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Calculation of Coulomb interaction strengths for 3*d* transition metals and actinides

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Coulomb interaction strengths (U_{dd} and U_{ff}) have been calculated from Hartree-Fock-Slater atomic calculations for 3*d* transition and 5*f* actinide elements, respectively. By decomposing the different contributions to the response (screening) to the 3*d* charge fluctuation, we show that a substantial reduction in U_{dd} arises due to the relaxation of the 3*d* charge distribution itself. This, combined with the screening due to the response of the 4*s* charge density, is shown to provide a very compact screening charge comparable to the metallic case, explaining the success of the atomic calculations for estimating *U* even in the metals. A pronounced dependence of U_{dd} (or U_{ff}) on the number of electrons n_d (n_f) or the electronic configuration is also shown here.

INTRODUCTION

The diverse electronic and magnetic properties of correlated systems (3*d* transition metals, actinides, and rare earths) are largely dominated by a competition between a tendency towards delocalization due to band formation and a tendency towards localization due to Coulomb interaction between the electrons. Thus, any microscopic description of electronic structure of these systems involves an estimation of Coulomb interaction strengths between the electrons. There have been several calculations for these quantities, *U*, for the rare earths[1-4] and the actinides.[5,6] The most extensive evaluation of U_{ff} for the rare earths and the actinides has been done by Herbst *et al.*[1,5] Comparatively, there are fewer calculations[7-9] for U_{dd} in the case of 3*d* transition elements. Gunnarsson *et al.*[9] have calculated U_{dd} specifically for Mn in CdTe. Herring,[7] using atomic spectroscopic data, estimated U_{dd} for Ni to be between 1.8 and 2.7 eV. Arguing that the screening is more compact in the metal compared to the case of the atom (contrary to the argument put forward by van Vleck[10]), Herring suggested that U_{dd} is likely to be even smaller than 1.8 eV for Ni metal. This expectation has not been fully supported by the experimental estimate[11] of U_{dd} in Ni metal ($\sim$2 eV). Since screening is expected to be nearly complete within the Wigner-Seitz radius (r_{WS}) in a metal, Cox *et al.*[8] have calculated U_{dd} for all transition metals from atomic Hartree-Fock calculations truncating the atomic wave functions at r_{WS}. This approach enforces complete screening within r_{WS}. Interestingly, this calculation, instead of leading to lower estimates of U_{dd}, has actually led to larger values. For example, U_{dd} of Ni was calculated to be about 3.4 eV, considerably larger than both the estimates based on atomic data[7] and experiment.[11] Recently, we have shown[2] that Hartree-Fock-Slater atomic calculations lead to a very good estimate of various Coulomb interaction strengths (including U_{ff}) for the rare-earth metals. This indicates that even atomic calculations can simulate the screening energetics quite satisfactorily, contrary to the arguments put forward by Herring.[7] We have now applied this method to calculate U_{dd} for the entire 3*d* transition series and have obtained fairly accurate estimates. We have also critically looked into the screening charge distribution as obtained from these atomic calculations and established that the screening in this case is nearly as complete as is expected in the case of metals, explaining the success of the present approach. This method has also been applied to calculate U_{ff} for the first eight actinides.

METHOD OF CALCULATION

We have extensively discussed the method of calculating various electron-electron interaction strengths from Hartree-Fock-Slater calculations in Ref. 2. The basic ideas follow from a Taylor-series expansion of the total energy $E(n_i)$, in terms of the electron occupancy, n_i, of various levels (i). Thus

$$E=E_0+\sum_i b_i n_i+\tfrac{1}{2}\sum_{i,j} a_{ij}n_i n_j+\cdots \; . \tag{1}$$

It can be easily shown[2] that the various U_{ij}'s are given directly by the corresponding coefficients, a_{ij}, if we truncate the expansion (1) at the second order. The various a_{ij}'s are then conveniently calculated[2] from the variation in the orbital energies (ϵ_i) in the following way:

$$U_{ij}=a_{ij}=\frac{\partial\epsilon_i}{\partial n_j} \; .$$

This approximation leads to U_{ij}'s being independent of the various occupancies, n_k. This level of approximation was found to be satisfactory for the case of rare earths.[2] However, we find that the same approximation is not valid in the case of 3*d* transition elements, since U_{dd} is strongly dependent on the occupancy of the *d* level, n_d. This important dependence has to be taken into account particularly for the transition elements, since it is possible to vary n_d by alloying transition metals with suitable partner elements. In an attempt to include the dependence of U_{dd} on n_d, we have included the third- and fourth-order terms in the expansion (1) of total energy. This leads to a linear and quadratic dependence of U_{dd} on n_d, respectively. Thus we can write

