Ab initio calculations of the Hubbard U for the early lanthanides using the constrained random-phase approximation

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In this work we have calculated U from first principles for the early lanthanides (Ce-Gd) using the constrained random phase approximation (cRPA). We compare the static limit of U with experimental estimations from x-ray photoemission spectroscopy (XPS) and bremsstrahlung isochromat spectroscopy (BIS) spectra and also discuss the frequency dependence of U across the series. The localized subspace is constructed using maximally localized Wannier functions (MLWFs). We discuss the choice of parameters used to construct the Wannier functions and show that in the case of Eu and Gd, where the local density approximation does not yield the correct position of the 4f bands, a physically motivated choice gives better agreement with experiment.

DOI: 10.1103/PhysRevB.88.125123

PACS number(s): 71.20.Eh

I. INTRODUCTION

The lanthanide series covering 15 elements starting from lanthanum with atomic number 57 to lutetium with atomic number 71 occupy a special place in the periodic table. Despite their more commonly known names as "rare earths," they are quite abundant in nature. Cerium is among the most abundant element in the Earth's crust and neodymium is more abundant than gold. Their electron configurations are rather unusual in that after lanthanum with one 5d electron, the energy of the 4f shell lies lower than the energy of the 5d shell so that starting from cerium electrons start to occupy the 4f shell rather than the 5d shell. The 4f electrons therefore lie deep inside the core and they are shielded by the 5d as well as 5s-5p electrons. When the lanthanide atoms form crystals, the very localized nature of the 4f electrons and their vicinity in energy with the 5d and 5s-5p electrons result in hybridization with many intriguing properties. Among the most interesting properties of the lanthanides is magnetism, which arises from unpaired 4 f electrons and strong spin-orbit coupling that can lead to higher magnetic moment than the unpaired electron spins alone would suggest. This is the case, for example, with Dy^{+3} and Ho⁺³ with magnetic moments in the range 10.4–10.7 bohrs magneton.

The lanthanides have found their way to many industrial applications ranging from catalysts in oil refining, control rods in nuclear reactors, Nd:YAG solid-state lasers, optical fibers, and the well-known neodymium-iron-boron high-flux magnets. The lanthanides are not only interesting from the point of view of applications but also from a fundamental theoretical point of view. It is by now well recognized that mean-field or one-particle theories are far from adequate to provide a sound description of the electronic structure of these elements and their compounds. Thus, for example, the much studied isostructural α to γ phase transition in cerium can hardly be understood within the conventional local density approximation (LDA) of density functional theory, which predicts almost identical density of states for the two phases, whereas experimentally there is a substantial reduction in quasiparticle weight around the Fermi level in going from the smaller α phase to the larger volume γ phase accompanied by an increase in satellite weight. The α - γ phase transition in cerium has been a subject of debate for many years and only recently a consensus is emerging regarding the correct description underlying the phase transition, which requires a sophisticated many-body treatment like dynamical meanfield theory $(DMFT)^1$ well beyond one-particle description. Although DMFT can provide a coherent description of the electronic structure of cerium, the treatment is usually based on a Hubbard or Anderson impurity model Hamiltonian and a fully first-principles scheme comparable to LDA is still lacking.

Due to the open-shell and localized nature of the 4fvalence electrons in the lanthanides these materials exhibit strong electronic correlations. A recent fully first-principles attempt to go beyond the LDA using the GW approximation $(GWA)^{2,3}$ fails to provide a correct description of the α - γ phase transition in cerium. Like in the LDA, the calculated oneparticle spectra of both phases are almost identical, revealing a fundamental problem inherent in the GWA when applied to strongly correlated systems. Quasiparticle self-consistent GW (QSGW)⁴ has been shown to improve the one-shot GW result for a number of 4f systems but the position of the unoccupied 4 f bands are overestimated by 1–4 eV compared to the experimental spectra.⁵ Also, QSGW is a one-particle theory and therefore many-body phenomena such as Mott transitions and multiplet structures are not accounted for in this model. It seems clear that to describe strongly correlated systems the GWA is not sufficient and it is necessary to develop more accurate methods. A natural first step is to determine the parameters in model Hamiltonians from first principles and then solve the models to all orders in the effective interaction between the localized electrons using many-body techniques such as DMFT. A suitable platform for this line of approach is already available. In the LDA + DMFT method, the oneparticle spectrum is supplied from first principles by the LDA and it remains to determine the effective interaction or the Hubbard U^6 of the correlated electrons from first principles. Usually U is taken as a parameter and fitted to experiment which severely reduces the predictive power of the model. Instead it would be desirable to calculate U from basic physical principles. One of the earliest attempts initiated by Herring is to estimate U from atomic data.⁷⁻¹⁰ Dederichs *et al.*¹¹ used a constrained LDA (cLDA) method with later improvement by Hybertsen *et al.*¹² and Cococcioni and de Gironcoli¹³ by taking into account the change in the kinetic energy of the electrons. A cLDA approach using a supercell calculation, $^{14-17}$ where hopping integrals from the orbital with localized electrons are cut off for the central atom in the supercell, has been widely used to calculate *U* from first principles.

In the present work we use the constrained random-phase approximation (cRPA).^{18–20} In this method U is identified as the partially screened interaction (W_r) where the transitions between the localized states defined in the model have been removed. This makes it possible to calculate the matrix elements of U from the band structure alone by calculating the partially screened interaction within the random phase approximation (RPA). Since a large part of the short-range correlations have been excluded from W_r one may expect that it is relatively well described within the RPA. The cRPA method has been applied with success to a wide range of materials from transition metals,¹⁹ iron-based superconductors,²¹ graphene,²² transition metal oxides,^{23,24} to metal and insulator surfaces.²⁵

In this work we do a systematic study of the Hubbard U calculated using the cRPA for the lanthanides. We look both at the static limit and frequency dependence and discuss how the cRPA values compare with experimental estimations from BIS and XPS spectra. We discuss in detail how to choose the energy window used to construct the localized subspace and show that for certain cases a physically motivated choice of parameters can improve the result substantially.

II. METHOD

A. Constrained RPA

By dividing the Hilbert space into two parts, the subspace of the model which is called the *f* subspace containing the localized 4*f* states and the *r* subspace spanning the rest of the space, it is possible to express the polarization as $P = P_f + P_r$. Here P_f contains the polarization within the *f* subspace and P_r contains the rest of the polarization. The main idea of the cRPA¹⁸ is to identify the Hubbard *U* as the partially screened Coulomb interaction

$$U = \frac{v}{1 - vP_r} \tag{1}$$

which, if further screened by the polarization P_f of the model, will reproduce the fully screened interaction

$$W = \frac{v}{1 - vP} = \frac{U}{1 - UP_f}.$$
 (2)

The polarization is calculated within the random phase approximation, which for a given spin is given by

$$P(\mathbf{r},\mathbf{r}';\omega) = \sum_{\mathbf{k}n}^{\operatorname{occ}} \sum_{\mathbf{k}'n'}^{\operatorname{unocc}} \frac{\psi_{\mathbf{k}n}^{*}(\mathbf{r})\psi_{\mathbf{k}'n'}(\mathbf{r})\psi_{\mathbf{k}'n'}(\mathbf{r}')\psi_{\mathbf{k}n}(\mathbf{r}')}{\omega - \epsilon_{\mathbf{k}'n'} + \epsilon_{\mathbf{k}n} + i\delta} - \frac{\psi_{\mathbf{k}n}(\mathbf{r})\psi_{\mathbf{k}'n'}(\mathbf{r})\psi_{\mathbf{k}'n'}(\mathbf{r}')\psi_{\mathbf{k}n}(\mathbf{r}')}{\omega + \epsilon_{\mathbf{k}'n'} - \epsilon_{\mathbf{k}n} - i\delta}.$$
 (3)

The total polarization is the sum over the spin channels.

For the lanthanides the localized 4f bands are mixed with the crossing s and p bands. In order to get a well defined f subspace the hybridization is removed by disentangling the f subspace from the r subspace.²⁰ In practice this is accomplished by removing all coupling between the f and r subspaces in the Hamiltonian and diagonalizing the two blocks separately:

$$\tilde{H} = \begin{pmatrix} H_{ff} & 0\\ 0 & H_{rr} \end{pmatrix}.$$

The *r*-subspace polarization is then calculated as $P_r = P - P_f$, where the full polarization *P* and the *f*-subspace polarization P_f are calculated *for the disentangled band structure* according to Eq. (3). There is some arbitrariness in defining the *f* subspace which depends on the choice of the energy window when constructing the Wannier orbitals. A physically motivated choice of the energy window is therefore needed. The fully screened interaction [*W* in Eq. (2)] can be calculated both for the original LDA band structure (W_{orig}) and for the disentangled band structure is close to the original one, these two quantities will be nearly identical but if there is a large hybridization between the *f* and *r* subspaces there could be substantial differences.

