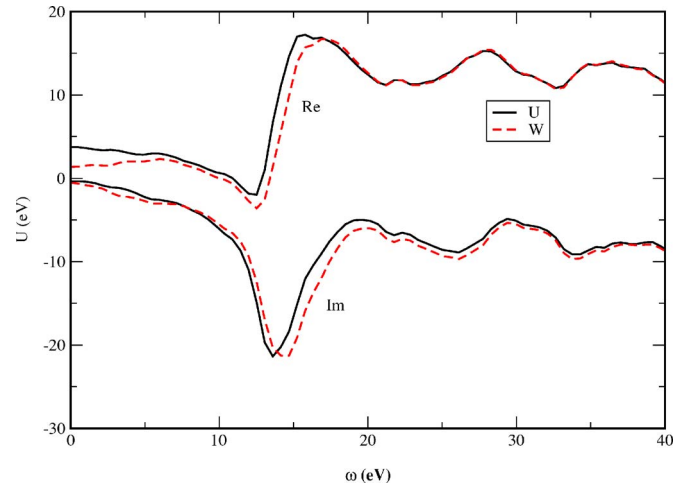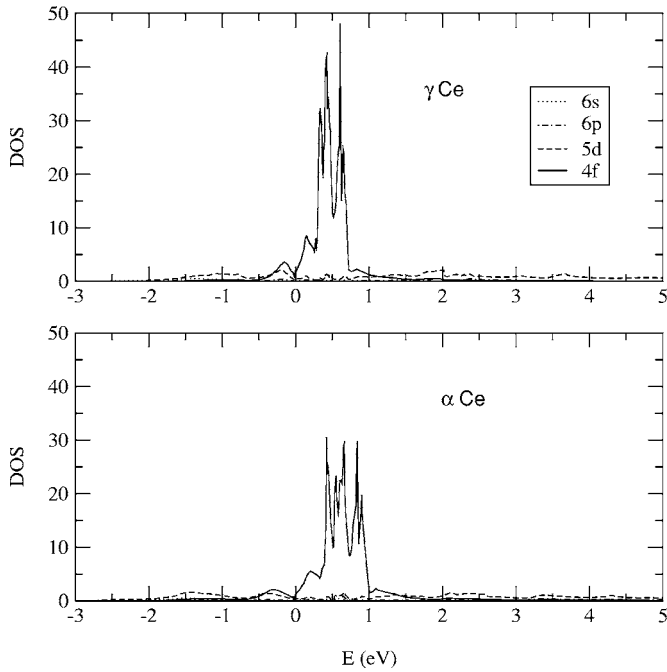

FIG. 3. (Color online) Frequency dependent U and W of $SrVO_3$.

able result because $t_{2g} \rightarrow t_{2g}$ screening is metallic, which is very efficient. Similarly, when the oxygen $2p$ electrons are allowed to screen first (case 3), there is little left for the t_{2g} electrons to screen. Thus, cases 3 and 9 are not contradictory.

It is interesting to compare the value of U calculated using CRPA and CLDA. The value of U for the t_{2g} and e_g bands obtained from CLDA is 9.5 eV and the modified CLDA yields a value of 8.8 eV. Since in the implementation of CLDA, hopping to the $3d$ orbitals on a given impurity site in a supercell is prohibited, a fair comparison with CRPA would be to eliminate transitions from and to the $3d$ orbitals (both t_{2g} and e_g). In this interpretation of cLDA, we should therefore make comparison with case 5, corresponding to the case where transitions from O_{2p} to $3d$ bands (both t_{2g} and e_g) are also prohibited. Indeed the value corresponding to case 5 is very close to the modified CLDA value. We should also eliminate the $t_{2g} \rightarrow$ non-t_{2g} screening but as shown by cases 1, 2, and 3 in Fig. 2, this screening channel is not important.

The frequency-dependent U and W are displayed in Fig. 3. There is a qualitative difference in the frequency dependence of the imaginary part of U of $SrVO_3$ and late transition metals. In the former the imaginary part is dominated by a single plasmon excitation while the latter is characterized by a broad excitations with no distinct plasmon excitation. This is a consequence of the small polarization contribution of the t_{2g} electrons to non-$3d$ orbitals in the former so that the plasmon excitation is dominated by the free-electron-like O_{2p}. In late transition metals, such as nickel, the $3d$ electrons themselves contribute very significantly to screening in the form of polarization to non-$3d$ orbitals. The localized non-free-electron-like nature of the $3d$ electrons may be responsible for the broad excitation energies observed in Im U and Im W.

