

## Estimation of electron-electron interaction strengths for the rare-earth metals from $X\alpha$ calculations

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We give a simple method within the  $X\alpha$  approximation to calculate various electron-electron and -hole interaction strengths  $U$  from variation in the one-electron orbital energies with respect to changes in the orbital occupancies. The values of different  $U$ 's such as  $U_{ff}$  and  $U_{fc}$ , calculated within the present scheme for the rare-earth series compare well with previously obtained experimental as well as theoretical estimates, wherever available. The present estimation of  $U_{fd}$  is considerably lower than the values suggested earlier in the literature.

### INTRODUCTION

Electronic structure of the early rare earths (in particular, La and Ce) and their compounds have been successfully explained combining the electron spectroscopic observations and calculations based on single-impurity Anderson Hamiltonian.<sup>1</sup> Three important interaction strengths that enter these calculations as parameters are the hybridization strength,  $V$ , Coulomb interaction within the  $f$  electrons,  $U_{ff}$ , and the stabilization of the  $f$  level energy in presence of a core hole,  $U_{fc}$ . The values of these parameters that are obtained from fitting the experimental results to the calculation in turn determine the electronic structure of the system. In principle it should be possible to estimate these quantities in a given system from calculations based on single-particle approximation rather than treating them as parameters, as has been convincingly shown by Herbst *et al.*<sup>2</sup> for the case of  $U_{ff}$ .  $U_{ff}$  as well as the valence-band spectra for Ce have also been successfully calculated within one-electron approximation by Norman *et al.*<sup>3</sup> One intrinsic problem of treating these quantities as parameters is manifest in three different calculations for  $\text{CeO}_2$ .<sup>4-6</sup> These three different works have arrived at different sets of parameter values and interpretations, while each group has simulated the experimental spectra equally satisfactorily. This nonuniqueness of the results can be avoided if one is able to estimate the interaction strengths reliably from one-electron calculations of the electronic structure. One such attempt was in fact made in the case of  $\text{CeO}_2$ ,<sup>4</sup> where results of the multiple-scattering (MS)  $X\alpha$  calculation of the  $\text{CeO}_8^{12-}$  cluster,<sup>7</sup> typical of  $\text{CeO}_2$ , were used to deduce the parameter values. However, it was concluded that while the hybridization strength,  $V$ , could be evaluated from the MS  $X\alpha$  cluster calculations, the values of  $U_{ff}$  and  $U_{fc}$  were completely unsatisfactory.

We have reinvestigated this question starting from atomic calculations base on the  $X\alpha$  approximation for the exchange interaction (rather than starting with clusters within MS  $X\alpha$  formalism). When using calculations base on  $X\alpha$  approximation, one has to be careful in extracting the interaction strengths from the orbital energies, as the interpretation of orbital energies between  $X\alpha$

approximation and Hartree-Fock approximation are qualitatively different.<sup>8,9</sup> Thus we first give a simple formalism to show how these strengths can be estimated from atomic  $X\alpha$  calculations. This formalism is then used to calculate various interaction strengths. Comparison with experimental and theoretical estimates of these quantities, whenever available, shows a fair degree of success of the present calculations. This at first appears surprising, since we completely neglect the solid state and correlation effects; however, it has been shown that these effects are comparatively small and furthermore these cancel each other to a large extent.<sup>2</sup> This way we obtain values correct within 10% of experimental and other estimates.

One reason for choosing  $X\alpha$  approximation rather than Hartree-Fock method is the computational efficiency with which these can be performed; particularly so, since we have derived a method of evaluating these interaction strengths from variation of  $X\alpha$  orbital energies with respect to a small variation in the occupancy of the orbitals. More important is the ease with which this method in the form of MS  $X\alpha$  calculations can be extended to study clusters, representing a typical fragment of the solid, in order to derive  $V$ ,  $U_{ff}$ , and  $U_{fc}$  in any environment, determining the electronic structure of the system. Such an approach within Hartree-Fock scheme often is prohibitive in all but the most modern computers. In passing we would like to point out our contention that  $X\alpha$  (in case of the atom) and MS  $X\alpha$  (in case of a cluster) methods provide reliable estimates of the interaction strengths is at variance with the conclusion of Ref. 4 where the MS  $X\alpha$  approach was found to be unsatisfactory for  $\text{CeO}_2$ . This was so as the particular MS  $X\alpha$  calculation<sup>7</sup> that was used was not properly converged; we have converged the calculation properly and have indeed obtained very satisfactory estimates of  $U_{ff}$  and  $U_{fc}$  for  $\text{CeO}_2$  from MS  $X\alpha$  calculations.<sup>10</sup>