The matrix elements of U are given by

$$U(n_{1}\sigma, n_{2}\sigma, n_{3}\sigma', n_{4}\sigma'; \mathbf{R}; \omega)$$

$$= \int \int d^{3}r d^{3}r' [\phi_{n_{1}0}^{\sigma}(\mathbf{r})]^{*} \phi_{n_{2}0}^{\sigma}(\mathbf{r}) U(\mathbf{r}, \mathbf{r}'; \omega)$$

$$\times [\phi_{n_{3}\mathbf{R}}^{\sigma'}(\mathbf{r}')]^{*} \phi_{n_{4}\mathbf{R}}^{\sigma'}(\mathbf{r}'), \qquad (4)$$

where $\{\phi_{n_i \mathbf{R}'}^{\sigma}\}\$ are the Wannier functions spanning the *f* subspace and σ reflects the fact that these functions, in general, are different for the two spin channels.

In this work we mainly consider the on-site direct components $(U_{nm}^{\sigma\sigma'})$ and the on-site exchange $(J_{nm}^{\sigma\sigma})$ as well as spin-flip and pair-hopping $(J_{nm}^{\sigma\bar{\sigma}})$ components of the partially screened interaction:

$$U_{nm}^{\sigma\sigma'} = \int \int d^3r d^3r' |\phi_{n0}^{\sigma}(\mathbf{r})|^2 U(\mathbf{r},\mathbf{r}';0) |\phi_{m0}^{\sigma'}(\mathbf{r}')|^2, \quad (5)$$
$$J_{nm}^{\sigma\sigma'} = \int \int d^3r d^3r' \left[\phi_{n0}^{\sigma}(\mathbf{r})\right]^* \phi_{m0}^{\sigma}(\mathbf{r}) U(\mathbf{r},\mathbf{r}';0)$$
$$\times \phi_{n0}^{\sigma'}(\mathbf{r}') [\phi_{m0}^{\sigma'}(\mathbf{r}')]^*. \quad (6)$$

Further on we will denote the average diagonal element of $U_{nm}^{\sigma\sigma'}$ by U and the average exchange element of $J_{nm}^{\sigma\sigma}$ $(n \neq m)$ by J. The corresponding quantities of the bare and the fully screened interaction will be denoted by v (bare direct) and W (screened direct) as well as v^x (bare exchange) and W^x (screened exchange).

B. Computational details

As a starting point we use the LDA band structure calculated with the full-potential linearized augmented planewave (FLAPW) code FLEUR.²⁶ The *f* subspace is constructed using maximally localized Wannier functions^{27,28} (MLWFs) calculated with the WANNIER90 code^{29,30} and finally the matrix elements of *U* are calculated using the cRPA as implemented in the SPEx code.³¹ For the elements between Pr and Gd spin-polarized calculations were done including the 5*s* and 5*p* core states as local orbitals. For Ce the calculations were



FIG. 1. (Color online) U calculated for hcp Gd and fcc Gd with the same electron density. The energy windows with a width of 2.6 eV were used for both the majority and minority spin.

done without spin polarization, since Ce is not spin polarized within the LDA. For these calculations it was also sufficient to only include the 5p core states as local orbitals. In the cRPA calculations we used $8 \times 8 \times 8 k$ points.

In the present work the disentanglement approach²⁰ described in the previous section is used rather than the more recent weighting approach of Ref. 32. The disentanglement scheme has the advantages that a larger part of the low energy excitations are removed from P_r and that there are well defined one particle bands associated with the model. This simplifies the construction of effective Hamiltonians using, e.g., the Hubbard model.

For all calculations the lattice parameters taken from Ref. 33 were used. In order to reduce the computational time for the elements with close-packed structures and more than one atom per unit cell (such as hcp and dhcp structures, etc.) we used fcc structures with a unit-cell volume chosen to preserve the atomic density. Since the static value of U is largely determined by the coupling to the plasmon excitation and the plasma frequency is determined by the electron density through the f-sum rule this approximation is not expected to affect any of the main features of U. Furthermore, since the 4 f orbitals are highly localized they are not much affected by the crystal structure. Especially, the 4 f bandwidth is expected to be the same for the unit cells chosen in this work and the experimental unit cells. Due to the similarities of the fcc and the hcp, dhcp as well as Sm structures (all are close packed but with different stacking), one would also expect the main features of the *r*-subspace DOS to be well represented by the density preserving fcc cell. Considering these arguments the errors introduced by our choice of unit cells are expected to be much smaller than the errors introduced by other factors, such as removing the coupling between the f and r subspace. In Fig. 1 we show U calculated for hcp Gd and the corresponding phenomenological fcc Gd used in this work. From this figure one can see that U is indeed very similar for the two cases which confirms that the choice of a density preserving fcc cell rather than the experimental close-packed cell does not have much influence on U.

In the lanthanides the localized 4f bands are mixed with the crossing 6s and 5d bands. In order to determine which states should be used to construct the MLWFs a combination of energy window and band index is used. That is, only states belonging to certain bands and with energies within a given energy interval are used to construct the MLWFs. Naturally, the choice of energy window will affect both the Wannier basis functions and the disentangled band structure. In principle it would be desirable to remove all hybridization and thus keep the energy window and number of bands unrestricted. However, this often leads to unphysically narrow bands and substantial overestimations of U. Instead, one often looks at the disentangled band structure and chooses the energy window so that this gives a good representation of the original band structure. Such a choice is well motivated if the LDA band structure is close to the true band structure. For the middle and later lanthanides, however, the LDA is a rather poor starting point and the choice of energy window is therefore associated with a certain amount of arbitrariness. Therefore we will put some emphasis on the choice of energy window in this work, especially for the case of Eu and Gd where the LDA is particularly poor.

III. RESULTS AND DISCUSSION

A. Eu and Gd: Determining the energy window

The electronic configuration of Eu is $4f^76s^2$. Within the LDA, the majority spin bands will be filled but close to the Fermi energy and there will be some hybridization with the crossing 6s and 5d bands (r subspace). The minority spin bands are empty and are centered at approximately 4 eV above the Fermi energy (see Fig. 2).

 P_r , which determines U, contains both the r-r and the f-r screening channels. However, in the disentangled band structure for Eu, since the f-r hybridization is removed, the *f*-subspace DOS will be zero at the Fermi energy. Hence the low energy part of P_r will only contain r-r polarization. The r-r polarization depends strongly on how much hybridization that is removed from the r subspace, which makes the value of U for Eu extremely sensitive to the choice of (majority spin) energy window, much more so than U for the earlier lanthanides where the screening due to r-rpolarization is negligible compared to the contribution from the f-r polarization. The f-r polarization is less sensitive to the disentanglement, as can be understood intuitively by noting that removing a large part of the hybridization reduces the *r*-subspace DOS at the Fermi energy but correspondingly increases the f DOS which keeps the f-r contribution to P_r roughly constant.

In Fig. 3 we can see how the value of the fully screened interaction (*W*) as well as the partially screened interaction (*U*) varies for different widths of the majority spin energy window. The fully screened interaction is calculated both for the original (W_{orig}) and for the disentangled states (W_{dis}). (For definitions see Sec. II A.) Since the *f* subspaces of the majority and minority spins are, respectively, completely filled and empty, there is no polarization within these *f* subspaces so that W_{dis} and *U* are identical.³⁴ The bare Coulomb interaction across the series is also shown in the the inset of Fig. 3.

Key to understanding the behavior of U is the recognition that the value of U depends on two factors; the localization of the Wannier functions and the screening by P_r . On the other hand, for a given material the bare interaction and the original



FIG. 2. (Color online) LDA band structure of Eu (left) and Gd (right).

screened interaction W_{orig} depend only on the shape and extent of the Wannier orbitals. Since W_{orig} is approximately constant and the bare interaction only increases slightly as the energy window is widened, we may conclude that the change in the localization of the Wannier orbitals does not have much direct influence on U. Thus, the increase of U in Fig. 3 can be attributed to decreased screening. As the energy window is widened a larger part of the hybridization with the r subspace is removed and therefore the screening associated with P_r is reduced so that U increases.