$$U_{dd}(n_d)=U_0+U_1(\delta n_d)+U_2(\delta n_d)^2 \ , \tag{2}$$

with

$$(\delta n_d)=n_d-n_d^0 \text{ and } U_0=U_{dd}(n_d^0) \ .$$

In this way, if we know U_{dd} at a particular n_d^0 as well as U_1 and U_2, we shall be able to estimate U_{dd} for any arbitrary n_d. However, instead of calculating U_0, U_1, and U_2 by the atomic calculations after expressing them in terms of the various coefficients in the expansion (1), we have calculated U_{dd} directly for three different n_d values by expressing

$$\begin{aligned} U_{dd}(n_d)&=E(n_d+1,\, n_s-1)+E(n_d-1,\, n_s+1)-2E(n_d,n_s) \\ &=(1/\delta)[\{\epsilon_d(n_d+\delta/2,\, n_s-\delta/2)-\epsilon_s(n_d+\delta/2,\, n_s-\delta/2)\} \\ &\qquad +\{\epsilon_s(n_d-\delta/2,\, n_s+\delta/2)-\epsilon_d(n_d-\delta/2,\, n_s+\delta/2)\}] \ . \end{aligned} \tag{3}$$

In the final step of the expression (3), we made use of the transition-state concept.[12,13] It should be noted here that the charge fluctuation in $3d$ level has been compensated for by the charge in $4s$ level. Thus evaluated values of screened U_{dd} for three different n_d were fitted to expression (2) to obtain the values of U_0, U_1, and U_2. While varying the n_d, we have kept the total number of outer electrons (n_d+n_s) fixed. A value of 0.2 has been used throughout for δ and n_d^0 has been taken to correspond to the configuration $3d^n4s^1$ of the transition metal. This enables us to compare our results with those of Cox *et al.*,[8] who used the same configuration. We have also calculated the $U_{dd}(n_d^b)$, where n_d^b corresponds to the number of d electrons obtained in band-structure calculations for the transition metals.[14]

The calculations for screened U_{ff} in the actinide series have been performed in an analogous way. In this case we have taken n_f^0 to correspond to $5f^n(6d7s)^3$ configuration (except in the cases of Th and Am, where $4f^0$ and $4f^7$ configurations have been used, respectively). The occupancy of $6d$ and $7s$ levels were obtained by minimizing the total energy. In this case, we have not calculated any $U_{ff}(n_f^b)$, as reliable estimates of n_f^b are not available for all these elements.

RESULTS AND DISCUSSION

In Table I we show the values of U_0, U_1, and U_2 for the $3d^n4s^1$ configuration of the elements Sc–Cu and for the $3d^{10}4s^2$ of Zn. (For Zn, the values of U_0, U_1, and U_2 were calculated within charge fluctuations of the type $3d^{10-\delta}4s^24p^\delta$.) In the same table we have also given the U_{dd} for the $3d$ occupancy (n_d^b) corresponding to the band-structure calculations.[14] The U_{dd} values, for n_d^0 as well as for n_d^b, exhibit a monotonic increase across the transition-metal series (Fig. 1), indicating the increasing tendency towards localization of the d electrons. However, it is not U_{dd} alone that determines the electronic and magnetic properties of the system. The more relevant parameter in this respect is the ratio U_{dd}/W, where W is the d-band width. For the purpose of comparison, we also show in Fig. 1 the ranges of W estimated for the transition metals[15] and the corresponding range of U_{dd}/W. U_{dd}/W clearly shows a pronounced monotonic increase across the series, in conformity with the well-known magnetic properties of the transition metals.

Table I clearly shows that while the quadratic dependence (U_2) of U_{dd} on n_d is small, the linear term (U_1) is very large. This implies that U_{dd} is markedly reduced (by

TABLE I. Values (in eV) of Coulomb interaction strengths U_0 and $U(n_d^b)$ in presence of n_d^0 and n_d^b electrons in the $3d$ level of transition elements from Sc through Zn.