### METHOD OF CALCULATION

It has been shown that the total energy,  $E$ , of the atom within  $X\alpha$  approximation can be expanded in Taylor series as a function of the occupancies,  $n_i$ , of the  $i$ th orbital and that terms beyond the second order do not contribute significantly.<sup>9</sup> Thus we can write

$$E = \sum_{i,j} a_{ij} n_i n_j + \sum_i b_i n_i, \quad (1)$$

where the summations over  $i$  and  $j$  run over all the occupied orbitals. Then it can be easily shown that the coefficients  $a_{ij}$  in Eq. (1) are directly related to various unscreened interaction strengths. In the following we illustrate this point by explicitly deriving the expression for  $U_{ff}^{\text{uns}}$ , the unscreened Coulomb interaction strength between the  $f$  electrons. Assuming that there are  $n_f$  electrons in the  $f$  orbital and  $n_i$  electrons in the  $i$ th orbital ( $i \neq f$ ) in the ground state of the system, we have

$$\begin{aligned} U_{ff}^{\text{uns}} &= E(n_f + 1, n_i) + E(n_f - 1, n_i) - 2E(n_f, n_i) \\ &= 2a_{ff}. \end{aligned}$$

Similarly, it can be easily shown that the unscreened interaction strength,  $U_{fc}^{\text{uns}}$ , between the  $f$  electron and the hole in core orbital,  $c$ , is  $2a_{fc}$ . Here we have defined  $U_{fc}^{\text{uns}}$  (or, in general,  $U_{ic}^{\text{uns}}$ ) as follows:

$$\begin{aligned} \sum_i U_{ic}^{\text{uns}} n_i &= E(n_i, n_c = 0) - E(n_i, n_c = 1) \\ &\quad + E(n_i = 0, n_c = 1), \end{aligned}$$

where the left-hand term denotes the energy gain of the system due to the stabilization,  $U_{ic}$ , of the orbitals  $i$  ( $i \neq c$ ) due to a core hole in orbital  $c$  ( $n_c = 1$ ). The first and second terms on the right-hand side are the total energies of the system without and with the core hole. The third term gives the energy of the core hole in absence of its interaction with other levels.

Thus we find that all the bare interaction strengths are given directly by the coefficients  $a_{ij}$ . This formalism can be easily extended to express the screened interaction strengths in terms of the  $a_{ij}$ 's. Thus if we are primarily interested in screening by  $d$  electron (as in rare earth metals), we have for the screened Coulomb interaction

$$\begin{aligned} U_{fd} &= [E(n_f, n_d, n_s, n_i) - E(n_f - 1, n_d + 1, n_s, n_i)] - [E(n_f, n_d, n_s, n_i) - E(n_f - 1, n_d, n_s + 1, n_i)] + E_{\text{corr}} \\ &= [E(n_f - 1, n_d, n_s + 1, n_i) - E(n_f - 1, n_d + 1, n_s, n_i)] + E_{\text{corr}}. \end{aligned}$$

Here we have introduced a term  $E_{\text{corr}}$  [ $= \varepsilon_d(n_f, n_d, n_s, n_i) - \varepsilon_s(n_f, n_d, n_s, n_i)$ ] in order to correct the fact that the orbital energies,  $\varepsilon$ , of  $s$  and  $d$  orbitals are not equal in the atomic calculations of the ground state. The ground-state orbital energy of an  $s$  orbital is found to be always more stable than that of a  $d$  orbital and thus,  $E_{\text{corr}}$  in fact increases the magnitude of  $U_{fd}$  for the rare-earth metals in the present calculation.

