# Corrected atomic limit in the local-density approximation and the electronic structure of $d$ impurities in Rb

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We propose an energy functional for localized electron systems that corresponds to the constrained-local-density approximation (LDA) but includes some corrections for spin and orbital polarization to take Hund's first and second rules into account. The discontinuity of the one-electron potential known for an exact density functional can be easily incorporated in LDA in the scope of our formalism. Applications of the method to the electronic structure and configurational stability of $d$ impurities in Rb are presented.

## I. INTRODUCTION

It is well know now that the local-spin-density approximation (LSDA) fails to describe properties of systems with localized $d$ and $f$ electrons. Typical examples of such failures are Mott insulators like $3d$-transition-metal oxides, where the LSDA cannot reproduce the well-established correlation gaps nor the antiferromagnetic ground states. Several different attempts [SIC-LSDA,[1-3] LDA+$U$ (Ref. 4)] have been undertaken to overcome these limitations and repair the LSDA by introducing some corrections for localized states.

On the other hand, there is a paradox that despite of all limitations of LSDA it gives reasonable values for the parameters characterizing the localized states. Indeed, the values of the Coulomb interaction parameters ($U$) obtained in the constrained-LSDA calculations for a variety of strongly correlated systems[5-11] are surprisingly accurate. This means that as long as we manipulate with total energies in constrained-LSDA, we are quite successful in describing the behavior of localized electrons, even if we consider excited-state properties. But as soon as we start using single-particle energies obtained in LSDA for the ground state all deficiencies of such a treatment become evident. This is not very surprising since LSDA-eigenvalues themselves (at least for the ground state) do not have a direct physical meaning. Some other representations for one-electron spectra which would better reflect the nature of the localized states are more prefered.[12] But, is the transformation to another set of one-electron states very important and what is the *nature of the localized states*? Let us consider a system consisting of two well-separated atoms. We will neglect any hybridization effects between the wave functions but allow for charge transfer from one atom to the other.[13] If we still stay within the framework of the one-electron picture this process can be described only as a transition of an electron from a well-defined *one-electron orbital* at one atom to the corresponding *one-electron orbital* at

the other atom and the physical origin of the one-electron states involved in such a process becomes very important here. Perdew et al.[14] have shown that an attempt to use one-electron states like those of LSDA, which are simply derivatives of a smooth function (total energy in LSDA) with respect to orbital populations, to describe the behavior of two different well-separated atoms leads to a paradox: fractional electron occupations on each atom of the considered system will minimize the total energy. The only possible choice to avoid this is to use such a set of one-electron orbitals on every site for which the energy of the highest occupied or lowest empty state (thus, we unavoidably must introduce some gap between these two energies) would exactly agree with the cost to remove or to add one electron to the shell of localized states, i.e., with the ionization energy or electron affinity, respectively.

Now, let us look again at the total energy functional in LSDA for isolated atoms to get some feeling of what one should improve and how it could be done. First, we note that the values of the total energy obtained in LSDA for isolated atoms do not differ drastically from those obtained in Hartree-Fock (HF) calculations. As the most striking example, we can remind ourselves of the $X_\alpha$ approximation proposed by Slater,[15] where the parameter $\alpha$ was chosen from the equality between total energies in $X_\alpha$ and HF approaches for isolated atoms. It looks like that we should not change LSDA total energy at all except for some small corrections arising from orbital-polarization effects. This fact was intensively used by Eriksson et al.,[16] Norman,[17] and Severin et al.[18] to include the orbital-polarization effects (which are also a consequence of localized states) into density-functional formalism. But the localized nature of the states is also omitted in such a consideration. What else can we do if we do not want to change (drastically) the total energy of LSDA? The answer is very simple if we look at the total energy as an one-electron part minus double-counting term : $E^{\mathrm{LSDA}} = \sum_i \varepsilon_i^{\mathrm{LSDA}} n_i - E_{\mathrm{dc}}$. The only

one possible choice is to introduce some redefinition both for the one-electron energies $\varepsilon'_i = \varepsilon_i^{\text{LSDA}} + \Delta V_{\text{cor}}^i$ and for the double-counting term $E'_{\text{dc}} = E_{\text{dc}} + \sum_i \Delta V_{\text{cor}}^i n_i$. Of course, the one-electron states $\varepsilon'_i$ are then no longer related to the LSDA-total energy as its derivatives with respect to occupations $n_i$. However, we will show that this relation can be still fulfilled for our *corrected*-LDA total energy functional, the LDA+$U$ energy.