Elements	n_d^0	U_0	U_1	U_2	n_d^b	$U(n_d^b)$
Sc	2	0.78	−1.05	0.24	1.76	1.05
Ti	3	1.15	−1.16	0.10	2.90	1.27
V	4	1.47	−1.20	0.03	3.98	1.49
Cr	5	1.74	−1.17	0.11	4.96	1.79
Mn	6	2.00	−1.25	−0.03	5.99	2.02
Fe	7	2.24	−1.23	0.03	6.93	2.33
Co	8	2.47	−1.26	0.00	7.87	2.63
Ni	9	2.69	−1.32	0.05	8.97	2.73
Cu	10	2.89	−1.37	−0.13	9.91	3.01
Zn	10	6.45	−0.99	−0.21	10.00	6.45

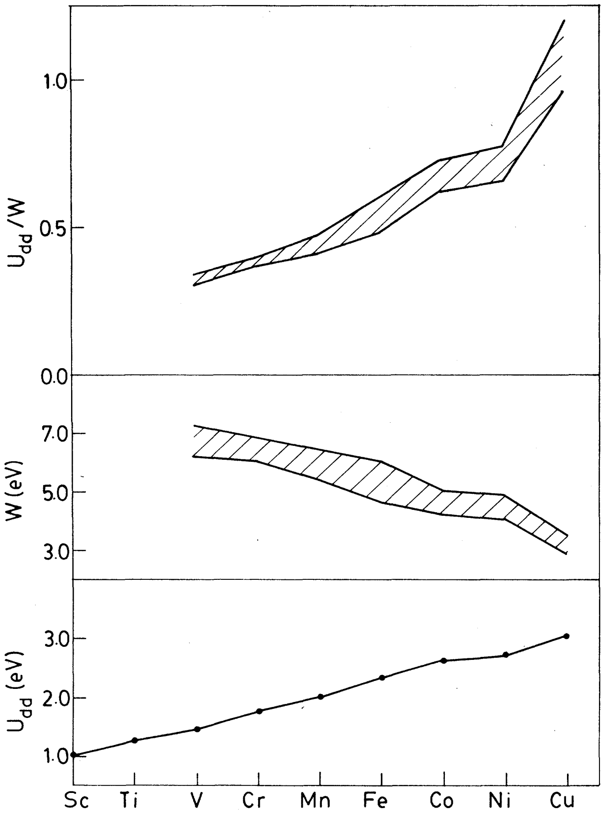

FIG. 1. The variation of intra-atomic Coulomb strength, U_{dd}, across the transition-metal series. The ranges of bandwidths (W) from Ref. 15 as well as U_{dd}/W are also shown.

~ 1 eV per electron) with increasing n_d. We find that, with increasing n_d, the 3*d* orbital becomes more diffused due to the increased Coulomb repulsion within 3*d* electrons. This increase in the spatial extent in turn reduces U_{dd}.

It should be noticed here that the present values of $U_{dd}(n_d^0)$ ($=U_0$) are considerably smaller than the corresponding values obtained in Ref. 8. For example, we obtain 0.8 and 2.7 eV for Sc and Ni, respectively, while Cox *et al.*[8] obtained 1.3 and 3.4 eV. This discrepancy can be understood in the light of the previous discussion on U_1. By restricting the atomic wave functions within the Wigner-Seitz radius, the calculations in Ref. 8 effectively increased the *d*-electron density at shorter distances. As a consequence, U_{dd} is also increased in these calculations, compared to our calculation where the atomic wave functions are not renormalized within the Wigner-Seitz radius.

Our evaluation of U_{dd} of Ni in $3d^94s^1$ configuration (2.7 eV) will be considerably reduced (to 2.2 eV) if we assume a ground-state configuration of $3d^{9.4}4s^{0.6}$ in Ni metal. This value is in good agreement with the experimental estimate[11] for Ni metal as well as that estimated[7] from atomic spectral data. According to the arguments put forward by Herring,[7] one would have expected the value of U_{dd} for the Ni metal to be considerably lower than 1.8 eV. The arguments are based on the expectation that the screening charge in response to a 3*d* charge fluctuation is more compact in the case of a metal than in an atom. It was estimated[7] that as much as 65% of the screening charge lies outside the Wigner-Seitz radius in the case of an atom, whereas the corresponding amount in the case of a metal is less than 35%. However, since the experimentally obtained U_{dd} for Ni metal[11] is in good agreement with the values obtained from the present atomic calculations as well as the ones obtained from atomic spectral data,[7] it appears that there cannot be a very drastic difference in the extent of screening between the atomic and metallic cases. In order to resolve this point, we have calculated the portion of the screening charge that lies outside the Wigner-Seitz radius. For this purpose, we integrate the charge density up to r_{WS} and obtain the total charge Q within the Wigner-Seitz radius for a given configuration. Then we define

$$q_+ = |Q(3d^n4s^1) - Q(3d^{n+1}4s^0)|$$

and

$$q_- = |Q(3d^n4s^1) - Q(3d^{n-1}4s^2)| \; .$$

Thus, q_+ (q_-) corresponds to the missing portion of the screening charge within r_{WS}, in response to a positive (negative) charge fluctuation in 3*d* occupancy. We have evaluated q_+ and q_- for the 3*d* transition-metal series and the result is shown in Table II. For all 3*d* transition elements we find that the atomic calculations provide approximately 80% of complete screening within the Wigner-Seitz radius. Such a nearly complete screening in the case of the atoms explains why the atomic spectral data[7] as well as the present calculation provide a fairly accurate estimate of U_{dd} for Ni metal as obtained experimentally.[11]