Now we turn to the question of how to evaluate the coefficients  $a_{ij}$ . First we note the orbital energies,  $\varepsilon_i$ , of the  $i$ th orbitals in  $X\alpha$  approximation are somewhat differently related to the total energy than that in the Hartree-Fock approximation. (In the latter, the total energy,  $E = \sum_i n_i \varepsilon_i +$  two-electron term.) In  $X\alpha$  approximation<sup>8,9</sup>

$$\varepsilon_i = \frac{\partial E}{\partial n_i}. \quad (2)$$

strength,  $U_{ff}$ ,

$$\begin{aligned} U_{ff} &= E(n_f + 1, n_d - 1, n_i) + E(n_f - 1, n_d + 1, n_i) \\ &\quad - 2E(n_f, n_d, n_i) \\ &= 2a_{ff} + 2a_{dd} - 4a_{fd}. \end{aligned}$$

This can be easily extended for other interaction strengths as well.

Note that  $U_{fc}$  here is somewhat different from the definition of the similar quantity  $\rho_c$  ( $c = 3d/4d$ ) by Herbst and Wilkins.<sup>11</sup>  $\rho_c$  is defined, in our terms, as

$$\begin{aligned} \rho_c &= [E(n_f, n_d, n_c = 0) - E(n_f, n_d + 1, n_c = 1)] \\ &\quad - [E(n_f + 1, n_d - 1, n_c = 0) \\ &\quad - E(n_f + 1, n_d, n_c = 1)]. \end{aligned}$$

Thus  $\rho_c$  refers to two different electron configurations ( $n_f, n_d$ ) and ( $n_f + 1, n_d - 1$ ), in the ground state and the corresponding final states in presence of the core hole. This quantity is particularly relevant in the core-level spectroscopy of mixed-valence rare-earth systems (based on Ce, Sm, Eu, Tm, and Yb) and has also been calculated within the present scheme for these five rare-earth metals along with La.

In the context of  $f$ -shell photoionization, it has been recently argued<sup>12-15</sup> that different screening channels for the  $f$  hole can explain the experimentally observed two peak structure in the light rare-earth metals (e.g., Ce, Pr, and Nd). Since in a metal a hole in a localized level will be locally screened by the conduction band, there are two distinct screening channels (viz.  $d$  screening and  $s$  screening) existing for the  $f$  hole in rare-earth metals. We can calculate the energy difference  $U_{fd}$  associated with these two screening channels within the present scheme by noting that

Using Eq. (1), we can rewrite Eq. (2) as

$$\varepsilon_i = 2 \sum_j a_{ij} n_j + b_i. \quad (3)$$

Equation (3) provides us a simple and effective way of extracting the coefficients  $a_{ij}$  from the variation of the orbital energies,  $\varepsilon_i$ , with respect to a variation in the occupancies,  $n_j$ . Thus to evaluate  $2a_{ff}$  (which is equal to  $U_{ff}^{\text{uns}}$ ), we have from Eq. (3)

$$2a_{ff} = \frac{\varepsilon_f(n_f + \delta) - \varepsilon_f(n_f)}{\delta}, \quad (4)$$

where  $\varepsilon_f(n_f)$  and  $\varepsilon_f(n_f + \delta)$  correspond to the  $f$ -orbital energies in two calculations, one with  $n_f$  electrons and the other with  $n_f + \delta$  electrons in the  $f$  orbital, while all the other electrons are kept unchanged. From the same calculations, we can also extract all other  $2a_{fi}$  and, in

TABLE I. Values of different interaction strengths in eV for the trivalent rare-earth metals, values in parantheses are for the divalent rare-earth metals: intra-atomic Coulomb interaction within the  $f$  states in the ground state ( $U_{ff}$ ) and in presence of a  $3d$  core hole ( $U_{ff}^{-1}$ ); the stabilization of the energy of an  $f$  electron ( $U_{fc}$ ) and the total system ( $\rho_{3d}$ ) in presence of a  $3d$  core hole.