The derivation of the functional will be given in Sec. II. A first description of the method and its applications to the calculation of the photoemission and Bremsstrahlung isochromat spectra of NiO, were presented in Ref. 19. Very recently, this functional has been successfully applied to the investigation of electronic structure and magneto-optical effects in CeSb (Ref. 20) and Gd (Ref. 21). The aim of this paper is to give a more extended analysis of the LDA+$U$ formalism and show how it is related to the model HF and LDA approaches. In particular, we will show that it is simply a constrained LDA with some additional corrections corresponding to the spin and orbital polarization. We will also show that the discontinuity of the one-electron potential known for an "exact" density functional can be easily incorporated in LSDA. Applications of the method to the electronic structure and configurational stability analysis of $d$ impurities in Rb host will be presented in Sec. III. Many experimental[22–26] and theoretical[27,28] efforts have been concerned with these systems in recent years mainly due to the discovery of a typically localized behavior for the $d$ states of transition-metal atom impurities in the $sp$ hosts leading to strong orbital moments and possibly to mixed-valence behavior. The conclusions of our paper will be summarized in Sec. IV.

## II. METHOD

In general we will follow the LDA+$U$ scheme proposed in Ref. 4. We will also call our present formalism LDA+$U$ since it is based on the same ideas as its original version[4] despite the fact that some differences between these two approaches exist, especially in the choice of a reference point between the LDA and the model-HF description for the localized states. We start with the normal total energy functional in the framework of LDA [in principle, the choice of the (non-spin-polarized) LDA as a starting point is not very important and absolutely the same manipulations can be performed for the total energy functional in LSDA]. Our main idea is to modify that part of the LDA-total energy which is responsible for the interaction between localized electrons and present it in the same way as it appears in model (Anderson[29] or Hubbard[30]) Hamiltonians. As a first step, we will remove the hybridization between the localized states and the rest of the system and consider the so-called atomic limit. We allow only for charge transfer between these two subsystems and assume them to relax self-consistently on such fluctuations. We will introduce a total energy functional and show that for an integer number of localized electrons this leads simply to a redefinition of the single-particle energies by splitting them up into two parts for

occupied and empty states, which represent the energy costs to remove and to add one localized electron, i.e., the ionization energy and the electron affinity. The total energy itself is that of a constrained LDA but including some corrections for spin and orbital polarization to take Hund's first and second rules into account which are not included in LDA.

Thus, we introduce a correction for localized states and write down a total energy functional as

$$E[\rho, \{n_i\}] = E^{\text{LDA}}[\rho] + \Delta E_{\text{cor}}[\{n_i\}], \qquad (1)$$

where $\rho$ is the total charge density, $\{n_i\}$ is the set of orbital occupancies for the localized states. Then, we will look for the $\Delta E_{\text{cor}}$ in the form

$$\Delta E_{\text{cor}}[\{n_i\}] = -E_{dd}^{\text{LDA}}[n_d] + E^H[\{n_i\}], \qquad (2)$$

where $E_{dd}^{\text{LDA}}$ is the electron-electron interaction for the localized states in LDA which depends only on the total number of localized electrons $n_d = \sum_i n_i$ (in the following, we will refer to the localized states as $d$ states). We suppose this dependence to be unsatisfactory and subtract it from the LDA-total energy. Instead, we add the Hartree expression for $d$-$d$ interaction with a renormalized Coulomb parameter $U$ (here, for a while, we drop the exchange interaction and nonspherical terms):