The growing difference between W_{orig} and W_{dis} implies that the disentangled and original band structures become increasingly different as the energy window is increased. If the LDA had been a good starting point it would have been natural to keep this difference small and choose a narrow energy window. However, for Eu the majority spin bands will be pushed down in a more accurate treatment like the LDA + U (see, e.g., Ref. 35), which reduces the hybridization between the 4*f* orbitals and the 5*d* and 6*s* orbitals substantially. Therefore, removing a large part of the hybridization by choosing a wide energy window for the majority spin channel will give a disentangled band structure that better mimics the properties of the true band structure. In the 4 *f* -partial density of states shown in Fig. 4 one can see that there are small 4f components even at energies higher than 10 eV above the Fermi energy which further motivates a wide energy window. In this work we do not use an energy window for Eu, instead we only use states with band indices between 5 and 18 to create the Wannier functions. This choice excludes the core states from the Wannier functions and also provides a high-lying upper bound in form of the 18th energy band at an approximate energy of 10 eV. It should be noted that from the DOS in Fig. 4 any energy window with a width from 3 to 12 eV could be motivated, which would give values of U ranging from 6 to 9 eV. The reason that we choose a relatively large window in this work is to better mimic the properties of a self-consistent calculation using, e.g., LDA + U. However, the present choice is associated with a certain amount of arbitrariness and to obtain a more accurate value one should do a self-consistent calculation, using, e.g., LDA + U.

The sensitivity of U with respect to the energy window for Eu is an inherent problem with the disentanglement approach



FIG. 3. (Color online) Left: The static average direct diagonal matrix element of the fully screened interaction (W) and the partially screened interaction (U) for Eu for different majority spin energy windows. W is calculated using both the original states (W_{orig}) and the disentangled states (W_{dis}). The majority spin energy window is centered at -0.5 eV and the minority spin energy window is kept constant at 2.5–5.5 eV. The inset shows the values of the bare interaction calculated for the same energy windows. Right: W_{orig} , W_{dis} , and U calculated for Gd. The minority spin energy window is centered at 0.4 eV and the majority spin energy window is kept constant at -5.6 to -3 eV.



FIG. 4. (Color online) Left: Interpolated band structure for the minority spin of Gd. Right: Partial f density of states for the majority spin of Eu and the minority spin of Gd, respectively.

for this particular material. In the more recent weighting approach,³² where the *f*-subspace polarization is calculated for the original band structure but each transition is weighted by the probability that the electron will reside in the *f* subspace before and after the transition, *U* is less sensitive to the choice of energy window. Since the hybridization between the 4f states and the 6s and 5d bands is included in the model the value of *U* is also much smaller using this approach (\approx 3.2 eV). It is also much smaller than the experimentally deduced value in Fig. 5. However, in a self-consistent calculation the two methods are expected to give a similar result since the hybridization is smaller in the self-consistent band structure.

Gd has the electronic configuration $4f^{7}5d^{1}6s^{2}$. For this element the majority spin bands are situated well below the Fermi level resulting in a small hybridization and U is therefore rather insensitive to the choice of a majority energy window. The minority spin bands, on the other hand, are close to the Fermi energy and will become slightly filled in the disentangled band structure. Looking at Fig. 3 one can see that W_{dis} and W_{orig} coincide for an energy window with a width around 2.2–2.4 eV, which could motivate a choice within this energy range. However, such an energy window would exclude a substantial amount of 4f states from the f subspace (see DOS Fig. 4). By choosing a slightly wider energy window with a width of 3 eV we include a larger part of the 4f states which results in a smoother band structure, still close to the original one, while keeping the difference between W_{dis} and W_{orig} smaller than 1 eV.

B. Static values for the entire series

We begin by discussing the diagonal elements of the Coulomb interactions shown in the inset of the left plot of Fig. 5. The bare interaction increases monotonically through the series. It is clear from Eq. (5), with U replaced by the bare interaction, that the increase in the bare Coulomb interaction reflects the increasing localization of the Wannier functions (see Fig. 6).

We now consider the fully screened interaction. When going from Ce to Pr the fully screened interaction W experiences a decrease of approximately 50%. This may be understood from the substantial increase of metallic screening within the 4fband (f subspace) when going from one 4f electron/atom (Ce) to three (Pr). The increase in screening is large enough to overcome the opposing effect of increasing Wannier



FIG. 5. (Color online) Left: The static average direct diagonal matrix element of the fully screened interaction (W) and the partially screened interaction (U) for the lanthanides. W is calculated using both the original states (W_{orig}) and the disentangled states (W_{dis}). The energy windows presented in Table I were used. The experimental data are taken from Ref. 36 and are estimations of U from XPS and BIS spectra. Karlsson *et al.* is U calculated using a cRPA based self-consistent LDA + U scheme.³⁸ The inset shows the average diagonal element of the bare interaction (U), and the bare interaction (v^x) for the lanthanides.



FIG. 6. (Color online) Average spread of the Wannier functions for the different elements.

localization which should increase W. Between Pr and Sm W is approximately constant, showing a small increase of only 0.04 eV, indicating that the increase in W due to the effect of Wannier localization is almost compensated by the decrease in W due to the increase in total screening, associated with the increase in the number of 4f electrons in the majority band. At Eu the 4f majority band becomes fully occupied, whereas the 4f minority band becomes completely empty so that the polarization within the 4f band, or f-subspace polarization P_f , vanishes which causes a substantial decrease of the total screening and we can therefore see an abrupt increase of W for this element. P_f is partially restored for Gd due to the small filling of the f-subspace minority spin bands in the disentangled band structure (Fig. 4). This yields an increased screening which lowers the value of W. Although less pronounced, this decrease is also seen in the original fully screened interaction and can be attributed to the LDA band structure which places the minority band too close to the Fermi level.

The partially screened interaction U exhibits a more complicated behavior and one can identify three main features:

- 1. The difference between the two phases of Ce,
- 2. the slight decrease from Ce- γ to Sm, and
- 3. the rapid increase between Sm and Gd.

The Ce γ - α phase transition is an isostructural volume collapse from the larger γ phase to the smaller α phase. The larger atomic spacing for Ce- γ enables the formation of more localized Wannier functions that in turn gives increased values of the matrix elements of the Coulomb interactions. However, seeing the small effect it has on the bare interaction (≈ 0.55 eV), the localization of the Wannier functions are not sufficient to explain the relatively large difference of U between the two phases. The larger lattice constant for Ce- γ will, apart from leading to more localized Wannier states, also lead to a smaller 4f (f subspace) bandwidth. A smaller 4f bandwidth implies a larger 4f DOS at the Fermi energy and thus also a larger screening by P_f . From Eq. (2) we can see that the fully screened interaction is obtained by letting U be further screened by the f-subspace polarization P_f . Seeing that W is approximately equal for the two phases and the screening associated with P_f is larger for the γ phase, this implies that also U is larger for $Ce-\gamma$, in agreement with the results in Fig. 5. In other words, the f-subspace polarization, which is excluded from U, contains a smaller part of the total screening for Ce- α , which indicates a substantial hybridization also in the disentangled band structure for this element.

From Ce- γ to Pr U follows the same trend as the fully screened interaction implying that also the screening associated with P_r increases, which decreases U as can be seen from Eq. (1). The increase in P_r can be understood by noting that P_r includes both the r-r and the f-r polarization channels. An increase of the 4f (f subspace) DOS at the Fermi energy will tend to increase the screening due to the f-r polarization and therefore also decrease the value of U. From this argument one would also expect U to be smaller for Pr than for Ce- α , contrary to what can be observed in Fig. 5. This discrepancy further emphasizes the large ratio of P_r/P for Ce- α , due to hybridization.

Between Pr and Sm the fully screened interaction W is approximately constant, whereas U decreases slowly. This suggests that in the case of U, the cancellation between the decrease in the screened interaction as a result of an increase in the polarization due to an increase in the DOS around the Fermi energy and the increase in the screened interaction due to the increase in Wannier localization is not as complete as for W. In other words, in the case of U the effects of the increase in the polarization P_r slightly dominates the effects of the increased localization of the Wannier orbitals.

As discussed in detail in the previous section the value of U for Eu is highly dependent on the choice of energy window. By choosing a large (majority spin) energy window the 4f Wannier orbitals become more localized and consequently we remove a large part of the hybridization between the 4f and the 5d-6s orbitals resulting in a decrease in P_r and consequently in a larger value of U. Between Eu and Gd the increase in U can be ascribed to the increased localization of the Wannier functions.

