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Electronic structure of 4d impurities in Rb: a local-spin-density approximation + U density-functional study

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Abstract. The electronic structure of the 4d substitutional impurities in Rb is studied by means of self-consistent density-functional calculations. Exchange and correlation corrections for localized orbitals, as included in the mean-field solution of Anderson's model, are superimposed on the spin-dependent potential of the traditional local-spin-density approximation. We find ionic-like d^n configurations and a quite important spin polarization of the extended sp states. For Nb and Ru impurities we obtain two stable configurations in each case and their energetic stability is studied by means of constrained density-functional calculations. Our results are compared with the results of other calculations and with the available experimental data.

1. Introduction

Transition-metal impurities in alkali-metal hosts constitute a new class of local-moment systems, which attract a growing experimental [1–6] and theoretical [6–12] interest. Owing to the extremely large atomic volumes and, consequently, the low electron densities of the late alkali metals, transition-metal impurities exhibit atomic-like configurations in these hosts, although hybridization effects leading to non-integer occupancies of the localized impurity states cannot be neglected.

The first theoretical calculations of the electronic structure of these systems were based on the local-spin-density approximation (LSDA) of the density-functional theory and obtained large impurity spin moments which are in good quantitative agreement with the experimental findings [6–9]. In addition to the d moment, which is more or less saturated in the heavier alkali metals, these calculations also yield sizable s moments, showing that also the sp electrons experience the effect of the localization [8]. However, orbital polarization, which is normally connected with atomic-like configurations, cannot be obtained from these calculations, since orbital degeneracy is inherent in the LSDA.

It is well known that, although the LSDA has been proved very successful for calculating ground-state properties of a wide range of materials [13], it tends to lose accuracy or it breaks down in cases where local correlations are strong. This failure has its origin mainly in the incomplete cancellation of self-interactions in the LSDA. As a result of this, for instance, d orbitals with the same spin directions are always almost equally occupied, in contrast with the full occupation of specific d orbitals, as is required by Hund's second rule for atoms. Several attempts have been made to overcome the problem of spurious self-interactions, such as the self-interaction-corrected (SIC) LSDA [14–17] or the local-density approximation (LDA) + U [12, 18] methods, and to improve the traditional LSDA by introducing some corrections for the localized states. These methods are successful in essentially solving the metal–insulator problem [15, 18].

Recently, the LDA+ U approach was applied to the calculation of the electronic structure of transition-metal impurities in Rb [10]. The main result was that ionic d^n configurations turned out to be more stable than the LSDA configurations with equally occupied d orbitals. In addition, in some cases, more than one stable ionic configuration was obtained with very small energy differences, thus suggesting the occurrence of mixed-valence behaviour. However, within the LDA + U approach, the possibility for spin and orbital polarization enters only for the localized d electrons, and therefore the rather large polarization of the sp electrons occurring in these systems [8] cannot be obtained.

In this work we use a new local-density-functional scheme, by superimposing exchange and correlation corrections for the localized orbitals on the spin-dependent potential of the LSDA, to study the electronic structure of 4d impurities in Rb. This 'LSDA+ U ' scheme allows one explicitly to incorporate correlations due to electron–electron interactions between the localized orbitals, in maintaining the spin degree of freedom in an average (LSDA) treatment of all the states, both localized and extended.

2. The method

The main idea in the LDA + U approach is to modify that part of the traditional LDA energy functional which is responsible for the interaction between localized electrons. This interaction is described fairly well in relevant model Hamiltonians. Therefore, comparing with the mean-field solution of such a model Hamiltonian, one can see which part of the interaction is missing in the LDA energy functional.

Anderson's [19] impurity model has been found to provide a satisfactory description of different properties of many systems which have a localized state interacting with a continuum of extended states. In order to be consistent with the mean-field character of the LDA, we consider the Hartree–Fock solution of Anderson's model. For a degenerate impurity state, this solution is obtained from the one-electron Hamiltonian

$$\hat{H} = \sum_{k,\sigma} \varepsilon_k \hat{n}_{k\sigma} + \sum_{m,\sigma} \varepsilon_{\ell m\sigma} \hat{n}_{\ell m\sigma} + \sum_{k,m,\sigma} (V_{k\sigma;\ell m\sigma} \hat{c}_{k\sigma}^+ \hat{c}_{\ell m\sigma} + V_{\ell m\sigma;k\sigma} \hat{c}_{\ell m\sigma}^+ \hat{c}_{k\sigma}) \quad (1)$$