$$E^H[\{n_i\}] = \frac{1}{2}U\sum_{i \neq j} n_i n_j. \qquad (3)$$

Of course, the main question of such a consideration is what is the reference point between LDA and Hartree-Fock description for the localized states or in other words what is a reasonable explicit form for the $d$-$d$ interaction in LDA? To answer this question let us consider more thoroughly the scheme for calculating Coulomb and exchange ($J$) parameters based on the constrained-LSDA formalism. As a first step in such an approach, the total energy as a function of occupation number and spin magnetization $m_d$ of localized states should be extracted from LSDA by applying a variety of constraints. These results can be mapped then on an analytical dependence of the total energy $E(n_d, m_d)$ known for the considered model. For instance, if we will restrict ourselves to the Hartree-Fock approximation for the electron-electron interaction and neglect orbital polarization effects, $E(n_d, m_d)$ for the integer occupations will be simply given by[15]

$$E(n_d, m_d) = \frac{1}{2}U n_d(n_d - 1) - \frac{1}{4}J n_d(n_d - 2) - \frac{1}{4}J m_d^2. \qquad (4)$$

The parameters of the electron-electron interaction ($U$ and $J$) can be considered as those which give the best fit to constrained-LSDA results and the parametrization (4). Thus, we come to the conclusion that despite of all limitations of LSDA the parametrization (4) works quite well and gives reasonable estimations for $U$ and $J$ parameters in many cases. So, if we will return to the previous consideration for $\Delta E_{\text{cor}}$, it is quite reasonable to define the energy of $d$-$d$ interaction in LDA as

$$E_{dd}^{\text{LDA}} = \frac{1}{2}Un_d(n_d - 1). \tag{5}$$

From the first point of view this decision looks strange, because on the one hand, we blame L(S)DA and state that this approach describes the behavior of localized electrons much worse than the model Hartree-Fock approximation with renormalized parameters, and on the other hand, we try to use for the interaction between localized electrons in LDA the same form as in the Hartree-Fock method. But it is not exactly the same since in Hartree-Fock approximation equation (4) is valid only for integer occupation numbers and since only for integer values $n_i$ equal 0 or 1 expression (3) is identical to (5) [the form of the Hartree approximation with fractional number of electrons differs from (5) and will be discussed later] whereas in LSDA, we suppose that the dependence (5) is valid for arbitrary values of $n_d$ and $m_d$ and even numerical differentiation can be used to extract the $U$ and $J$ parameters from LSDA:

$$U = \left.\frac{\partial^2 E[n_d, m_d]}{\partial n_d^2}\right|_{m_d = \text{const}} - \left.\frac{\partial^2 E[n_d, m_d]}{\partial m_d^2}\right|_{n_d = \text{const}}, \tag{6}$$

$$J = -2\left.\frac{\partial^2 E[n_d, m_d]}{\partial m_d^2}\right|_{n_d = \text{const}}. \tag{7}$$

Finally, we come to the following form of LDA correction

$$\Delta E_{\text{cor}}[\{n_i\}] = -\frac{1}{2}Un_d(n_d - 1) + \frac{1}{2}U\sum_{i \neq j}n_i n_j. \tag{8}$$

A few remarks concerning the new functional are appropriate. If we will look at the energy of Hartree interaction alone as a function of number of $d$ electrons in the interval $N \leq n_d \leq N + 1$ (where $N$ is integer) it is easy to show (we suppose that the occupations for lowest $N$ states in Eq. (3) are $n_i = 1$ and the last partially occupied state contains $x = n_d - N$ electrons) that it can be presented as

$$E^H[n_d] = \frac{1}{2}UN(N - 1) + UNx. \tag{9}$$

By taking into account the values at the edges of interval, we come to the following $x$ dependence of $E^H$,

$$E^H[N + x] = (1 - x)E^H[N] + xE^H[N + 1]. \tag{10}$$

This means that the curve $E^H$ versus $n_d$ is a series of straight-line segments and its derivative $\partial E^H[n_d]/\partial n_d$ has discontinuities at the integer values of $n_d$. This result has very important fundamental consequences concerning the description of a system with fractional electron numbers (for example, a system which could exchange electrons with a reservoir). In quantum mechanics, an open system with a fluctuating numbers of particles cannot be described by a pure state. Instead of this, a statistical mixture or ensemble of states with their respective probabilities must be used. In this case, as it has been shown by Perdew et al.,[14] for the exact density func-

tional the only allowed dependence of the total energy on the number of electrons has the form of Eq. (10), i.e., consists of series of straight-line segments. Thus, we see that the Hartree expression for the interaction of localized electrons automatically satisfies the property of the *exact* density-functional formalism. This is the key for the successful applications of Anderson[29] or Hubbard[30] models for strongly correlated systems and at the same time the basic limitation of LSDA being characterized by a smooth dependence of total energy on occupation numbers.