We have also calculated U for $YTiO_3$ with a result equal to 4.0 eV. This value is significantly smaller than the value of 5.0 eV used in LDA+dynamical mean-field theory (DMFT) calculations.[18] The value of 5.0 eV is needed in order to open up a gap when starting from a metallic state in the LDA. While a smaller value of $3-4$ eV would still be acceptable in the case of $SrVO_3$ or $CaVO_3$ since they are

FIG. 4. Partial density of states of αCe and γCe.

TABLE I. U of γCe and αCe as a function of energy window.

Energy window (eV)	γCe U (eV)	Energy window (eV)	αCe U (eV)
$(-2.0, 1.5)$	7.9	$(-2.0, 1.7)$	6.6
$(-1.5, 1.5)$	7.6	$(-1.5, 1.7)$	5.4
$(-1.0, 1.5)$	5.7	$(-1.0, 1.7)$	4.3
$(-0.5, 1.5)$	3.3	$(-0.7, 1.7)$	3.2
$(-0.5, 1.0)$	2.9	$(-0.7, 2.0)$	3.3
$(-0.5, 1.7)$	3.3	$(-0.7, 3.0)$	3.4

both metals, such value of U would just barely open up a gap in the case of YTiO$_3$. This poses a fundamental question concerning the value of the Hubbard U that is appropriate for DMFT. It could well be that due to the mapping to an impurity model, DMFT requires a larger U than the corresponding value for a lattice model. However, this runs counter to our intuition because by mapping to an impurity model one would expect that part of the screening process arising from the impurity's neighboring sites should already be included in the impurity U, which should therefore be smaller than the lattice U. Another possibility is that the RPA is not sufficient for treating local screening and more accurate approximation beyond the RPA may be needed. This question is now under study. We have also performed CLDA calculations giving a value of $U = 7.5$ eV and 6.3 eV with a modified CLDA. We have not analyzed in detail the various transitions in YTiO$_3$ since we believe they are essentially similar to those of SrVO$_3$.

B. Cerium

Another interesting case to consider is cerium although it is less ideal than SrVO$_3$ due to a mixing between the $4f$ and $5d$ orbitals in the valence states. The partial densities of

states of αCe and γCe are shown in Fig. 4. In Table I the values of U for a number of energy windows are shown.

A reasonable choice of energy window for αCe and γCe are $(-0.7, 1.7)$ and $(-0.5, 1.5)$, respectively, since these cover the $4f$ states. This choice gives a value of about 3.2–3.3 eV. It is clear from the tables that the value of U is very sensitive to the choice of the lower energy bound. Thus U is more than doubled when the lower bound is taken to be -2.0 eV, which corresponds to covering the entire occupied valence states. On the other hand, due to the small number of $4f$ electrons, U is not sensitive to the upper energy bound. This result is in reasonable accord with CLDA result of about 6 eV, which in our language corresponds to eliminating all transitions to and from the $4f$ states. Due to a slightly more extended $4f$ orbital, the result for αCe is somewhat smaller than that of γCe but otherwise they are very similar.

C. 3d transition metal series

The Hubbard U for the $3d$ metals is difficult to determine unambiguously because of the strong hybridization between the $3d$ and $4s$-$4p$ orbitals. Thus the result can depend strongly on the energy window or on what we choose as our one-particle band in the Hubbard model. This is especially true in the early transition metals, as can be seen, for example, in Table II for vanadium. The dependence on the energy window is less strong for the late transition metals Fe and Ni, as shown in Tables II. For this reason we have adopted the following procedure for defining the $3d$ band: it is defined to be those states from the second lowest band (the lowest band is of $4s$ character), up to states below an energy, just above the Fermi level, corresponding to a sharp drop in the density of states. Figure 5 shows the partial density of states of V, paramagnetic Fe, and paramagnetic Ni.

TABLE II. U of V, paramagnetic Fe and Ni as a function of energy window.