where $\hat{n}_{k\sigma} = \hat{c}_{k\sigma}^+ \hat{c}_{k\sigma}$ denotes the electron number operator for the continuum states with energies ε_k , labelled by some quantum number k and spin σ ; $\hat{n}_{\ell m\sigma} = \hat{c}_{\ell m\sigma}^+ \hat{c}_{\ell m\sigma}$ is the corresponding quantity for the localized orbitals, characterized by angular momentum quantum numbers ℓm and spin σ ; $V_{k\sigma;\ell m\sigma}$ are the hopping matrix elements between the two sets of states. Correlations due to electron–electron interactions are explicitly included only between localized orbitals through the single-particle energies

$$\varepsilon_{\ell m\sigma} = \varepsilon_{\ell} + \sum_{m'} U_{mm'} n_{\ell m' -\sigma} + \sum_{m' \neq m} (U_{mm'} - J_{mm'}) n_{\ell m'\sigma} \quad (2)$$

where $n_{\ell m\sigma}$ is the occupancy of the localized orbital $\ell m\sigma$, and $U_{mm'}$ and $J_{mm'}$ are the Coulomb and exchange integrals, respectively, between the orbitals m and m' . For simplicity we assume hereafter that the Coulomb and exchange integrals do not depend on the particular orbitals m and m' and, consequently, they are taken as constant parameters (U and J). Under these assumptions, we consider that the single-particle energies $\varepsilon_{\ell m\sigma}$ are derived from the energy functional

$$E_{\text{loc}} = \sum_{m,\sigma} \varepsilon_{\ell} n_{\ell m\sigma} + \frac{1}{2} U \sum_{m,m'} n_{\ell m\sigma} n_{\ell m' -\sigma} + \frac{1}{2} (U - J) \sum_{\substack{m,m',\sigma \\ m' \neq m}} n_{\ell m\sigma} n_{\ell m'\sigma} \quad (3)$$

through Janak's [20] theorem

$$\varepsilon_{\ell m \sigma} = \frac{\partial E_{\text{loc}}}{\partial n_{\ell m \sigma}}. \quad (4)$$

In the LDA, exchange and correlation effects for a localized state are taken into account on the average, thus neglecting the possibility of orbital and spin polarization. In the LDA+ U approach the total energy expression as calculated in the LDA is combined with the exchange and correlation energy of the Hartree-Fock solution of Anderson's model [19]. Therefore, it is clear that, within the LDA+ U density-functional scheme, spin and orbital polarizations are allowed only for the localized state, and not for the extended states. In some cases, however, spin polarization of extended states is also important and it must be taken into account. This is for instance the case of transition-metal impurities in late alkali-metal hosts, where spin polarization of the sp electrons is quite large [8]. In order to treat such cases, the LSDA can be generalized by including correlations due to electron-electron interactions between the localized orbitals, in the same way as these are taken into account within the LDA+ U approach. In this respect, we expand the orbital occupancies in equation (3) around the average occupancy for a given spin direction σ :

$$n_{\ell m \sigma} \equiv n_{\sigma}^0 + (n_{\ell m \sigma} - n_{\sigma}^0) \quad (5)$$

with

$$n_{\sigma}^0 = \frac{1}{2\ell + 1} \sum_m n_{\ell m \sigma} \equiv \frac{n_{\ell \sigma}}{2\ell + 1} \quad (6)$$

and we obtain

$$\begin{aligned} E_{\text{loc}} = & \left(\sum_{m, \sigma} \varepsilon_{\ell} n_{\sigma}^0 + \frac{1}{2} U \sum_{m, m', \sigma} n_{\sigma}^0 n_{-\sigma}^0 + \frac{1}{2} (U - J) \sum_{\substack{m, m', \sigma \\ m' \neq m}} n_{\sigma}^0 n_{\sigma}^0 \right) \\ & + \frac{1}{2} (U - J) \sum_{\substack{m, m', \sigma \\ m' \neq m}} (n_{\ell m \sigma} - n_{\sigma}^0) (n_{\ell m' \sigma} - n_{\sigma}^0). \end{aligned} \quad (7)$$