If we subtract from (9) the $d$-$d$ interaction energy in LDA parametrized in the form (5), we find out that inside the interval $N \leq n_d \leq N + 1$, $\Delta E_{\text{cor}}$ behaves as

$$\Delta E_{\text{cor}}[x] = -\frac{1}{2}Ux(x - 1), \tag{11}$$

and its derivative $\partial \Delta E_{\text{cor}}/\partial x$ (correction for one-electron potential) is

$$\Delta V_{\text{cor}}(x) = \frac{\partial \Delta E_{\text{cor}}}{\partial x} = U(\tfrac{1}{2} - x) \tag{12}$$

(see Fig. 1). Thus, for integer occupations $\Delta E_{\text{cor}}$ vanishes but its first derivative undergoes a jump of hight $U$. It means that in these points our correction gives a *redefinition of the one-particle energies* for the localized states:

$$\varepsilon_d^{\text{LDA}+U}(N) = \varepsilon_d^{\text{LDA}}(N) \pm \frac{U}{2}, \tag{13}$$

where the signs "+" and "−" correspond to the empty and occupied states. By taking into account that $U = \partial \varepsilon_d^{\text{LDA}}/\partial n_d \,|_{n_d = N}$, we find
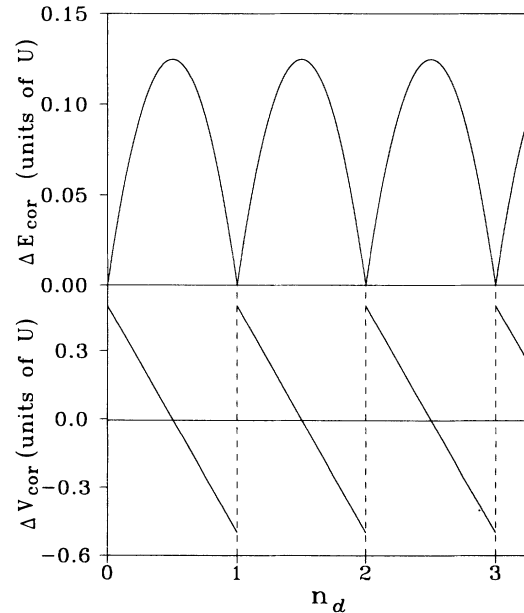


FIG. 1. The dependence of the LDA+$U$ corrections for the total energy ($\Delta E$) and for the one-electron potential on the number of localized electrons.

$$\varepsilon_d^{\mathrm{LDA}+U}(N) \simeq \varepsilon_d^{\mathrm{LDA}}(N \pm \tfrac{1}{2}). \tag{14}$$

If we compare this expression with Slater's transition state formalism one can see that the eigenvalues for $d$ states in the LDA+$U$ have the meaning of ionization and affinity energies for the occupied and empty orbitals, respectively. Any deviations of the total number of localized electrons from the integer values increase the total energy in accordance with the parabolic dependence (11). Therefore, the effect of the term $\Delta E_{\mathrm{cor}}$ can be also considered as an additional constraint enforcing an integer population of the localized states.