We can partition the various contributions to the screening charge from different orbitals. The screening charge would, of course, involve a large contribution from the active screening orbital (4*s*). As discussed earlier, the addition (removal) of a 3*d* electron would also lead to an expansion (contraction) of the 3*d* wave function, leading to an effective screening from within the 3*d*

TABLE II. Screening charge (q_+ and q_-) lying outside r_{WS} in response to 3*d* charge fluctuations in 3*d* transition elements.

Elements	r_{WS} (a.u.)	q_+	q_-
Sc	3.42	0.06	0.18
Ti	3.03	0.12	0.23
V	2.82	0.15	0.26
Cr	2.68	0.17	0.27
Mn	2.69	0.18	0.26
Fe	2.66	0.19	0.25
Co	2.63	0.19	0.25
Ni	2.60	0.20	0.24
Cu	2.67		0.22
Zn	2.90		0.35

TABLE III. Total and the $3d$ and $4s$ components of the charge within $r_{\rm WS}$ for Sc, Mn, and Ni in different configurations.

	Configuration	$Q_{\rm tot}$	Q_{3d}	Q_{4s}
Sc	$3d^1 4s^2$	19.82	0.91	0.92
	$3d^2 4s^1$	20.00	1.61	0.40
	$3d^3 4s^0$	20.06	2.07	0.0
Mn	$3d^5 4s^2$	23.59	4.78	0.81
	$3d^6 4s^1$	23.85	5.51	0.35
	$3d^7 4s^0$	24.03	6.03	0.0
Ni	$3d^8 4s^2$	26.75	7.81	0.94
	$3d^9 4s^1$	27.00	8.60	0.40
	$3d^{10} 4s^0$	27.20	9.20	0.0

electrons. The spectator orbitals (orbitals other than $3d$ and $4s$) would also respond to the charge fluctuation; however, we find this effect to be very small. We have evaluated the different (i.e., $4s$ and $3d$) contribution to screening for the cases of Sc, Mn, and Ni as typical examples. We show in Table III the total charge ($Q_{\rm tot}$), and total $3d$ and $4s$ charges (Q_{3d} and Q_{4s}) within $r_{\rm WS}$ for the $3d^{n-1}4s^2$, $3d^n 4s^1$, and $3d^{n+1}4s^0$ configuration of these three elements. From this table it is clear that there is only about 0.4 electron in the $4s$ level within $r_{\rm WS}$ for these elements in $3d^n 4s^1$ configuration. This led Herring to conclude[7] that an excess charge in the $3d$ level ($3d^{n+1}4s^0$ configuration) can only be screened to the extent of about 0.4 electron within $r_{\rm WS}$ (by the removal of the $4s$ electron) with around 60% of the screening charge lying outside $r_{\rm WS}$. Table III shows that when a positive charge fluctuation takes place within $3d$, the $3d$ charge within $r_{\rm WS}$ increases only by about 0.4 for Sc, 0.5 for Mn, and 0.6 for Ni due to the relaxation of the $3d$ in response to the charge fluctuation. Thus the removal of only 0.4 electron within $r_{\rm WS}$ via the $4s$ orbital leads to very compact screening with only 20% or less of the screening charge being outside $r_{\rm WS}$. Table III shows that the case for a negative charge fluctuation in $3d$ (i.e., $3d^n 4s^1 \rightarrow 3d^{n-1}4s^2$) is also similar, in that the removal of a $3d$ electron reduces the $3d$ charge by only about 0.7 electron within $r_{\rm WS}$.

TABLE IV. Values (in eV) of Coulomb interactions strengths U_0 in presence of a core hole in the $2p$ level of transition elements.

Elements	n_d^0	U_0	U_1	U_2
Sc	3	1.54	−1.44	−0.05
Ti	4	1.85	−1.41	−0.08
V	5	2.12	−1.40	−0.09
Cr	6	2.37	−1.35	−0.02
Mn	7	2.61	−1.39	−0.11
Fe	8	2.83	−1.37	−0.07
Co	9	3.01	−1.38	−0.09
Ni	10	3.25	−1.41	−0.13
Cu	10	6.82	−0.91	−0.18
Zn	10	7.86	−0.64	−0.02

TABLE V. Values (in eV) of Coulomb interaction strength U_0 in the presence of n_f^0 electrons in the $5f$ level of the actinides (Ac–Cm).