We identify the terms in the large parentheses as the Hartree-Fock energy of the localized state, if orbital polarization is neglected. This part of the interaction is taken into account in the LSDA and for integer occupations it reduces to the well known result [21]

$$\varepsilon_{\ell} n_{\ell} + \frac{1}{2} U n_{\ell} (n_{\ell} - 1) - \frac{1}{4} J n_{\ell} (n_{\ell} - 2) - \frac{1}{4} J m_{\ell}^2 \quad (8)$$

with $n_{\ell} \equiv n_{\ell \uparrow} + n_{\ell \downarrow}$ and $m_{\ell} \equiv n_{\ell \uparrow} - n_{\ell \downarrow}$. Therefore, what is essentially missing from the LSDA energy functional for the localized state is described by the last term in equation (7). Analogously to the LDA+ U approach this term may be incorporated into the LSDA total energy functional E_{LSDA} and the new total energy functional is defined as

$$E_{\text{LSDA}+U} = E_{\text{LSDA}} + \frac{1}{2} (U - J) \sum_{\substack{m, m', \sigma \\ m' \neq m}} (n_{\ell m \sigma} - n_{\sigma}^0) (n_{\ell m' \sigma} - n_{\sigma}^0). \quad (9)$$

Minimization of this total energy functional leads to the usual LSDA Kohn–Sham equations for the extended states, whereas for the localized state the minimization procedure gives rise to a spin- and orbital-dependent effective potential

$$V_{\ell m \sigma}(\mathbf{r}) = V_{\text{LSDA}}(\mathbf{r}) + (U - J) \sum_{m' \neq m} (n_{\ell m' \sigma} - n_{\sigma}^0). \quad (10)$$

This means that the usual LSDA single-particle potential V_{LSDA} is augmented with orbital (and spin) dependences, as one would find in a mean-field calculation using Anderson's model containing on-site U and J (Hunds rule exchange) interactions. A similar density-functional scheme has been recently used by Czyżyk and Sawatzky [22] to calculate the electronic structure of La_2CuO_4 and LaCuO_3 .

U and J are constant parameters which are determined for a given system using constrained LSDA methods [23–26], thus ensuring an overall consistency of the approach. Recent calculations by Solovyev and co-workers [11, 12] for transition-metal impurities in Rb showed that U and J depend also on the impurity configuration d^n . Here, the slight differences occurring in U and J for different configurations of 4d impurities in Rb are ignored. Our results are compared with those of Anisimov and Dederichs [10] and thus we use their values of U and J . In addition, we use the parametrization of Vosko *et al* [27] for the exchange and correlation contribution to V_{LSDA} .

For the calculations we employ the jellium model to treat the Rb host. A substitutional impurity in Rb jellium is created by excavating a spherical hole with the volume of the Rb Wigner–Seitz cell in the positive background density and inserting the nuclear charge of the impurity in the centre of the vacancy. The electron cloud will be redistributed to screen the perturbation induced by the impurity. The electronic structure of the system is determined self-consistently using a Green function approach. This involves the iterative solution of the corresponding Kohn–Sham single-particle equations for the LSDA + U effective potential. Relativistic effects are taken into account within the scalar-relativistic approximation [28]. Details of our method of calculation can be found elsewhere [7]. An angular momentum cut-off $\ell_{\text{max}} = 3$ and a range of perturbing potential $S = 10$ au are sufficient to obtain convergence in all cases examined.

3. Results and discussion

Systematic calculations of the electronic structure of all 4d impurities in Rb are carried out self-consistently within the LSDA + U scheme. The results for the impurity magnetic moments and their configurations are reported in table 1, together with the corresponding LSDA results as well as the LDA + U results of Anisimov and Dederichs [10]. We find ionic d^n configurations to be more stable than the LSDA configurations which have equal orbital occupations of all d states for a given spin. These d^n configurations are in agreement with the LDA + U results. However, hybridization between the impurity d localized states and the host free-electron gas is not negligible. This leads to the occurrence of d virtual bound states and non-integer occupation numbers within the impurity Wigner–Seitz sphere. Nevertheless, the occupancies of the impurity d localized orbitals are close to either 1 or 0, so that formal ionic d^n configurations can be assigned.

The local d moments obtained generally agree well with both the LSDA and the LDA + U results, although the LDA + U values are a little higher. The main qualitative difference, however, with the LDA + U results is that we also obtain a rather large polarization of the

Table 1. The local sp and d magnetic moments of 4d impurities in Rb, according to different density-functional calculations. The impurity ionic configurations d^n , obtained from the LDA + U and the LSDA + U calculations, are also given.