Thus, we have shown how the discontinuity of the one-electron potential existing in an *exact* density-functional formalism can be incorporated in LDA. Now let us turn to a more realistic treatment of electron-electron interaction in the atomic limit and explicitly include the exchange and orbital polarization terms in the functional (1). In the Hartree-Fock approximation, the $d$-$d$ interaction energy can be expressed in the general case as

$$E^{HF}[\{n_i\}] = \frac{1}{2}\sum_{i \neq j}(U_{ij} - J_{ij})n_i n_j, \tag{15}$$

where $U_{ij}$ and $J_{ij}$ are orbital dependent Coulomb and exchange parameters:

$$U_{ij} = \left\langle ij \left| \frac{1}{r_{12}} \right| ij \right\rangle, \qquad J_{ij} = \left\langle ij \left| \frac{1}{r_{12}} \right| ji \right\rangle. \tag{16}$$

Integration in (16) assumes also summation over spin variables. The parameters $U_{ij}$ and $J_{ij}$ can be expressed through Slater's integrals $F^k$,[15]

$$F^k = e^2 \int_0^\infty r^2 dr [\varphi_d(r)]^2 \int_0^\infty (r')^2 dr' [\varphi_d(r')]^2 \frac{r_<^k}{r_>^{k+1}} \tag{17}$$

and Clebsch-Gordan coefficients (a concrete form of these expressions can be found, for example, in Ref. 19). $\varphi_d(r)$ in (17) is the wave function for localized states and $r_<$ ($r_>$) is the smaller (larger) of $r$ and $r'$. The index $k$ takes the values $0, 2, 4$ and $0, 2, 4, 6$ for states of $d$ and $f$ symmetry. Thus, in fact only three and four independent parameters, respectively, are needed to define all values of $U_{ij}$ and $J_{ij}$ (16). The principal question here is the choice of $F^k$. It is known that direct calculations of Slater's integrals [Eq. (17)] based on the atomic wave functions strongly overestimate them due to the neglect of renormalization effects. This is especially important for the $F^0$ integral being identical with the Coulomb $U$ parameter. Sometimes the use of LDA wave functions gives quite reasonable values for $F^2$, $F^4$, and $F^6$ integrals,[16,17] because the overestimation arising from the neglect of renormalization effects is approximately canceled by the larger spatial extension of the LDA wave functions (due to the improper cancelation of self-interaction in the LDA potential) in comparison with HF ones. But this is a rather accidental fact. This problem cannot be straightforwardly solved by mapping results of constrained LSDA total energy calculations on the model (15) (even with integer occupation numbers) since, the former has only two

degrees of freedom for all possible constraints (number of electrons and spin magnetization) and since, therefore, only two parameters characterizing the interaction in the system of localized electrons can be extracted. Usually, these are the Coulomb and exchange interaction parameters which can be related to Slater's integrals as[15]

$$U = F^0, \tag{18}$$

$$J = \frac{1}{14}(F^2 + F^4). \tag{19}$$

However, in the following, we will exploit the well-known fact that usually the ratios between $F^2, F^4$ (and $F^6$) integrals are reasonably well-defined constants. For example, HF calculations[31] for $3d$ ions give values for the ratio $F^4/F^2$ varying between 0.621 and 0.629. Analytical result for this case obtained with hydrogenlike functions yield the value $F^4/F^2 = 0.6514$.[32,33]

With all parameters $U_{ij}$ and $J_{ij}$ determined, we can perform now the same manipulations as in the simplified scheme developed above where intra-atomic exchange and orbital-polarization contributions where neglected. We suppose that in LDA the interaction energy between the localized electrons can be expressed in the form (4) with $m_d = 0$ and replace it by (15). Finally, we come to the following expression for the total energy correction for localized states:

$$\Delta E_{\mathrm{cor}}[\{n_i\}] = -\frac{1}{2}Un_d(n_d - 1) + \frac{1}{4}Jn_d(n_d - 2)$$
$$+ \frac{1}{2}\sum_{i \neq j}(U_{ij} - J_{ij})n_i n_j \tag{20}$$

and therefore the potential acting on the $i$th localized orbital is

$$V_i(\mathbf{r}) = V^{\mathrm{LDA}}(\mathbf{r}) + \Delta V_{\mathrm{cor}}^i, \tag{21}$$

where

$$\Delta V_{\mathrm{cor}}^i = -U\left(n_d - \frac{1}{2}\right) + \frac{1}{2}J(n_d - 1)$$
$$+ \sum_j (U_{ij} - J_{ij})n_j. \tag{22}$$