Energy window (eV)	V U (eV)	Energy window (eV)	Fe U (eV)	Energy window (eV)	Ni U (eV)
$(-2.0, 4.0)$	3.7	$(-3.0, 1.2)$	4.0	$(-5.0, 0.5)$	3.7
$(-3.0, 4.0)$	6.3	$(-4.0, 1.2)$	4.8	$(-5.0, 1.0)$	3.7
$(-4.0, 4.0)$	7.0	$(-5.0, 1.2)$	5.0	$(-5.0, 2.0)$	6.3
$(-2.0, 5.0)$	3.8	$(-3.0, 2.0)$	4.3	$(-6.0, 0.5)$	3.7
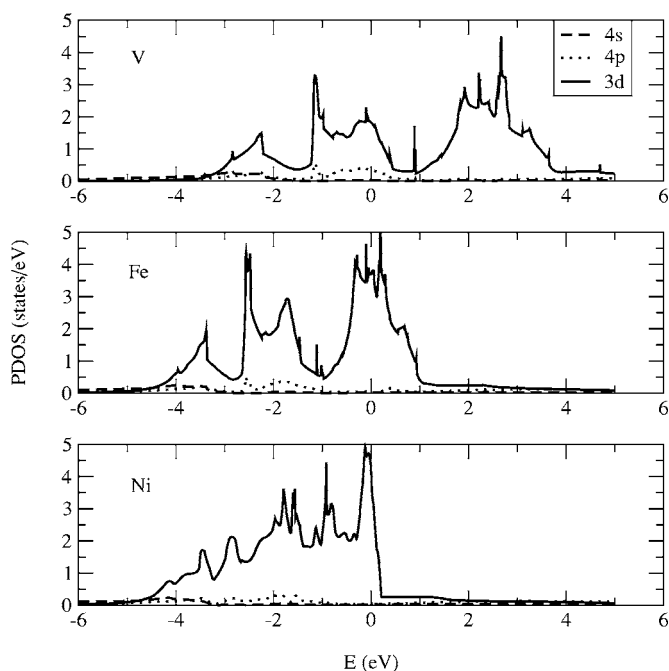
FIG. 5. Partial density of states of vanadium, paramagnetic iron, and nickel.

FIG. 6. (Color online) The Hubbard U for the $3d$ series obtained by eliminating transitions among the $3d$ bands. The empty circles correspond to the case where the $3d$ bands are defined to be band 2 to 6 and the filled circles to the case where the $3d$ bands are defined to be band number 2 up to bands below an energy cut off above the Fermi level corresponding to a sharp drop in the $3d$ density of states, as described in the text. The filled circles are what we define to be the Hubbard U.

One might wonder if it would not be better to project out the $3d$ orbitals in calculating P_r in Eq. (3). This procedure turned out to be mathematically unstable resulting in negative static U and an ad hoc procedure was employed to avoid this problem.[19] It is also tempting to adopt a simple procedure whereby one eliminates bands 2 to 6 (corresponding to the five "$3d$ states") when calculating the polarization. This procedure is untenable because band number 6, for example, can be very high in energy, up to 8.0 eV, which clearly cannot be regarded as $3d$ states. The result using this procedure is illustrated in Fig. 6. The procedure in fact works quite well for the early elements but the result deviates widely from that calculated using the procedure adopted in the present work. The reason for the wide deviation is due to the increasing number of $3d$ electrons as we go to the later elements. Transitions from the occupied states to unoccupied states just above the Fermi level where the hybridization between the $3d$ and $4p$ is strong become increasingly numerous since the number of occupied states increases.