	$U_{ff}$	$U_{ff}^{-1}$	$U_{fc}$	$\rho_{3d}$
La	5.0	6.2	9.2	8.5
Ce	5.1	6.2	9.0	9.5
Pr	5.2	6.4	8.9	
Nd	5.3	6.4	8.8	
Pm	5.4	6.5	8.7	
Sm	5.5	6.6	8.7	8.2
	(4.9)	(5.9)	(7.3)	
Eu	5.6	6.7	8.7	8.2
	(10.7)	(15.4)	(8.5)	
Gd	11.9	15.8	8.6	
Tb	5.8	6.8	8.6	
Dy	5.9	6.9	8.6	
Ho	6.0	7.0	8.6	
Er	6.1	7.1	8.6	
Tm	6.2	7.2	8.6	8.4
Yb	6.3	7.3	8.6	8.5

particular  $2a_{fd}$  as

$$2a_{fd} = \frac{\epsilon_d(n_f + \delta) - \epsilon_d(n_f)}{\delta},$$

which is the rate of change of  $d$ -orbital energy with respect to a change in the  $f$  occupancy.

We would like to point out here that the interaction strengths can also be estimated via calculations based on the transition-state<sup>8,9</sup> concept, instead of relating them to the coefficients in the expansion of total energy [Eq. (1)] as done here. For example, the expression for the unscreened  $U_{ff}^{\text{uns}}$  can be written as

$$\begin{aligned} U_{ff}^{\text{uns}} &= [E(n_f + 1, n_i) - E(n_f, n_i)] \\ &\quad + [E(n_f - 1, n_i) - E(n_f, n_i)] \\ &= \epsilon_f(n_f + 0.5, n_i) - \epsilon_f(n_f - 0.5, n_i), \end{aligned}$$

and can be directly evaluated by performing two separate transition-state calculation. This approach is in fact a special case of Eq. (4) with  $\delta=1$ . However, adopting  $\delta=1$  often leads to problems of convergence in the calculation and thus we have performed the calculations of  $U_{ff}$  and  $U_{fc}$  with  $\delta=0.2$  within the scheme presented here. However, we calculate the values of  $\rho_{3d}$  and  $U_{fd}$  with transition-state calculation, as these quantities do not reduce to a combination of a few  $a_{ij}$ . The results presented here are obtained with a ground-state electron configuration  $[\text{Xe}]4f^n 5d^{m-1} 6s^1$  where  $m$  is the valency. To calculate the screened interaction strengths, we have always considered  $d$  screening in these calculation.

## RESULTS AND DISCUSSION

Values of different interaction strengths for the rare-earth series, calculated here, are tabulated in Table I. In Fig. 1 we have plotted the values of screened  $U_{ff}$  in the rare-earth series obtained by the present method. For comparison we also show the values obtained experimen-

tally from x-ray photoemission (XPS) and bremsstrahlung isochromat spectroscopy (BIS) measurements.<sup>16</sup> It is clear from the figure that the values calculated within the present scheme do not show the detail variations exhibited by the experimentally obtained values. The present values of screened  $U_{ff}$  only show a monotonic increase across the series. The sudden increase in the values of  $U_{ff}$  for  $f^7$  configurations (Eu<sup>2+</sup> and Gd<sup>3+</sup>) are related to the large exchange splitting of the  $f$  orbitals. Though  $U_{ff}$ 's calculated here do not show the detail of the experimentally observed variation across the series, the present values are within 10% of the experimental values in every case. This fact is very encouraging con-

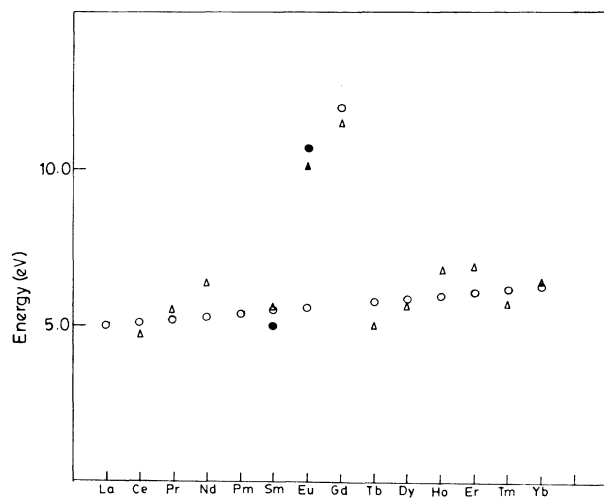


FIG. 1. Comparison of calculated (circles) and experimentally obtained (triangles) values of  $U_{ff}$ . The open symbols are for trivalent rare-earth metals and the filled symbols for the divalent ones. Experimental results for Ce–Tm from Ref. 16. The value of  $U_{ff}$  in YbP (Ref. 17) is shown for Yb.