Both intra-atomic exchange and orbital-polarization terms are included in expression (20) in the framework of the one-electron approximation [thus, we do not pretend here to describe properly all atomic multiplet structure which is based entirely on the many-determinant approach. It is well known that, in general, a many-electron wave function in the form of a single Slater's determinant is not an eigenstate of the operators $S^2$ and $L^2$. Therefore, the energy (20) cannot be presented as a pure term and has contributions arising from different terms]. To illustrate the role of intra-atomic exchange and orbital polarization we list in the Table I the values of the correction (20) for the case of two $d$ electrons, one of which occupies the one-electron orbital with azimuthal quantum number $-2$ and the other one an arbitrary orbital. It is evident that the total energy now depends on which states are exactly occupied by the electrons and takes

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TABLE I. Corrections for the total energy in LDA obtained for the configuration $d^2$ with different pairs of occupied states (the ratio $F^4/F^2 = 0.625$ between the Slater's integrals has been used).

| Occupied states | $\Delta E_{cor}$ |
|---|---|
| $(-2\uparrow, -1\uparrow)$ | $-1.5165J$ |
| $(-2\uparrow, 0\uparrow)$ | $-1.5165J$ |
| $(-2\uparrow, 1\uparrow)$ | $-0.8278J$ |
| $(-2\uparrow, 2\uparrow)$ | $-0.1392J$ |
| $(-2\uparrow, -2\downarrow)$ | $0.7155J$ |
| $(-2\uparrow, -1\downarrow)$ | $-0.4005J$ |
| $(-2\uparrow, 0\downarrow)$ | $-0.6300J$ |
| $(-2\uparrow, 1\downarrow)$ | $-0.4005J$ |
| $(-2\uparrow, 2\downarrow)$ | $0.7155J$ |

its minimal value when both have the same projection of spin and the highest possible values of azimuthal quantum numbers (an one-electron analog of Hund's rules). Moreover, we can see now that the lowest value of the total energy is obtained for two different determinants $(-2\uparrow, -1\uparrow)$ and $(-2\uparrow, 0\uparrow)$. It is not surprising because both belong to the same many-electron ground-state term $^3F$ (for these determinants there is no admixture of the next $^3P$ term) and, therefore, should have the same expectation values of the total energy (equal $-8/49F^2 - 9/441F^4$). This effect was omitted in the attempts to include the orbital polarization effects in LSDA in the form of the *anzatz* $-BL_z^2$ (where $B$ is Racah parameter) undertaken by Eriksson et al.[16] and Norman.[17]

Since the description of electron-electron interaction in the LDA+$U$ approach is based on a model similar to the Hartree-Fock method (with renormalized parameters), we inevitably come to the necessity to handle state-dependent potentials and problems connected with the appropriate choice of orbitals for corrections like (23). Sometimes this can be done starting from some physical assumptions (for example, the choice of real harmonics is quite suitable for transition-metal oxides[4] due to the strong crystal-field effects). But unfortunately this becomes practically impossible for more complicated systems (as an example of this, we can refer to the problem of the formation of orbital magnetic moments which is usually a result of the competition between the crystal-field and spin-orbit interactions which have different sets of eigenvectors) and some numerical scheme is needed for these aims. We will divide this problem in two steps. First, we look for the subspace of occupied states minimizing the total energy functional (1). This problem is very close to the one appearing in the SIC-LSDA formalism[2] and the steepest descent method[34] can be used to solve it. In this minimization scheme, we define a set of occupied one-electron states as

$$| \varphi_i^{n+1} \rangle = | \varphi_i^n \rangle - \alpha P(h^{\mathrm{LDA}} + \Delta V_{\mathrm{cor}}^i) | \varphi_i^n \rangle \qquad (23)$$

and iterate this equation to self-consistency. $h^{\mathrm{LDA}}$ in (23) is the LDA part of the Hamiltonian, $P$ is the operator projecting vectors on the subspace of empty states

$$P = 1 - \sum_i^{\mathrm{occ}} | \varphi_i^n \rangle\langle \varphi_i^n | , \qquad (24)$$