For the average exchange element J in Fig. 5 the screening is small and J therefore follows the same trend as the average exchange element of the bare interaction (v^x) . This is due to the fact that it is much harder to screen an exchange charge distribution which has no spherical component than to screen a spherical charge distribution so that, as has been commonly assumed for a long time, the value of J in a crystal is approximately the same as its atomic value. Since both J and v^x are relatively constant the structure that can be seen for W^x reveals the variation of P_f across the series. A small value of W^x corresponds to a large f -subspace screening which further confirms that P_f is larger for Ce- γ than for the α phase and also indicates that the screening due to P_f reaches its maximum for Nd. The static values of U and J for all elements are given in Table I.

When comparing the cRPA results with the experimental estimations in Fig. 5 one can see that both the theoretical and experimental values follow the same basic trend. It is noteworthy that both the experimental estimates and the theoretical predictions of U across the series reveal a structure at Nd. We speculate that the origin of this structure is due to the fact that at Nd the majority 4f band becomes half-filled and the polarization P_f reaches its maximum. We observe that the fully screened interaction W is rather constant across the series and by examining Eq. (2) we may conclude that to maintain a constant W with an increase in P_f , the value

TABLE I. Static U, J, and energy window used for the calculations. Win 1/2 are the majority/minority spin windows in eV. U and J are given in eV.

| | U | J | Win 1 | Win 2 |
|------|-----|-----|------------------------|------------------------|
| Ce-α | 4.3 | 0.5 | $-1.1 \rightarrow 2.3$ | _ |
| Ce-y | 5.4 | 0.6 | $-1.0 \rightarrow 2.0$ | _ |
| Pr | 4.8 | 0.6 | $-1.4 \rightarrow 1.6$ | $0.0 \rightarrow 3.0$ |
| Nd | 4.8 | 0.6 | $-1.5 \rightarrow 1.5$ | $0.4 \rightarrow 3.8$ |
| Pm | 4.3 | 0.6 | $-1.7 \rightarrow 1.3$ | $0.8 \rightarrow 4.2$ |
| Sm | 4.0 | 0.6 | $-1.7 \rightarrow 1.3$ | $1.8 \rightarrow 5.2$ |
| Eu | 9.1 | 0.7 | ∞ | $2.5 \rightarrow 5.5$ |
| Gd | 9.6 | 0.8 | $-5.6 \rightarrow -3$ | $-1.1 \rightarrow 1.9$ |

of U for Nd should be larger than those of its neighboring elements.

The cRPA yields slightly smaller values of U than the values obtained from the experimental spectra. This underestimation may be explained by two factors. First, the experimentally deduced value of U may be regarded as an *effective* static value which is not necessarily the same as the calculated static limit of U $[U(\omega = 0)]$. When estimating an effective static U one should in principle include the effects of the frequency dependence of U by downfolding the high-energy part of Uinto the static value. However, there is, to our knowledge, no known way to do this and therefore we have simply taken the static limit of $U[U(\omega = 0)]$ in this work. A different point of view concerning this important issue was recently proposed by Casula et al.³⁷ In their work it is formally shown that the static value of U obtained within the cRPA is the appropriate value to use provided one first renormalizes the one-particle dispersion. In this approach, the effects of the frequency dependence of Uis taken into account in the one-particle dispersion so that the effective static value of U for the renormalized quasiparticle band is just the static value of U calculated in cRPA. Another possible source of underestimation of U is that the LDA band structure is not a sufficiently good starting point for the lanthanides. Thus, in order to get an improved result for these elements U has to be calculated in a self-consistent manner. That a self-consistent calculation indeed increases the value of U in the case of Gadolinium was shown by Karlsson et al.³⁸ within a self-consistent LDA + U scheme. Here one could see that the self-consistent U showed a smoother frequency dependence at low energies and also a higher static value $[U(\omega = 0)]$ than the original cRPA result. The peaks in the imaginary part of U corresponding to the f-r transitions were pushed up in energy towards self-consistency, which effectively gave a smoother low frequency structure of the real part of U through the Kramers- Kronig relation. However, as will be discussed in the next section, this effect is expected to be smaller for the parameters chosen in this work since a larger part of the hybridization is removed already in the initial cRPA calculation.

In Refs. 39 and 40 a number of the rare-earth metals were studied using the Hubbard-I formalism. Of special interest to this work are the results for Pr, Nd, and Sm where a value of U of 7 eV was used for all elements. The calculated spectral function reproduced experimental XPS and BIS spectra well, except for one peak which was concluded to be of nonlocal

character and therefore not well described by the model. However, the peaks in the spectral function corresponding to the unoccupied f states were positioned slightly higher in energy than the corresponding experimental BIS peaks. This is understandable since U determines the separation between the occupied and unoccupied 4f states and the value of U used in Ref. 39 is slightly larger than what one would estimate from the experimental spectra (see, e.g., Fig. 5). Correspondingly, since the static values of U presented in this work are slightly smaller than the experimental estimations a straightforward use of these parameters, without accounting for the frequency dependence of U, is expected to give a small underestimation of the splitting between the occupied and unoccupied 4f states.

C. Frequency dependence

In Fig. 7 the full frequency dependent U and W are displayed.

Since all transitions within the f subspace have been removed from U it has a much smoother behavior at low frequencies than the fully screened interaction. The remaining low frequency structure, mainly in Ce, comes from low frequency f-r transitions. This structure could be reduced by increasing the energy window in the calculation. However, a larger energy window would also increase the difference between the disentangled and original band structures. For high frequencies $U(\omega) \rightarrow W(\omega)$ since the screening associated with P_f vanishes for energies much larger than the bandwidth of the f subspace.

The peaks in the imaginary part of the screened interaction correspond to the zeros of the dielectric function. The large peak at approximately 12 eV originates from a collective plasma oscillation. The position of the plasmon peak could roughly be estimated from an electron gas model as $\omega_p = \sqrt{4\pi\rho}$, where ρ is the valence electron density. This gives a value ranging from 12.7 eV (Ce) to 16.1–20.4 eV (Eu-Gd). However, due to their localized nature, the 4 *f* electrons do not contribute fully to the plasmon oscillation which explains the overestimation by the electron gas model compared to Fig. 7.

The two subsequent peaks at approximately 20 and 35 eV originates from particle-hole transitions from the two shallow 5s and 5p core orbitals. The poles of the response function for a two level system provides a rough estimation of the position of these peaks:⁴¹

$$\Omega_{nn'} = \sqrt{\Delta \epsilon_{nn'}^2 + 2J_{nn'}\Delta \epsilon_{nn'}} \approx \begin{cases} 18 \text{ eV} & (5p) \\ 37 \text{ eV} & (5s), \end{cases}$$
(7)

where $\Delta \epsilon_{nn'}$ is the energy difference between the 4*f* states and the 5*s* (5*p*) core states and the exchange interaction between the states $J_{nn'}$ has been approximated to zero in the last step. In Fig. 8 we present calculations of *U* for Nd where all transitions from the 5*s* and 5*p* orbitals have been excluded from the polarization function. From this figure we can see that the high energy peaks indeed disappears, as expected from the above analysis.

A resonance with the 5p orbital is also clearly visible for J in Fig. 9. Apart from this peak J follows the expected trend, there is some low frequency structure due to f-r polarization but J quickly approaches its atomic value.



FIG. 7. (Color online) U and W for the entire series. W was calculated using the disentangled band structure.

In the self-consistent LDA + U calculations for Gd by Karlsson *et al.*³⁸ it was found that the self-consistent treatment increases the static value of U and also removes some of the low frequency structure. However, the result from the initial cRPA calculation by Karlsson *et al.*³⁸ shows significant differences from the result in this work; a smaller static U is found and U also exhibits a more pronounced low

frequency structure. These differences can be understood from the differences in the methods. Although U as defined in Eq. (1) is basis independent, the matrix elements of U will inevitably depend on the basis in which these are taken. Karlsson *et al.* use a basis composed of the head of the LMTO basis functions. Since the head of the LMTO is by construction localized within a muffin-tin sphere it is expected to be more



FIG. 8. (Color online) The partially screened interaction U for Nd. The 5s and 5p core states have been excluded from the calculation.

localized than the Wannier orbitals used in the present work, so that the matrix elements of U are also expected to be larger than those of the present work, contrary to the obtained results. We think that this discrepancy lies in the calculation of P_r . In this work, by using the disentanglement approach combined with a large energy window in defining the Wannier functions, the screening due to P_r is reduced. This yields an increased value of the static U with less pronounced low frequency structure. Thus, with the method used in the present work we include some of the effects of a self-consistent LDA + U calculation already in the initial cRPA calculation.