sidering the computational ease of the present scheme compared to that of Herbst *et al.*<sup>2</sup> who obtained a very accurate description of  $U_{ff}$ . Moreover, it should be noted that we have not included corrections for correlation effects derived from spectroscopic data, and the calculations were performed nonrelativistically in contrast to the scheme of Herbst *et al.*<sup>2,18</sup> In spite of these limitations, the reasonable agreement between the present calculation and the experimental values has prompted us to calculate the interaction strength of a  $3d$  core hole and the  $f$  electron,  $U_{fc}$ , for all the rare-earth metals. We have also calculated  $\rho_{3d}$  for five rare-earth metals that exhibit valence fluctuation. This interaction strength plays an important role in determining the core-level spectra of the rare-earth metals as well as the actinides, and has been treated as a parameter in the modified impurity Anderson Hamiltonian for the description of core-level spectra in these systems.<sup>19-21</sup>

In Fig. 2 we show the calculated screened  $U_{fc}$  value for the rare-earth series. Here we find a monotonic decrease of  $U_{fc}$  across the series. Unfortunately,  $U_{fc}$  values have not been calculated for the rare-earth series by anyone else, unlike the case of  $U_{ff}$ . However, the values of  $\rho_{3d}$  that were required to describe the core-level spectra of La and Ce within the impurity Anderson model are 9.0 and 10.0 eV, respectively.<sup>19,20</sup> This is in good agreement with the values of  $\rho_{3d}$  (8.5 and 9.5 eV) calculated here (see Table I).  $\rho_{3d}$  values calculated in the present scheme are very similar to that obtained by Herbst and Wilkins,<sup>11</sup> the difference between the two being less than 1 eV in every case.

The values of  $\rho_c$  are found to be very close to the values of screened  $U_{fc}$  with the core hole ( $c$ ) in the  $3d$  orbital for the rare-earth metals. This can be easily understood, as within the present scheme  $\rho_c$  and  $U_{fc}$  are

related as follows:

$$\rho_c = (2a_{fc} - 2a_{fd}) - (2a_{dc} - 2a_{dd}),$$

where the first term is the screened  $U_{fc}$ . We find that the value of the second term, representing the  $U_{dc}$  in the presence of  $d$  screening, is always small ( $\sim 0.5$  eV) for all the rare-earth metals. This is consistent with the assumption ( $U_{dc} = 0$ ) made in Ref. 22.

Besides stabilizing the  $f$  level (by  $U_{fc}$ ), a  $3d$  core hole in principle should also affect the spatial extent of the  $f$  orbitals and make it more localized. One way that this spatial contraction should manifest itself is by increasing the value of  $U_{ff}$  in the presence of a core hole, compared to that in the ground state. Thus we have calculated the screened  $U_{ff}$  in presence of a  $3d$  core hole ( $U_{ff}^{-1}$ ) for the rare-earth series and the results are shown in Fig. 2. The trend is the same monotonic increase across the series, as found for the ground state  $U_{ff}$ ; however, the value of  $U_{ff}^{-1}$  is larger by  $\sim 1$  eV than  $U_{ff}$  in each case. It is interesting to note that while for the description of valence-band spectra of Ce compounds,  $U_{ff}$  value of 5.5 eV was employed within the impurity Anderson Hamiltonian,<sup>23</sup> a value of 6.4 eV had to be used for the description of the core-level spectra.<sup>19</sup> The values are in good agreement with values of  $U_{ff}$  (5.1 eV) and  $U_{ff}^{-1}$  (6.2 eV) calculated here (Table I). Though the change in  $U_{ff}$  due to the presence of a  $3d$  core hole is small ( $\sim 1$  eV) and uniform for the rare-earth metals, one may anticipate more pronounced effects of a core hole in the case of actinides where the  $5f$  orbital is known to make a transition from a delocalized to a localized behavior in the middle of the series.