$\alpha$ is a admixture coefficient. It is evident that convergence of (23) will be achieved when the condition

$$\langle \varphi_k | h^{\mathrm{LDA}} | \varphi_i \rangle = 0 , \qquad (25)$$

determined by the symmetry properties of the operator $h^{\mathrm{LDA}}$, is fulfilled for every $i$ and $k$ from the subsets of occupied and empty states, respectively. Then, (23) is reduced to the set of regular one-electron equations with nondiagonal Lagrange multipliers $\varepsilon_{ij}$:

$$(h^{\mathrm{LDA}} + \Delta V_{\mathrm{cor}}^i) | \varphi_i^n \rangle = \sum_j \varepsilon_{ij} | \varphi_j \rangle. \qquad (26)$$

We should note here that in comparison with the SIC-LSDA formalism, the second minimization step (the minimization of the total energy with respect to unitary transformations among the occupied states[2]) is not needed in the framework of the LDA+$U$ method since the functional (20) is invariant (due to the well-known property of the Hartree-Fock approximation) under transformations of such kind. Thus, the one-electron spectra for the localized states can be found simply by the diagonalization of the Lagrange parameter matrix:

$$\|\varepsilon_{ji}\| = \|\langle \varphi_j | (h^{\mathrm{LDA}} + \Delta V_{\mathrm{cor}}^i) | \varphi_i \rangle\|. \qquad (27)$$

Due to the condition (26), all matrix elements between the occupied and empty states vanish and diagonalization of $\|\varepsilon_{ji}\|$ can be performed independently for both sets of states.

## III. RESULTS AND DISCUSSION

The calculations for the electronic structure of all $d$ impurities in Rb were performed in super-cell geometry using the ASA-LMTO method[35,36] in the scalar-relativistic approximation. The bcc-based super-cell $T\mathrm{Rb}_3$ ($T$ denotes a transition metal atom) has been used where a $T$ impurity atom has only Rb atoms as first and second nearest neighbors. The impurity-impurity distance is $d_{ii} = \sqrt{2}a$, corresponding to a third neighbor distance in the bcc lattice ($a$ - lattice constant). We have found this to be a quite reasonable approximation. For example, test calculations using the larger super cell $T\mathrm{Rb}_7$ with $d_{ii} = \sqrt{3}a$ led to small changes for the $U$ and $J$ parameters of about 3% (the values of $U$ for an Fe impurity in the configuration $d^7$ calculated using FeRb$_3$ and FeRb$_7$ super cells are 0.309 and 0.319 Ry, respectively). Thus, we might expect that the size of the super cell will be important only for such cases where a localized state appears very close to the Fermi level, for example, in systems which are candidates for a mixed-valence behavior. That is why in this paper we restrict ourselves only to a qualitative description of such processes.

### A. Calculations of Coulomb and exchange interaction parameters

The $U$ and $J$ parameters calculated in accordance with Eqs. (6),(7) for all $3d$, $4d$, and $5d$ impurities in Rb are

presented in the Figs. 2 and 3. The main result of these calculations is the strong dependence of the $U$ parameters on the valence configuration [in this work, we have considered only $T^{2+}$ and $T^{1+}$ states which correspond to the configurations $(sp)^2 d^n$ and $(sp)^1 d^{n+1}$] of the impurities. This effect appears to be most significant for $3d$ impurities where the difference between $U$ parameters for both configurations reaches 30% and can play a very important role in the determination of the ground-states configuration for these systems. The source of such an unusual behavior is the relaxation of the $d$ wave function which becomes more extended when the number of $d$ electrons increases (in more detail, this effect is discussed elsewhere[37]). Within every row the dependence of the Coulomb parameters on the atomic numbers can be well interpolated by the straight lines.

The values of $J$ parameters also depend on the valence configuration of the $d$ impurity but this dependence is somewhat less pronounced than that of the $U$ parameters (for example, in the $3d$-impurity case the effect is less than 20%). We also note that the $J$ values are practically the same for all $4d$ and $5d$ impurities in Rb as was already mentioned in Ref. 28.