IV. CONCLUSION

We have calculated the Hubbard U for the early lanthanides using the constrained random phase approximation. The static values of U show almost the same trend across the series as the experimental estimations, although there is a consistent underestimation. In this work we have simply taken the static limit of U [$U(\omega = 0)$], however, in principle, the effects of the frequency dependence should be incorporated into the static value by means of downfolding of the high-frequency part of U. A self-consistent calculation of U is expected to improve the result and it is probably the main reason for the underestimation.

We have discussed the choice of energy window used to construct the Wannier functions spanning the localized



FIG. 9. (Color online) The real and imaginary parts of the average matrix element of J for Ce- γ , Nd, and Eu.

subspace. For the late lanthanides the LDA is a rather poor starting point and the choice of energy window becomes increasingly arbitrary. We have discussed the choice of energy window in detail for Eu and Gd and shown that, based on physical arguments, it is possible to choose the energy window so that the disentangled band structure improves the LDA starting point by removing a larger part of the hybridization. This will give a disentangled band structure that is less similar to the LDA band structure but instead closer to the true one. Thus, although still a source of arbitrariness, the energy window can be used as a tool to improve the LDA band structure.

The frequency dependence of U has been studied in detail and we have explained the origins of the different structures. The frequency dependence is very similar across the series, the main difference being the low energy peaks that can be seen for Ce that are absent for the other elements. These peaks originate from low energy f-r transitions. The two distinct peaks at high energy are shown to originate from particle-hole transitions from the shallow 5s and 5p core states. This structure is also clearly visible in the average exchange element J.

In the Appendix all matrix elements U_{nm} and J_{nm} are given.

ACKNOWLEDGMENTS

This work was supported by Swedish Research Council. One of the authors (R.S.) acknowledges support from the Scandinavia-Japan Sasakawa Foundation.

APPENDIX: FULL INTERACTION MATRICES $U_{nm}^{\sigma\sigma'}$ AND $J_{nm}^{\sigma\sigma'}$

Here we present the full matrices

$$U_{nm}^{\sigma\sigma'} = \int \int d^3r d^3r' |\phi_{n0}^{\sigma}(\mathbf{r})|^2 U(\mathbf{r},\mathbf{r}';0) |\phi_{m0}^{\sigma'}(\mathbf{r}')|^2,$$

$$J_{nm}^{\sigma\sigma'} = \int \int d^3r d^3r' \left[\phi_{n0}^{\sigma}(\mathbf{r})\right]^* \phi_{m0}^{\sigma}(\mathbf{r}) U(\mathbf{r},\mathbf{r}';0)$$

$$\times \phi_{n0}^{\sigma'}(\mathbf{r}') [\phi_{m0}^{\sigma'}(\mathbf{r}')]^*.$$

From the above definition the conventional reduced matrices $\tilde{U}_{nm}^{\sigma\sigma'}$ are derived as

$$\begin{split} \tilde{U}_{nm}^{\sigma\bar{\sigma}} &= U_{nm}^{\sigma\bar{\sigma}}, \\ \tilde{J}_{nm}^{\sigma\sigma'} &= J_{nm}^{\sigma\sigma'}, \\ \tilde{U}_{nm}^{\sigma\sigma} &= U_{nm}^{\sigma\sigma} - J_{nm}^{\sigma\sigma}. \end{split}$$

The Wannier basis functions are labeled by the projection onto spherical harmonics in the following way:

1.
$$Y_{30}$$
 3. $-\sqrt{2}\text{Im}(Y_{31})$ 5. $\sqrt{2}\text{Im}(Y_{32})$
2. $-\sqrt{2}\text{Re}(Y_{31})$ 4. $\sqrt{2}\text{Re}(Y_{32})$ 6. $-\sqrt{2}\text{Re}(Y_{33})$.
7. $-\sqrt{2}\text{Im}(Y_{33})$.

See Tables II–IX.

=

| | | | U | | | | J | | | |
|------|-----|-----|-----|-----|-----|------|------------------|-----|-----|------|
| (4.4 | 3.7 | 3.7 | 3.2 | 3.2 | 2.7 | 2.7 | (4.4 0.4 0.4 0.9 | 0.9 | 0.4 | 0.4 |
| 3.7 | 4.4 | 3.1 | 3.2 | 3.3 | 2.8 | 2.8 | 0.4 4.4 0.7 0.5 | 0.5 | 0.5 | 0.5 |
| 3.7 | 3.1 | 4.4 | 3.2 | 3.3 | 2.8 | 2.8 | 0.4 0.7 4.4 0.5 | 0.5 | 0.5 | 0.5 |
| 3.2 | 3.2 | 3.2 | 3.9 | 3.3 | 3.2 | 3.2 | 0.9 0.5 0.5 3.9 | 0.3 | 0.7 | 0.7 |
| 3.2 | 3.3 | 3.3 | 3.3 | 4.0 | 3.2 | 3.2 | 0.9 0.5 0.5 0.3 | 4.0 | 0.7 | 0.7 |
| 2.7 | 2.8 | 2.8 | 3.2 | 3.2 | 4.6 | 4.0 | 0.4 0.5 0.5 0.7 | 0.7 | 4.6 | 0.3 |
| \2.7 | 2.8 | 2.8 | 3.2 | 3.2 | 4.0 | 4.6/ | 0.4 0.5 0.5 0.7 | 0.7 | 0.3 | 4.6/ |

TABLE II. Cerium- α .

TABLE III. Cerium- γ .

| | | | U | | | | | | | J | | | |
|------|-----|-----|-----|-----|-----|------|------|-----|-----|-----|-----|-----|------|
| (5.5 | 4.7 | 4.7 | 4.2 | 4.3 | 3.7 | 3.7 | (5.5 | 0.4 | 0.4 | 0.9 | 0.9 | 0.4 | 0.4 |
| 4.7 | 5.5 | 4.1 | 4.2 | 4.3 | 3.8 | 3.8 | 0.4 | 5.5 | 0.7 | 0.6 | 0.6 | 0.5 | 0.5 |
| 4.7 | 4.1 | 5.5 | 4.2 | 4.3 | 3.8 | 3.8 | 0.4 | 0.7 | 5.5 | 0.6 | 0.6 | 0.5 | 0.5 |
| 4.2 | 4.2 | 4.2 | 4.9 | 4.3 | 4.2 | 4.2 | 0.9 | 0.6 | 0.6 | 4.9 | 0.3 | 0.7 | 0.7 |
| 4.3 | 4.3 | 4.3 | 4.3 | 5.1 | 4.3 | 4.3 | 0.9 | 0.6 | 0.6 | 0.3 | 5.1 | 0.7 | 0.7 |
| 3.7 | 3.8 | 3.8 | 4.2 | 4.3 | 5.6 | 5.1 | 0.4 | 0.5 | 0.5 | 0.7 | 0.7 | 5.6 | 0.3 |
| 3.7 | 3.8 | 3.8 | 4.2 | 4.3 | 5.1 | 5.6/ | (0.4 | 0.5 | 0.5 | 0.7 | 0.7 | 0.3 | 5.6/ |

TABLE IV. Praseodymium.