Impurity	LSDA		LDA + U			LSDA + U		
	M_{sp} (μ_B)	M_d (μ_B)	M_{sp} (μ_B)	M_d (μ_B)	d^n	M_{sp} (μ_B)	M_d (μ_B)	d^n
Y	0.14	0.82	0	1.14	d^1	0.14	0.92	d^1
Zr	0.31	2.59	0	2.76	d^3	0.29	2.54	d^3
Nb	0.42	3.98	0	4.39	d^5	0.35	3.71	d^4
			0	4.39	d^5	0.42	3.98	d^5
Mo	0.39	4.78	0	4.84	d^5	0.39	4.78	d^5
Tc	0.23	4.05	0	3.95	d^6	0.26	3.89	d^6
Ru	0.16	2.64	0	2.96	d^7	0.16	2.92	d^7
						0.17	2.07	d^8
Rh	0.08	1.18	0	1.90	d^8	0.08	1.00	d^9
			0	1.17	d^9			
Pd	0	0	0	0	d^{10}	0	0	d^{10}

sp states, which is not included in the LDA + U treatment. Our results for the sp impurity moments are in very good agreement with those given by the LSDA calculations (see table 1).

Both the LSDA + U and the LDA + U calculations in the case of Y and Zr in Rb give d^1 and d^3 , respectively, as ground-state configurations. For Nb and also for Ru impurities we find two stable configurations in each case. The relative configurational stability can be accurately studied by means of constrained density-functional calculations where charge fluctuations on a particular orbital $\ell m \sigma$, denoted collectively by α are considered. This requires minimization of the generalized functional [23]

$$E_{\text{LSDA}+U} + \lambda_\alpha \left(\int_{V_s} d^3r \rho_\alpha(r) - n_\alpha \right). \quad (11)$$

Here $\rho_\alpha(r)$ is the charge density of the α orbital which should be constrained to give a total charge of n_α electrons within the impurity Wigner-Seitz sphere V_s . Minimization of the energy functional (11) leads to the LSDA + U one-particle equations, where a constant projection potential λ_α , acting only on the states α within V_s , is added in the expression for the effective potential. The lowest energy of the constrained system is

$$E(n_\alpha) = \min \left[E_{\text{LSDA}+U} + \lambda_\alpha \left(\int_{V_s} d^3r \rho_\alpha(r) - n_\alpha \right) \right]. \quad (12)$$

By taking advantage of the Hellmann-Feynman theorem

$$\frac{dE(n_\alpha)}{dn_\alpha} = -\lambda_\alpha \quad (13)$$

we can calculate the energy difference

$$E(n_\alpha^{(2)}) - E(n_\alpha^{(1)}) = - \int_{n_\alpha^{(1)}}^{n_\alpha^{(2)}} dn_\alpha \lambda_\alpha(n_\alpha) \quad (14)$$

between two configurations characterized by orbital occupancies $n_\alpha^{(1)}$ and $n_\alpha^{(2)}$. By applying this method of constraints, we find that in the case of Nb in Rb the d^4 configurations lies

0.23 eV below the d^5 configuration (see figure 1(a)), contrary to the LDA + U calculation which yields d^5 as the ground-state configuration. This can be explained as follows. In the LDA + U calculation, the splitting between occupied and empty states in the case of complete polarization (d^5) is the largest possible ($U + 4J$), which is more than twice the splitting ($U - J$) between occupied and empty states with the same spin direction. Consequently, the d^5 configuration is energetically more favourable than the d^4 configuration. On the other hand, in the LSDA + U approach, the energy splitting between the two fully spin-polarized states in the d^5 configuration is that of the LSDA. This is smaller than $U + 4J$ and turns out to be almost equal to $U - J$. In our LSDA + U calculation we find that the d^5 configuration is metastable (barely unstable as seen from figure 1(a)) and that the ground state has the d^4 configuration. Both the LSDA + U and the LDA + U calculations for Mo and Tc impurities give d^5 and d^6 , respectively, as ground-state configurations. In the case of Ru in Rb, we find the d^7 ground-state configuration, in agreement with the LDA + U results, whereas a second, d^8 , configuration (0.13 eV higher) appears as metastable (see figure 1(b)). For a Rh impurity we converge to a single solution d^9 , contrary to the LDA + U calculation, where d^9 appears as metastable and about 0.1 eV higher than the ground-state configuration d^8 . Finally, in the case of Pd in Rb, all the calculations converge to the fully occupied d^{10} configuration, which also occurs for the free Pd atom.