In Fig. 7 the Hubbard U for the $3d$ series calculated using the CRPA and CLDA method is shown. It is instructive to first consider the case when all transitions *from* the $3d$ band are eliminated from the polarization (empty circle), i.e., all screening comes from the $4s$ electrons. Note that we distinguish between transitions *from* and *to* the $3d$ band. The screened interaction increases almost monotonically from the early to late elements. Two factors are responsible for this monotonic increase. First, the $3d$ orbital contracts as we go from early to late elements. The effect of the contraction is illustrated by the bare Coulomb matrix element in Fig. 8. Since the bare Coulomb interaction is the same for all elements the increase must be due to the orbital contraction. Secondly, as more $3d$ states are filled as we go from early to late elements the transitions from the $4s$ to unoccupied $3d$
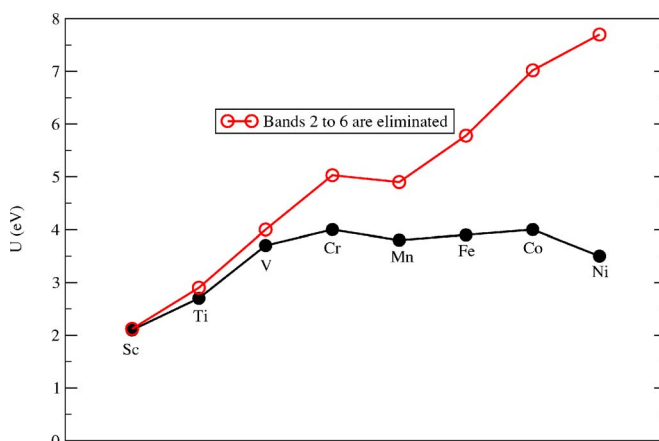
states is reduced resulting in larger screened interaction. To see the contribution of $4s$ to $3d$ transitions, the U values without these transitions are plotted in Fig. 8 (filled circle). The curve is somewhat more flat compared with the case where $4s$ to $3d$ transitions are included (empty circle) showing larger $4s$-$3d$ screening in early elements. The dominant effect, however, originates from orbital contraction. A similar conclusion was reached by Nakamura *et al.*[9]

The values of the Hubbard U (filled circle) calculated within the CRPA by eliminating $3d$ to $3d$ transitions lie between 2–4 eV across the series. It increases from the early transition metal Sc and reaches a maximum in the middle of
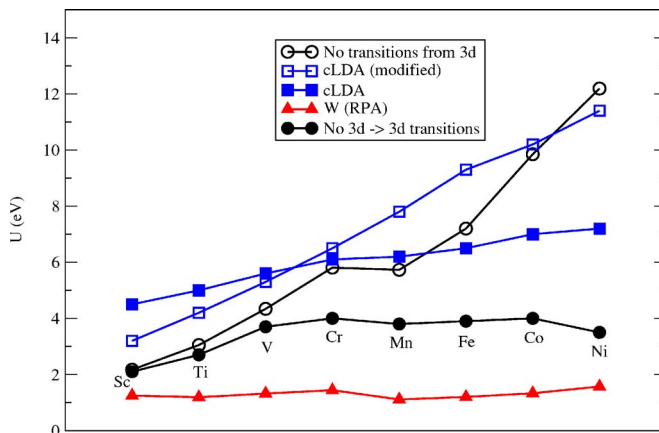

FIG. 7. (Color online) The Hubbard U for the $3d$ transition metal series calculated using the CRPA (filled circle, the same as the filled circles in Fig. 6) and CLDA (filled square). Empty circles correspond to the CRPA result excluding all transitions from the $3d$, i.e., only transitions from the $4s$ band are allowed. This should be compared with the modified CLDA result (empty square), as described in the text. For comparison, the fully screened interaction W is also plotted.
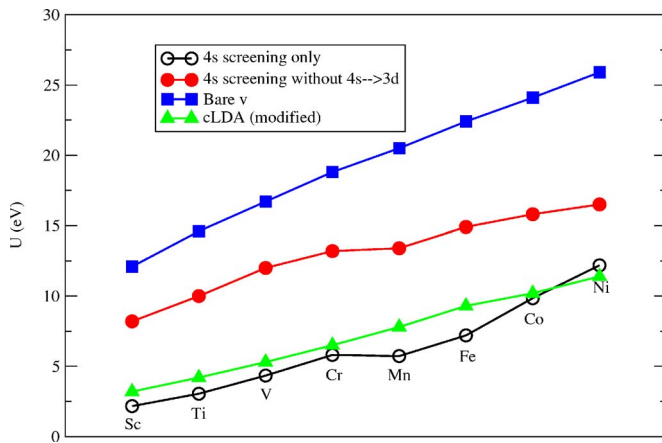
FIG. 8. (Color online) The effect of orbital contraction across the $3d$ series. Since the $3d$ orbital in nickel is most localized the bare Coulomb integral (filled square) is the largest. The bare Coulomb interaction is substantially reduced by the $4s$ screening (empty circle, the same as the empty circles in Fig. 7). The effect of $4s$ to $3d$ screening is illustrated by the filled circles. The effect, represented by the difference between the filled circles and the empty circles, is slightly more important in the early than in the late elements, due to the decreasing number of empty $3d$ states as we go from early to late elements.