| | | | $U^{\uparrow\uparrow}$ | | | | $U^{\downarrow\downarrow}$ | | | |
|------|-----|-----|----------------------------|-----|-----|------|----------------------------|-----|-----|------|
| (4.9 | 4.2 | 4.2 | 3.7 | 3.7 | 3.2 | 3.2 | (4.9 4.0 4.0 3.5 | 3.7 | 3.1 | 3.1 |
| 4.2 | 5.0 | 3.6 | 3.7 | 3.8 | 3.3 | 3.3 | 4.0 4.8 3.4 3.5 | 3.7 | 3.2 | 3.2 |
| 4.2 | 3.6 | 5.0 | 3.7 | 3.8 | 3.3 | 3.3 | 4.0 3.4 4.8 3.5 | 3.7 | 3.2 | 3.2 |
| 3.7 | 3.7 | 3.7 | 4.5 | 3.8 | 3.7 | 3.7 | 3.5 3.5 3.5 4.2 | 3.7 | 3.5 | 3.5 |
| 3.7 | 3.8 | 3.8 | 3.8 | 4.6 | 3.7 | 3.7 | 3.7 3.7 3.7 3.7 | 4.5 | 3.7 | 3.7 |
| 3.2 | 3.3 | 3.3 | 3.7 | 3.7 | 5.1 | 4.6 | 3.1 3.2 3.2 3.5 | 3.7 | 5.0 | 4.4 |
| \3.2 | 3.3 | 3.3 | 3.7 | 3.7 | 4.6 | 5.1) | 3.1 3.2 3.2 3.5 | 3.7 | 4.4 | 5.0) |
| | | | $U^{\uparrow\downarrow}$ | | | | $J^{\uparrow\uparrow}$ | | | |
| (4.9 | 4.1 | 4.1 | 3.5 | 3.7 | 3.1 | 3.1 | (4.9 0.4 0.4 0.9 | 0.9 | 0.4 | 0.4 |
| 4.1 | 4.9 | 3.5 | 3.6 | 3.7 | 3.2 | 3.2 | 0.4 5.0 0.7 0.6 | 0.6 | 0.5 | 0.5 |
| 4.1 | 3.5 | 4.9 | 3.6 | 3.7 | 3.2 | 3.2 | 0.4 0.7 5.0 0.6 | 0.6 | 0.5 | 0.5 |
| 3.6 | 3.6 | 3.6 | 4.3 | 3.8 | 3.6 | 3.6 | 0.9 0.6 0.6 4.5 | 0.4 | 0.7 | 0.7 |
| 3.7 | 3.7 | 3.7 | 3.7 | 4.6 | 3.7 | 3.7 | 0.9 0.6 0.6 0.4 | 4.6 | 0.7 | 0.7 |
| 3.1 | 3.2 | 3.2 | 3.6 | 3.7 | 5.1 | 4.5 | 0.4 0.5 0.5 0.7 | 0.7 | 5.1 | 0.3 |
| 3.1 | 3.2 | 3.2 | 3.6 | 3.7 | 4.5 | 5.1) | 0.4 0.5 0.5 0.7 | 0.7 | 0.3 | 5.1) |
| | | | $J^{\downarrow\downarrow}$ | | | | $J^{\uparrow\downarrow}$ | | | |
| (4.9 | 0.4 | 0.4 | 0.9 | 0.9 | 0.4 | 0.4 | (4.9 0.4 0.4 0.9 | 0.9 | 0.4 | 0.4 |
| 0.4 | 4.8 | 0.7 | 0.5 | 0.6 | 0.5 | 0.5 | 0.4 4.9 0.7 0.6 | 0.6 | 0.5 | 0.5 |
| 0.4 | 0.7 | 4.8 | 0.5 | 0.6 | 0.5 | 0.5 | 0.4 0.7 4.9 0.6 | 0.6 | 0.5 | 0.5 |
| 0.9 | 0.5 | 0.5 | 4.2 | 0.3 | 0.7 | 0.7 | 0.9 0.6 0.6 4.3 | 0.4 | 0.7 | 0.7 |
| 0.9 | 0.6 | 0.6 | 0.3 | 4.5 | 0.7 | 0.7 | 0.9 0.6 0.6 0.4 | 4.6 | 0.7 | 0.7 |
| 0.4 | 0.5 | 0.5 | 0.7 | 0.7 | 5.0 | 0.3 | 0.4 0.5 0.5 0.7 | 0.7 | 5.1 | 0.3 |
| 0.4 | 0.5 | 0.5 | 0.7 | 0.7 | 0.3 | 5.0) | 0.4 0.5 0.5 0.7 | 0.7 | 0.3 | 5.1) |

| | | | $U^{\uparrow\uparrow}$ | | | | U | ↓↓ | | |
|---|------------|-----|--------------------------|-----|-----|------|---|------------|------|-------|
| $\binom{4.9}{4.1}$ | 4.1 | 4.1 | 3.7 | 3.7 | 3.1 | 3.1 | $\begin{pmatrix} 4.9 & 4.0 & 4.0 & 3\\ 4.0 & 4.7 & 2.2 & 2 \end{pmatrix}$ | 4 3.6 | 3.0 | (3.0) |
| 4.1 | 5.1 | 3.6 | 3.7 | 3.7 | 3.3 | 3.3 | | .4 3.6 | 3.1 | 3.0 |
| 4.1 | 3.6 | 5.1 | 3.1 | 3.7 | 3.3 | 3.3 | 4.0 3.3 4.7 3 | 4 3.6 | 3.0 | 3.1 |
| 3.7 | 3.7 | 3.7 | 4.5 | 3.8 | 3.7 | 3.7 | 3.4 3.4 3.4 4 | .0 3.6 | 3.4 | 3.4 |
| 3.7 | 3.7 | 3.7 | 3.8 | 4.5 | 3.7 | 3.7 | 3.6 3.6 3.6 3 | .6 4.5 | 3.6 | 3.6 |
| 3.1 | 3.3 | 3.3 | 3.7 | 3.7 | 5.2 | 4.6 | 3.0 3.1 3.0 3 | .4 3.6 | 4.9 | 4.3 |
| \3.1 | 3.3 | 3.3 | 3.7 | 3.7 | 4.6 | 5.2) | $(3.0 \ 3.0 \ 3.1 \ 3)$ | .4 3.6 | 4.3 | 4.9/ |
| | | | $U^{\uparrow\downarrow}$ | | | | J | † † | | |
| (4.9 | 4.0 | 4.0 | 3.4 | 3.6 | 3.0 | 3.0 | (4.9 0.4 0.4 1 | .0 1.0 | 0.4 | 0.4 |
| 4.1 | 4.9 | 3.5 | 3.5 | 3.7 | 3.2 | 3.2 | 0.4 5.1 0.7 0 | .6 0.6 | 0.6 | 0.6 |
| 4.1 | 3.5 | 4.9 | 3.5 | 3.7 | 3.2 | 3.2 | 0.4 0.7 5.1 0 | .6 0.6 | 0.6 | 0.6 |
| 3.6 | 3.6 | 3.6 | 4.3 | 3.8 | 3.6 | 3.6 | 1.0 0.6 0.6 4 | .5 0.4 | 0.7 | 0.7 |
| 3.6 | 3.6 | 3.6 | 3.6 | 4.5 | 3.6 | 3.6 | 1.0 0.6 0.6 0 | 4 4.5 | 0.7 | 0.7 |
| 3.1 | 3.1 | 3.1 | 3.5 | 3.7 | 5.0 | 4.5 | 0.4 0.6 0.6 0 | 7 0.7 | 5.2 | 0.3 |
| 3.1 | 3.1 | 3.1 | 3.5 | 3.7 | 4.5 | 5.0/ | | 7 0.7 | 0.3 | 5.2 |
| (011 | 0.11 | 011 | ı↓↓ | 011 | | 2.0) | | ↑ 017 | 0.12 | 0.2) |
| (1.0 | 0.4 | 0.4 | 0.0 | 1.0 | 0.4 | 0.4) | | 0 10 | 0.4 | 0.4) |
| $\begin{bmatrix} 4.9\\ 0.4 \end{bmatrix}$ | 0.4 4 7 | 0.4 | 0.9 | 1.0 | 0.4 | 0.4 | | 6 0.6 | 0.4 | (0.4) |
| 0.4 | 4.7 | 0.7 | 0.5 | 0.0 | 0.5 | 0.5 | | 0.0 | 0.0 | 0.5 |
| 0.4 | 0.7 | 4.7 | 0.5 | 0.6 | 0.5 | 0.5 | | 0.0 | 0.5 | 0.6 |
| 0.9 | 0.5 | 0.5 | 4.0 | 0.3 | 0.7 | 0.7 | 0.9 0.6 0.6 4 | .3 0.4 | 0.7 | 0.7 |
| 1.0 | 0.6 | 0.6 | 0.3 | 4.5 | 0.7 | 0.7 | 1.0 0.6 0.6 0 | .4 4.5 | 0.7 | 0.7 |
| 0.4 | 0.5 | 0.5 | 0.7 | 0.7 | 4.9 | 0.3 | 0.4 0.6 0.5 0 | .7 0.7 | 5.0 | 0.3 |
| \0.4 | 0.5 | 0.5 | 0.7 | 0.7 | 0.3 | 4.9/ | 0.4 0.5 0.6 0 | 7 0.7 | 0.3 | 5.0/ |

TABLE V. Neodymium.