In spite of the success of Gunnarsson-Schönhammer theory employing the single impurity Anderson Hamiltonian in explaining the various spectroscopic observations of the early lanthanides, there have been several suggestions in the literature that the Coulomb attraction between the  $f$  hole and  $d$  electrons ( $U_{fd}$ ) following  $f$  photoemission is very important.<sup>12-15</sup>  $U_{fd}$  is assumed to be small in the rare-earth series and is completely neglected in the model of Gunnarsson and Schönhammer, while other workers have suggested that  $U_{fd}$  is as large as 2.5 eV in the early lanthanides.<sup>12,13</sup> We find that the  $U_{fd}$  values for all trivalent rare-earth metals are between 1.0 and 1.1 eV. In the divalent case the values are found between 0.8 and 0.9 eV. Thus the values of  $U_{fd}$  turn out to be considerably smaller than  $U_{ff}$  in the rare-earth metals. Moreover, the value of  $U_{fd}$  (2.5 eV) estimated from the  $f$  photoemission of the early lanthanide metals<sup>12,13</sup> is more than a factor of 2 too large compared to our estimates. Even if we calculate the energy difference between a totally unscreened and  $d$  screened  $f$  hole, the associated energy is about 1 eV; this value is also smaller than the value (2.5 eV) assumed earlier. This further indicates that there is no appreciable energy gain associated with  $s$  screening.

It has often been said in the literature that the atomic  $U_{ff}$  in the rare earth is reduced by a factor of 5 or 6 in the solid state.<sup>2</sup> This is based on the evaluation of atomic  $U_{ff}$  from the Slater integral  $F^0(4f, 4f)$ . This integral from relativistic Hartree-Fock calculation of the atom

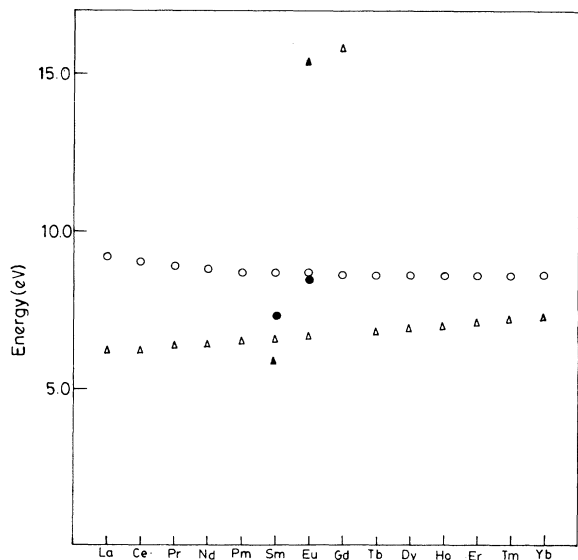


FIG. 2. Plot of  $U_{fc}$  (circles) and Coulomb interaction strength (triangles),  $U_{ff}^{-1}$ , in presence of a  $3d$  core hole in the rare-earth series. The open symbols are for the trivalent rare earth metals and filled symbols for the divalent ones.

turns out to be between 24 and 36 eV for the rare-earth metals. However when we calculate the unscreened  $U_{ff}$  for the atom within the present scheme, we find a value of  $12.0 \pm 0.5$  eV for all the rare-earth metals. Thus we find a reduction by a factor of only 2 between  $U_{ff}$  in the atomic case and the solid state. This discrepancy, we feel, is due to the neglect of polarization screening in equating the atomic  $U_{ff}$  to the Slater's  $F^0(4f, 4f)$  integral evaluated from ground-state orbitals. Unfortunately there is no experimental XPS-BIS data on the rare-earth atoms to date and thus the validity of our estimate of atomic  $U_{ff}$  could not be checked at this stage. The corresponding atomic  $U_{ff}$ 's in presence of a  $3d$  core hole range between 16.7 and 18.5 eV across the series.

Having shown that we obtain reasonable estimates of various interaction strengths that are relevant to the

electronic structure of rare-earth metals from atomic  $X\alpha$  calculation, we would like to point out that a great advantage of this approach is the ease with which it can also be extended to clusters (and thus beyond the limitations of the atomic case) by employing MS  $X\alpha$  approximations. This would, in principle, allow us to calculate these interaction strengths within a given local environment around the rare-earth atom. We have applied this approach in order to calculate the various  $U$ 's in  $\text{CeO}_2$  and then to calculate the core-level XPS of this compound. The preliminary results<sup>10</sup> are encouraging.

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