the series (Cr, Mn). Compared to the case with $4s$ screening only (empty circle) we have additional screening channels arising from transitions from $3d$ to non-$3d$ bands. Evidently in Sc, due to the small number of $3d$ electrons, these additional screening channels contribute little to screening. As the number of $3d$ electrons increases, these additional channels correspondingly increase their contribution to screening reaching a maximum in nickel. In the case of nickel, this contribution is so large that when eliminated the bare Coulomb interaction is only reduced to about 12 eV from the bare value of 25 eV. This is in stark contrast to Sc where the screened interaction without contribution to screening from the $3d$ electrons is close to the value of the fully screened interaction W, implying that the small number of $3d$ electrons contribute little to screening, as expected. Contrary to intuition, the screening for U in transition metals is not only affected by the $4s$ electrons but also by the $3d$ electrons, especially in the late transition elements.

We now include the remaining $3d$ to $3d$ transitions to reach the fully screened interaction W (triangle). Not surprisingly, the largest contributions from $3d$ to $3d$ transitions occurs around the middle of the series where the $3d$ band is half-filled while the early elements show smaller contribution. The late elements also show tendency for smaller $3d$ to $3d$ contribution although not as small as for the early elements. It is remarkable although not surprising that the fully screened interaction W is almost constant across the series. The fact that W is almost constant across the series can be understood generally in terms of metallic screening. Since metallic screening is very efficient, essentially independent of the number of $3d$ electrons, the bare Coulomb interaction is always completely screened. Unlike the case of the bare interaction, the effect of orbital contraction is small because the static screened interaction W is presumably short range.
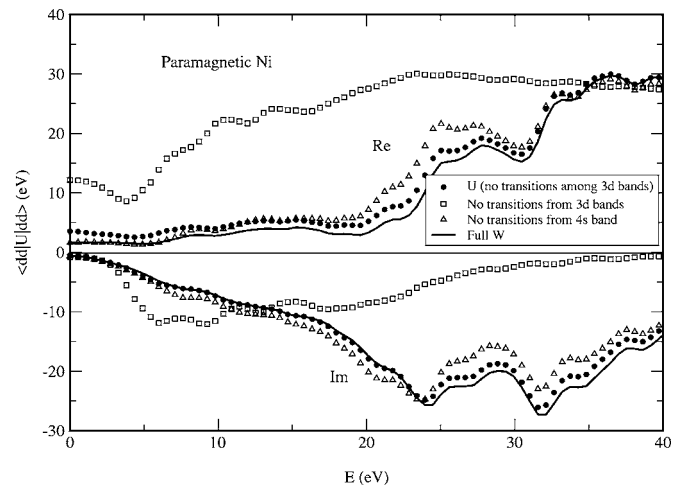

FIG. 9. Frequency dependent U (filled circle) and W (solid line) of paramagnetic nickel. Also shown are the results when all transitions from the $3d$ bands are eliminated (square) and when all transitions from the $4s$ band (lowest band) are eliminated (triangle).

The Hubbard U calculated using the CLDA method is significantly higher (>2 eV) than the value obtained using the RPA. This is rather puzzling because intuitively the procedure employed in the CLDA method is physically equivalent to that of the CRPA (apart from the neglect of exchange correlation, which is not expected to play a big role in this case and which can be incorporated within the LDA if necessary[20]). One possible source of difference may be due to the fact that by constraining the number of $3d$ electrons on one site in a supercell, one effectively cuts off the hopping from the $3d$ orbital to other orbitals. In the language of CRPA, this approximately corresponds to prohibiting transitions from the $3d$ bands to bands other than $3d$ as well as transitions from non-$3d$ bands to the $3d$ bands. For the early transition elements, the contribution of these transitions to screening is relatively small because of the small number of $3d$ electrons. For this reason CLDA result is close to that of CRPA. However, as we approach the late elements, $3d$ to non-$3d$ transitions contribute very significantly to screening. Since these are neglected in CLDA, the discrepancy between CLDA and CRPA results becomes much larger. This conclusion is however only semiquantitative. We emphasize that due to the strong hybridization between the $3d$ and $4s$-$4p$ orbitals, it is difficult to make a clear comparison between CLDA and CRPA.