TABLE VI. Promethium.

| | | | $U^{\uparrow\uparrow}$ | | | | $U^{\downarrow\downarrow}$ | | | |
|------|-----|-----|----------------------------|-----|-----|------|---|-----|-----|--------------|
| (4.4 | 3.6 | 3.6 | 3.1 | 3.1 | 2.6 | 2.6 | (4.3 3.4 3.4 2.8 | 3.0 | 2.4 | 2.4 |
| 3.6 | 4.6 | 3.1 | 3.2 | 3.2 | 2.7 | 2.7 | 3.4 4.1 2.8 2.8 | 3.0 | 2.5 | 2.5 |
| 3.6 | 3.1 | 4.6 | 3.2 | 3.2 | 2.7 | 2.7 | 3.4 2.8 4.1 2.8 | 3.0 | 2.5 | 2.5 |
| 3.1 | 3.2 | 3.2 | 4.1 | 3.2 | 3.2 | 3.2 | 2.8 2.8 2.8 3.5 | 3.0 | 2.8 | 2.8 |
| 3.1 | 3.2 | 3.2 | 3.2 | 3.9 | 3.1 | 3.1 | 3.0 3.0 3.0 3.0 | 3.9 | 3.0 | 3.0 |
| 2.6 | 2.7 | 2.7 | 3.2 | 3.1 | 4.7 | 4.1 | 2.4 2.5 2.5 2.8 | 3.0 | 4.3 | 3.8 |
| \2.6 | 2.7 | 2.7 | 3.2 | 3.1 | 4.1 | 4.7) | 2.4 2.5 2.5 2.8 | 3.0 | 3.8 | 4.3/ |
| | | | $U^{\uparrow\downarrow}$ | | | | $J^{\uparrow\uparrow}$ | | | |
| (4.3 | 3.4 | 3.4 | 2.9 | 3.1 | 2.5 | 2.5 | (4.4 0.4 0.4 1.0 | 1.0 | 0.4 | 0.4 |
| 3.6 | 4.3 | 2.9 | 3.0 | 3.2 | 2.6 | 2.6 | 0.4 4.6 0.8 0.6 | 0.6 | 0.6 | 0.6 |
| 3.6 | 2.9 | 4.3 | 3.0 | 3.2 | 2.6 | 2.6 | 0.4 0.8 4.6 0.6 | 0.6 | 0.6 | 0.6 |
| 3.1 | 3.1 | 3.1 | 3.8 | 3.2 | 3.1 | 3.1 | 1.0 0.6 0.6 4.1 | 0.4 | 0.8 | 0.8 |
| 3.0 | 3.0 | 3.0 | 3.0 | 3.9 | 3.0 | 3.0 | 1.0 0.6 0.6 0.4 | 3.9 | 0.8 | 0.8 |
| 2.5 | 2.6 | 2.6 | 2.9 | 3.1 | 4.5 | 3.9 | 0.4 0.6 0.6 0.8 | 0.8 | 4.7 | 0.3 |
| \2.5 | 2.6 | 2.6 | 2.9 | 3.1 | 3.9 | 4.5) | (0.4 0.6 0.6 0.8 | 0.8 | 0.3 | 4.7 / |
| | | | $J^{\downarrow\downarrow}$ | | | | $J^{\uparrow\downarrow}$ | | | |
| (4.3 | 0.4 | 0.4 | 0.9 | 1.0 | 0.4 | 0.4 | (4.3 0.4 0.4 0.9 | 1.0 | 0.4 | 0.4 |
| 0.4 | 4.1 | 0.7 | 0.5 | 0.6 | 0.5 | 0.5 | 0.4 4.3 0.7 0.6 | 0.6 | 0.6 | 0.6 |
| 0.4 | 0.7 | 4.1 | 0.5 | 0.6 | 0.5 | 0.5 | 0.4 0.7 4.3 0.6 | 0.6 | 0.6 | 0.6 |
| 0.9 | 0.5 | 0.5 | 3.5 | 0.3 | 0.7 | 0.7 | 0.9 0.6 0.6 3.8 | 0.4 | 0.7 | 0.7 |
| 1.0 | 0.6 | 0.6 | 0.3 | 3.9 | 0.7 | 0.7 | 1.0 0.6 0.6 0.4 | 3.9 | 0.7 | 0.7 |
| 0.4 | 0.5 | 0.5 | 0.7 | 0.7 | 4.3 | 0.3 | 0.4 0.6 0.6 0.7 | 0.7 | 4.5 | 0.3 |
| 0.4 | 0.5 | 0.5 | 0.7 | 0.7 | 0.3 | 4.3) | $\begin{pmatrix} 0.4 & 0.6 & 0.6 & 0.7 \end{pmatrix}$ | 0.7 | 0.3 | 4.5/ |

| | | | $U^{\uparrow\uparrow}$ | | | | $U^{\downarrow\downarrow}$ | | | |
|------|-----|-----|----------------------------|-----|-----|------|---|-----|-----|------|
| (4.2 | 3.4 | 3.4 | 2.9 | 2.8 | 2.3 | 2.3 | (3.9 3.1 3.1 2.6 | 2.6 | 2.1 | 2.1 |
| 3.4 | 4.4 | 2.8 | 3.0 | 2.9 | 2.5 | 2.5 | 3.1 4.0 2.5 2.6 | 2.6 | 2.2 | 2.2 |
| 3.4 | 2.8 | 4.4 | 3.0 | 2.9 | 2.5 | 2.5 | 3.1 2.5 4.0 2.6 | 2.6 | 2.2 | 2.2 |
| 2.9 | 3.0 | 3.0 | 3.9 | 3.0 | 2.9 | 2.9 | 2.6 2.6 2.6 3.4 | 2.7 | 2.6 | 2.6 |
| 2.8 | 2.9 | 2.9 | 3.0 | 3.7 | 2.9 | 2.9 | 2.6 2.6 2.6 2.7 | 3.4 | 2.6 | 2.6 |
| 2.3 | 2.5 | 2.5 | 2.9 | 2.9 | 4.5 | 3.8 | 2.1 2.2 2.2 2.6 | 2.6 | 4.1 | 3.5 |
| 2.3 | 2.5 | 2.5 | 2.9 | 2.9 | 3.8 | 4.5) | 2.1 2.2 2.2 2.6 | 2.6 | 3.5 | 4.1 |
| | | | $U^{\uparrow\downarrow}$ | | | | $J^{\uparrow\uparrow}$ | | | |
| (4.0 | 3.2 | 3.2 | 2.7 | 2.7 | 2.2 | 2.2 | (4.2 0.4 0.4 1.0 | 1.0 | 0.5 | 0.5 |
| 3.3 | 4.2 | 2.7 | 2.8 | 2.8 | 2.4 | 2.3 | 0.4 4.4 0.8 0.6 | 0.6 | 0.6 | 0.6 |
| 3.3 | 2.7 | 4.2 | 2.8 | 2.8 | 2.3 | 2.4 | 0.4 0.8 4.4 0.6 | 0.6 | 0.6 | 0.6 |
| 2.8 | 2.8 | 2.8 | 3.6 | 2.9 | 2.8 | 2.8 | 1.0 0.6 0.6 3.9 | 0.4 | 0.8 | 0.8 |
| 2.7 | 2.8 | 2.8 | 2.8 | 3.5 | 2.7 | 2.7 | 1.0 0.6 0.6 0.4 | 3.7 | 0.8 | 0.8 |
| 2.2 | 2.3 | 2.3 | 2.7 | 2.7 | 4.3 | 3.7 | 0.5 0.6 0.6 0.8 | 0.8 | 4.5 | 0.3 |
| 2.2 | 2.3 | 2.3 | 2.7 | 2.7 | 3.7 | 4.3/ | 0.5 0.6 0.6 0.8 | 0.8 | 0.3 | 4.5/ |
| | | | $J^{\downarrow\downarrow}$ | | | | $J^{\uparrow\downarrow}$ | | | |
| (3.9 | 0.4 | 0.4 | 0.9 | 0.9 | 0.4 | 0.4 | (4.0 0.4 0.4 1.0 | 1.0 | 0.4 | 0.4 |
| 0.4 | 4.0 | 0.7 | 0.6 | 0.6 | 0.6 | 0.5 | 0.4 4.2 0.7 0.6 | 0.6 | 0.6 | 0.6 |
| 0.4 | 0.7 | 4.0 | 0.6 | 0.6 | 0.5 | 0.6 | 0.4 0.7 4.2 0.6 | 0.6 | 0.6 | 0.6 |
| 0.9 | 0.6 | 0.6 | 3.4 | 0.4 | 0.7 | 0.7 | 1.0 0.6 0.6 3.6 | 0.4 | 0.8 | 0.8 |
| 0.9 | 0.6 | 0.6 | 0.4 | 3.4 | 0.7 | 0.7 | 1.0 0.6 0.6 0.4 | 3.5 | 0.7 | 0.7 |
| 0.4 | 0.6 | 0.5 | 0.7 | 0.7 | 4.1 | 0.3 | 0.4 0.6 0.6 0.8 | 0.7 | 4.3 | 0.3 |
| 0.4 | 0.5 | 0.6 | 0.7 | 0.7 | 0.3 | 4.1) | $\begin{pmatrix} 0.4 & 0.6 & 0.6 & 0.8 \end{pmatrix}$ | 0.7 | 0.3 | 4.3/ |

TABLE VII. Samarium.