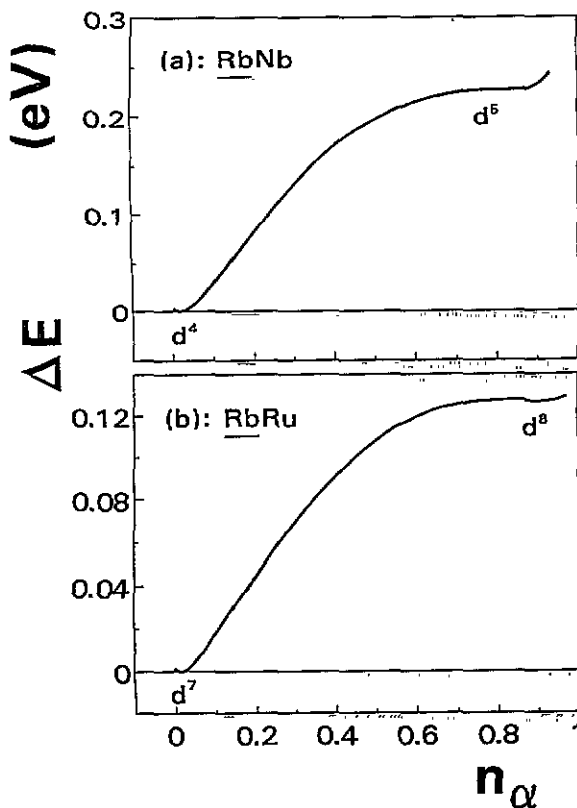


Figure 1. The energy difference ΔE relative to the ground state, versus the occupancy n_α of a specific localized orbital: (a) $\alpha = \{\ell = 2, m = 2, \sigma = \uparrow\}$ for Nb in Rb; (b) $\alpha = \{\ell = 2, m = 0, \sigma = \downarrow\}$ for Ru in Rb.

Our results confirm the general conclusion [1–6] that the transition-metal impurities in the heavy alkali metals exhibit ionic-like configurations although, because of hybridization effects, some itinerant character is still maintained. From the ionic-type analysis applied to the experimental data obtained by the time-differential perturbed γ -ray distribution method, the electronic structure of isolated impurities implanted by recoil into an alkali-metal host may be determined [1–6]. For Mo in Rb, the experiment yields the d^5 ground-state configuration [2] which is in agreement with our calculations. Moreover, the experimental data for Tc in Rb can be reproduced rather well by a mixture of the ionic d^5 and d^6 configurations, whereas the magnetic behaviour of Ru in Rb is consistent with a predominant d^7 state together with large spin fluctuations [3]. We recall that our results yield only the d^6 configuration for Tc in Rb, whereas for Ru in Rb a d^8 metastable configuration is found 0.13 eV higher than the ground-state configuration d^7 . The behaviour of 4d impurities from the beginning (Zr and Nb) and the end (Rh and Pd) of the 4d series in Rb has also been investigated experimentally [4]. Nb and Rh show a rather weak tendency for magnetism and, within the experimental uncertainties, Zr and Pd impurities are non-magnetic. While the behaviour of Pd in Rb is in line with our calculations, we obtain quite a large polarization for Zr and Nb in Rb, which makes the behaviour of these impurities difficult to understand.

When comparing these calculations with the experiments, one should have in mind that the interpretation of the experimental results is often rather ambiguous and strongly depends on the choice of the model parameters used. Moreover, in some cases, the theoretical calculations may also be sensitive to the different approximations involved, e.g. the approximate treatment of exchange and correlation or the neglect of the spin-orbit interaction in the scalar-relativistic treatment of the impurity states. Also, the important size differences between the impurity and the large atomic volume of Rb host might lead to unusually large lattice relaxations of the neighbouring atoms, as discussed by Gross *et al* [6]. Energy differences due to lattice relaxations are estimated to be of the order of the tenth of an electronvolt [12]. There is also experimental evidence that, in addition to substitutional configurations, transition-metal impurities can occupy interstitial positions [29]. Therefore, the local environment of the impurity may affect the energetic stability of the electronic configuration.

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