In Figs. 9 and 10 we show the frequency dependence of the Hubbard U of nickel and vanadium. We have also analyzed the role of the screening channels in these two systems. As already discussed before, the difference between nickel and vanadium when all transitions from the $3d$ are eliminated is very striking. More surprisingly, eliminating all transitions from the $4s$ band (triangles) has little effect on the fully screened interaction W for both Ni and V, implying that $4s$ screening is not important. On the other hand, when only the $4s$ electrons are allowed to screen [by eliminating all transitions from the $3d$ bands (squares)], the bare interaction is reduced from about 25 to 12 eV in the case of nickel, and from 20 to 4 eV in the case of vanadium, implying the im-
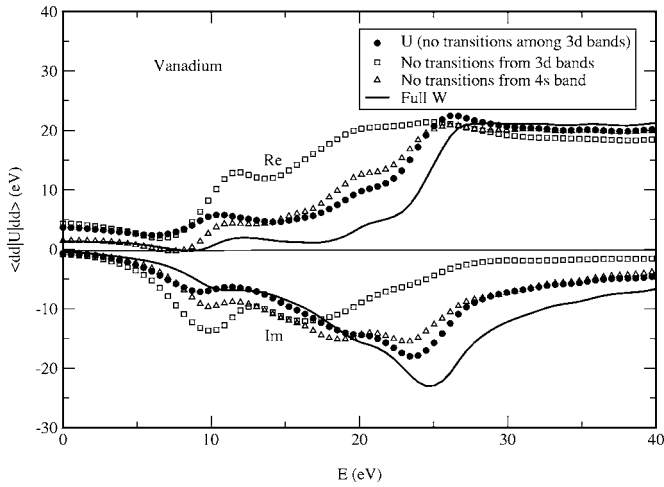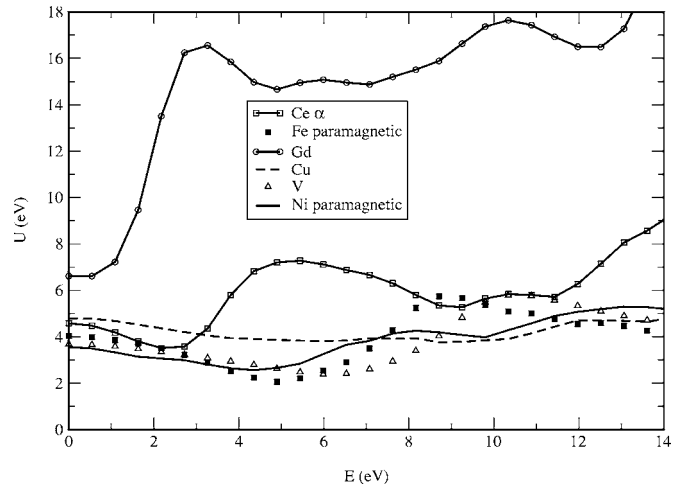
FIG. 10. The same as Fig. 9 but for vanadium.

FIG. 11. Frequency-dependent U of αCe, Fe, Gd, Cu, V, and Ni.

portance of 4s screening. The results appear at first sight to be contradictory but these results reflect the fact that the screening process is "nonadditive" in the sense that the effect of screening depends on what is to be screened. When the bare Coulomb interaction is already screened by the 3d electrons, the 4s electrons have little left to screen and vice versa when the 4s electrons have performed the screening there is not much left for the 3d electrons to screen.

D. Breathing or relaxation effects

Finally we comment on relaxation effects of the orbitals on the CLDA method. In calculating U the corresponding (localized) orbitals are usually allowed to breathe or relax in a self-consistency cycle. Constraining the number of electrons occupying the given orbitals is physically equivalent to applying a perturbing potential acting only on those orbitals such that the occupation number remains constant. The relaxation of the orbitals can therefore be regarded as the response to this perturbing potential. Since hopping from, say, the 3d orbitals is cut off, there are no relaxation to other non-3d orbitals and the relaxation corresponds therefore to (in the RPA language) transitions between 3d-3d, 3d-4d, etc. Transitions from 3d to higher d should be included but at least for the case of nickel 3d-4d transitions contribute little to the screening of U. This is in contrast to the atomic case where 3d-4d transitions can be significant.[21] However, 3d-3d transitions should not be allowed since they are implicit in the Hubbard model. The effect of 3d-3d screening can be large since this screening is metallic and may fortuitously compensate for the missing transitions to and from non-3d band. For this reason, we think that cLDA calculations for solids should not include relaxation of the constrained orbitals, as done in the modified cLDA in the present work.