TABLE VIII. Europium.

| $U^{\uparrow\uparrow}$ | $U^{\downarrow\downarrow}$ |
|--|--|
| (9.8 8.8 8.8 8.2 8.2 7.5 8.8 9.9 8.1 8.3 8.3 7.7 8.8 8.1 9.9 8.3 8.3 7.7 8.2 8.3 8.3 9.2 8.3 8.3 7.7 8.2 8.3 8.3 9.2 8.3 8.2 8.2 8.3 8.3 9.2 8.2 8.2 7.5 7.7 7.7 8.2 8.2 0.4 | $ \begin{array}{c} 7.5 \\ 7.7 \\ 7.7 \\ 8.2 \\ 8.2 \\ 9.4 \\ 9.4 \\ 101 \\ \end{array} $ |
| (1.5 1.1 1.1 8.2 6.2 9.4 | 10.1/ (0.5 0.7 0.7 7.2 7.0 0.2 0.8) |
| $ \begin{pmatrix} 9.1 & 8.2 & 8.2 & 7.7 & 7.4 & 7.0 \\ 8.2 & 9.3 & 7.6 & 7.7 & 7.5 & 7.2 \\ 8.2 & 7.6 & 9.3 & 7.7 & 7.5 & 7.2 \\ 7.6 & 7.7 & 7.7 & 8.6 & 7.5 & 7.7 \\ 7.7 & 7.8 & 7.8 & 7.8 & 8.4 & 7.7 \\ 7.0 & 7.2 & 7.2 & 7.7 & 7.5 & 9.4 \\ 7.0 & 7.2 & 7.2 & 7.7 & 7.5 & 8.8 \\ \end{pmatrix} $ | $ \begin{array}{c} 7.0\\ 7.2\\ 7.2\\ 7.2\\ 7.7\\ 7.7\\ 7.7\\ 8.8\\ 9.4 \end{array} \right) \begin{pmatrix} 9.8 & 0.5 & 0.5 & 1.2 & 1.2 & 0.5 & 0.5\\ 0.5 & 9.9 & 0.9 & 0.7 & 0.7 & 0.7 & 0.7\\ 0.5 & 0.9 & 9.9 & 0.7 & 0.7 & 0.7 & 0.7\\ 1.2 & 0.7 & 0.7 & 9.2 & 0.4 & 0.9 & 0.9\\ 1.2 & 0.7 & 0.7 & 0.4 & 9.2 & 0.9 & 0.9\\ 0.5 & 0.7 & 0.7 & 0.9 & 0.9 & 10.1 & 0.4\\ 0.5 & 0.7 & 0.7 & 0.9 & 0.9 & 0.4 & 10.1 \end{pmatrix} $ |
| $J^{\downarrow\downarrow}$ | $J^{\uparrow\downarrow}$ |
| $ \begin{pmatrix} 8.5 & 0.4 & 0.4 & 1.1 & 1.0 & 0.4 \\ 0.4 & 8.7 & 0.8 & 0.6 & 0.6 & 0.6 \\ 0.4 & 0.8 & 8.7 & 0.6 & 0.6 & 0.6 \\ 1.1 & 0.6 & 0.6 & 8.1 & 0.4 & 0.8 \\ 1.0 & 0.6 & 0.6 & 0.4 & 7.6 & 0.8 \\ 0.4 & 0.6 & 0.6 & 0.8 & 0.8 & 8.8 \\ 0.4 & 0.6 & 0.6 & 0.8 & 0.8 & 0.3 \\ \end{pmatrix} $ | $ \begin{array}{c} 0.4 \\ 0.6 \\ 0.6 \\ 0.8 \\ 0.8 \\ 0.3 \\ 8.8 \end{array} $ |

| $U^{\uparrow\uparrow}$ | | | $U^{\downarrow\downarrow}$ | |
|----------------------------|----------|-----------|----------------------------|---------------|
| (10.2 9.1 9.1 8.4 8.4 | 7.7 7.7 | (9.1 8.1 | 8.1 7.5 | 7.6 6.8 6.8 |
| 9.1 10.4 8.4 8.5 8.5 | 7.9 7.9 | 8.1 9.2 | 7.4 7.6 | 7.6 7.0 7.0 |
| 9.1 8.4 10.4 8.5 8.5 | 7.9 7.9 | 8.1 7.4 | 9.2 7.6 | 7.6 7.0 7.0 |
| 8.4 8.5 8.5 9.6 8.6 | 8.5 8.5 | 7.5 7.6 | 7.6 8.5 | 7.7 7.6 7.6 |
| 8.4 8.5 8.5 8.6 9.5 | 8.5 8.5 | 7.6 7.6 | 7.6 7.7 | 8.6 7.6 7.6 |
| 7.7 7.9 7.9 8.5 8.5 | 10.5 9.8 | 6.8 7.0 | 7.0 7.6 | 7.6 9.4 8.7 |
| 7.7 7.9 7.9 8.5 8.5 | 9.8 10.5 | 6.8 7.0 | 7.0 7.6 | 7.6 8.7 9.4 |
| $U^{\uparrow\downarrow}$ | | | $J^{\uparrow\uparrow}$ | |
| (9.6 8.6 8.6 8.0 8.0 | 7.2 7.2) | (10.2 0.5 | 0.5 1.3 | 1.3 0.6 0.6 |
| 8.6 9.8 7.9 8.0 8.1 | 7.4 7.4 | 0.5 10.4 | 1.0 0.8 | 0.8 0.8 0.8 |
| 8.6 7.9 9.8 8.0 8.1 | 7.4 7.4 | 0.5 1.0 | 10.4 0.8 | 0.8 0.8 0.8 |
| 8.0 8.0 8.0 9.0 8.2 | 8.0 8.0 | 1.3 0.8 | 0.8 9.6 | 0.5 1.0 1.0 |
| 7.9 8.0 8.0 8.1 9.0 | 8.0 8.0 | 1.3 0.8 | 0.8 0.5 | 9.5 1.0 1.0 |
| 7.2 7.4 7.4 8.0 8.1 | 9.9 9.2 | 0.6 0.8 | 0.8 1.0 | 1.0 10.5 0.4 |
| 7.2 7.4 7.4 8.0 8.1 | 9.2 9.9 | 0.6 0.8 | 0.8 1.0 | 1.0 0.4 10.5 |
| $J^{\downarrow\downarrow}$ | | | $J^{\uparrow\downarrow}$ | |
| (9.1 0.5 0.5 1.2 1.2 | 0.5 0.5 | (9.6 0.5 | 0.5 1.2 | 1.3 0.5 0.5 |
| 0.5 9.2 0.9 0.7 0.7 | 0.7 0.7 | 0.5 9.8 | 0.9 0.8 | 0.8 0.7 0.7 |
| 0.5 0.9 9.2 0.7 0.7 | 0.7 0.7 | 0.5 0.9 | 9.8 0.8 | 0.8 0.7 0.7 |
| 1.2 0.7 0.7 8.5 0.4 | 0.9 0.9 | 1.2 0.8 | 0.8 9.0 | 0.5 1.0 1.0 |
| 1.2 0.7 0.7 0.4 8.6 | 0.9 0.9 | 1.3 0.8 | 0.8 0.5 | 9.0 1.0 1.0 |
| 0.5 0.7 0.7 0.9 0.9 | 9.4 0.3 | 0.5 0.7 | 0.7 1.0 | 1.0 9.9 0.4 |
| 0.5 0.7 0.7 0.9 0.9 | 0.3 9.4/ | 0.5 0.7 | 0.7 1.0 | 1.0 0.4 9.9/ |

TABLE IX. Gadolinium.

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