Elements	n_f^0	U_0	U_1	U_2
Ac	0.0	2.35	−0.30	−0.16
Th	0.0	2.72	−0.20	−0.05
Pa	2.0	2.71	−0.22	−0.02
U	3.0	2.89	−0.20	−0.05
Np	4.0	3.07	−0.16	−0.01
Pu	5.0	3.24	−0.13	0.00
Am	7.0	3.34	−0.04	0.04
Cm	7.0	3.58	−0.08	0.02

In case of rare earths, we have earlier shown that the Coulomb interaction strength within $4f$ electrons in the presence of a core hole (denoted U'_{ff}) is higher than the ground state U_{ff} by about 1 eV. This distinction of the Coulomb interaction strength, in the absence and in the presence of a core hole, may play an important role in the high-energy spectroscopies (e.g., x-ray photoemission and absorption spectroscopies), where a hole is created in the core level. In view of this, we have calculated the corresponding U'_{dd} with the hole in the transition-metal $2p$ core level, in a way analogous to the calculation of the ground state U_{dd}. However, n_d^0 in this case corresponds to the $3d^{n+1}4s^1$ configuration (except for Cu and Zn with $3d^{10}4s^2$ and $3d^{10}4s^2 4p^1$ configurations, respectively) where the extra electron screens the $2p$ core hole. The values of U_0, U_1, and U_2 for U'_{dd} are listed in Table IV. Comparison of Tables I and IV shows that the U_0 value increases by 0.6 ± 0.1 eV due to the presence of a $2p$ core hole in the transition-metal series. This modest increase would have been somewhat larger, had it not been for the fact that the increase of n_d by 1 to screen the hole reduces the Coulomb interaction strength by more than 1 eV, as evidenced from the large U_1 values listed in Table IV. This is indeed the case for Zn, where the screening of the $2p$ core hole is provided by an extra electron in the $4p$ level and, consequently, we find an ~1.5-eV increase in U_{dd} of Zn in the presence of a core hole. The very large increase of U_{dd} in the presence of a core hole in Cu is due

TABLE VI. Values (in eV) of Coulomb interaction strengths U_0 in presence of a core hole in the $4f$ level of the actinides (Ac–Cm).

Elements	n_f^0	U_0	U_1	U_2
Ac	1.0	2.61	−0.23	−0.04
Th	1.0	2.93	−0.16	−0.02
Pa	3.0	2.96	−0.17	−0.01
U	4.0	3.13	−0.14	0.00
Np	5.0	3.30	−0.11	0.01
Pu	6.0	3.47	−0.09	0.02
Am	8.0	3.61	0.03	0.06
Cm	8.0	3.80	−0.04	0.04

to the fact that the $4p$ screening of the $3d$ charge fluctuation in the screened core-hole case (Table IV) is not as compact as that provided by $4s$ screening in the ground state (Table I). The same reason is responsible for a large U_{dd} value in the ground state of Zn (Table I).

The values of U_0, U_1, and U_2 obtained for U_{ff} in the actinide series are shown in Table V. The values of U_0 in this case range between 2.4 and 3.6 eV for the elements between Ac and Cm, in conformity with previous estimates.[5,6] The steady increase of U_0 across the series is indicative of an increasing extent of localization of the $5f$ orbital. This is further suggested by the decreasing value of U_1 across the series (Table V). Thus the magnitude of U_1 of about 0.3 for Ac decreases steadily to less than 0.1 for the elements beyond Pu. Earlier we have pointed out that U_1 arises primarily from the response of the active orbitals ($3d$ for the transition metals and $5f$ for the actinides) to the charge fluctuations. Thus, if the orbital relaxation (an expansion for an increase in charge or a contraction in the presence of a deficit charge) is larger, U_1 is also expected to be larger. In this sense, the decreasing U_1 value across the actinide series (Table V) is due to a "stiffness" or "rigidity" of the orbital wave function due to a greater extent of localization. From the calculation of q_+ and q_- in an analogous way to that for the transition elements, we find that the $5f$ charge fluctuation is always screened better than 80% within r_{WS}, indicating that the atomic calculations are expected to reliably simulate the screening energetics in the metal.

We have also calculated the U'_{ff} in the actinide series in the presence of a core hole in the $4f$ orbital. The $4f$ core hole was taken to be screened by the presence of an extra $5f$ electron. The results for the first eight actinides are shown in Table VI. From this table we find that U_{ff} increases by a small amount (~ 0.3 eV) due to core hole in comparison to the ground-state value.

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