E. Frequency dependence of U

Finally we comment on the possible importance of energy dependence of U. In Fig. 11 we show the frequency dependence of U for some elements within a relatively low energy range. It becomes clear from the figure that U can be far from a constant within the band width of each element. This suggests that taking the static value of U and using it in a model Hamiltonian may be inappropriate. Rather, some kind of averaging over some range of frequency may be necessary. Consider for example cerium. The commonly used value of 6 eV for U in model calculations falls within the minimum and the maximum value within a frequency range of 5 eV. For iron, the calculated static value of about 4 eV is considerably larger than the commonly used value of 2.0–2.5 eV, which lies in between the calculated static value and the minimum of 2.0 eV at about ω=5 eV. The case of Gd is even more striking, with U starting at $\sim$6.5 eV and shooting up to $\sim$16 eV within a frequency range of 3 eV. On the other hand, nickel and SrVO$_3$ appear to have a relatively constant value of U at low energy.

IV. SUMMARY AND CONCLUSION

We have calculated the Hubbard U for the 3d transition metal series as well as cerium, SrVO$_3$ and YTiO$_3$ using a recently proposed basis-independent CRPA method. Although the U values presented in this work may not be the ultimate ones, we nevertheless believe that they provide a useful guideline for reasonable values of U that should be used in the *lattice* Hubbard model. The precise values of U depends on the choice of the one-particle orbital defining the annihilation and creation operators of the model Hamiltonian, no matter what method we use to calculate U. Our scheme, however, allows the calculation of $U(\mathbf{r},\mathbf{r}')$, which is basis independent. But the matrix element in Eq. (5) entering the Hubbard model will inevitably depend on the choice of the one-particle basis ϕ_{3d} of the model.

We have studied systematically the role of the screening channels in a number of materials. In the case of cerium, $5d \rightarrow 4f$ polarization is important whereas $4f \rightarrow$ non-4f is much less important due to a small number of 4f electrons. In the case of SrVO$_3$, $O_{2p} \rightarrow V_{3d(t_{2g})}$ polarization plays a crucial role in reducing the Coulomb interaction. On the other hand, $t_{2g} \rightarrow e_g$ polarization is not important. The screening

properties of the 3*d* transition series are more difficult to analyze due to strong hybridization between the 3*d* and 4*s*-4*p* orbitals, which prevents a clear distinction between the various screening channels. Nevertheless, our results indicate that in early transition series, such as vanadium, most of the (static) screening of *U* can be attributed to the 4*s* electrons. The situation is very different for the late transition metals, where, in addition to the 4*s* electrons, the 3*d* electrons themselves contribute substantially to the screening of *U*. This can be understood from a simple fact that the number of 3*d* electrons is large so that $3d \rightarrow$ non-3*d* screening is substantial, in contrast to the early transition metals with a small number of 3*d* electrons. For the fully screened interaction *W*, $3d \rightarrow 3d$ screening alone is sufficient to obtain the static value due to a very efficient metallic screening for all the elements in the series. Screening from the 4*s* electrons alone are not sufficient to obtain the static *W*, contrary to what is commonly stated in the literature.

We have also studied the frequency dependence of *U* and found that it can be far from constant at low energy. This suggests that for some materials the calculated static value of *U* may not be appropriate and some kind of averaging over a frequency range may be necessary. For example, a simple energy averaging over the bandwidth is a possible choice.

We have also compared the CRPA values with those calculated using the well-known CLDA method. Significant discrepancy is observed particularly towards the end of the 3*d* series. A possible source of discrepancy may be attributed to *technical* difficulties of including polarization of the 3*d* electrons to other angular momenta in the CLDA method. We would like to emphasize that the two methods CLDA and CRPA theoretically ought to give the same results. In practical implementations, $3d \rightarrow$ non-3*d* polarization corresponding to transitions from the occupied 3*d* bands to unoccupied bands other than of 3*d* characters may not be properly included due to the constraint on the number of the 3*d* electrons, which effectively cuts off hopping of the 3*d* electrons to other bands. While this polarization is small for the early 3*d* elements, due to the small number of 3*d* electrons, the contribution becomes increasingly large as we go towards the end of the series. Our CRPA results for Ce and $SrVO_3$ are also consistent with the CLDA results but only when the screening channels associated with the cut off of the hopping in CLDA are correspondingly eliminated. It would be desirable to modify the CLDA method to include screening channels not included in current implementations.

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