### B. Ground-state configurations for $d$ impurities in Rb

In this section, we will turn directly to a discussion of the stability of different electronic configurations of
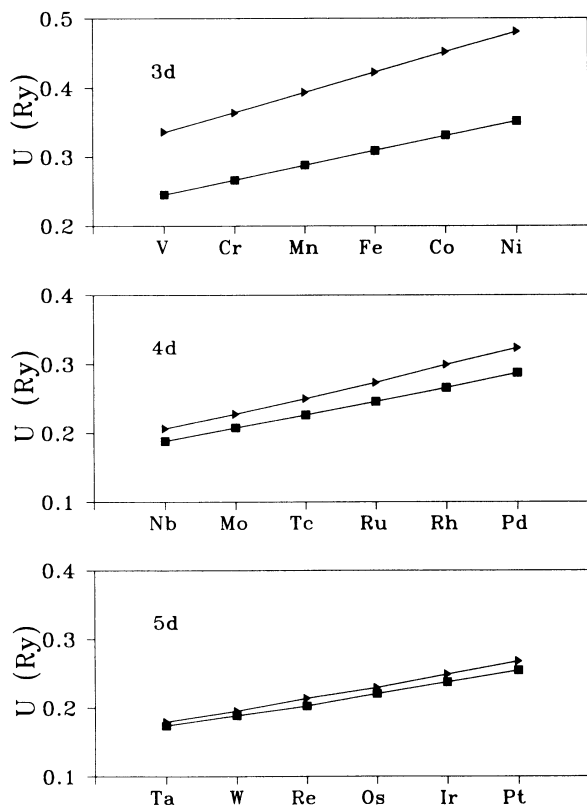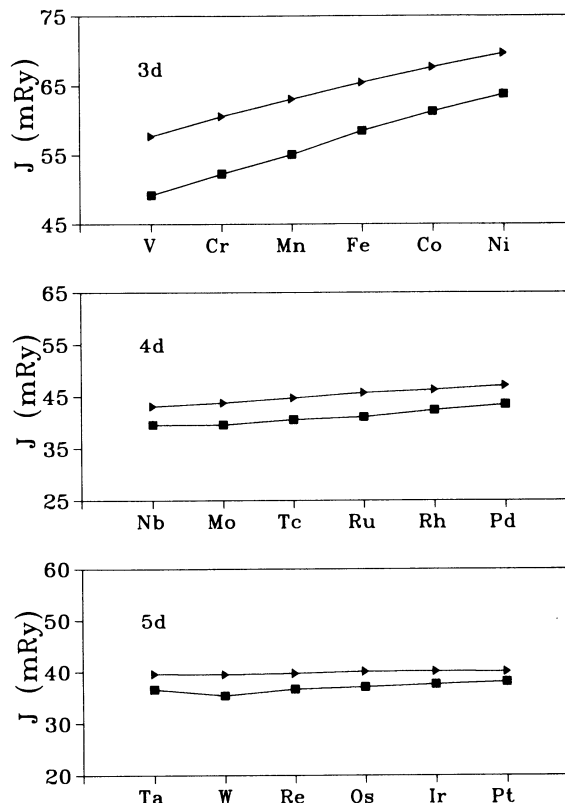


FIG. 3. The parameters of effective exchange interaction for $3d$, $4d$, and $5d$ impurities in Rb.

$d$ impurities in Rb within the LDA+$U$ formalism. In Table II, we show the typical values of LMTO-potential parameters,

$$\tilde{\Delta} = \frac{S}{2}[\varphi_d(C, S)]^2 \qquad (28)$$

for $d$ impurities in Rb (where $C$ is the band-center corresponding to the boundary condition that the logarithmic derivative of $\varphi_d$ at the Wigner-Seitz sphere $S$ is $-\ell - 1$), which can be considered as a measure of the hopping matrix elements in the Anderson model.[38,8] As example, we have chosen isoelectronic impurities from the middle of the $3d-$(Mn), $4d-$(Tc) and $5d-$(Re) series. One can see that the magnitude of $\tilde{\Delta}$ is rather small and has for all these series the same order as that of $4f$ states in rare-earth compounds. Thus, in a first approximation, we completely remove the hybridization between $d$ states at



FIG. 2. The parameters of the effective Coulomb interaction for $3d$, $4d$, and $5d$ impurities in Rb.

TABLE II. The potential parameter $\tilde{\Delta}$ for different configurations of Mn, Tc, and Re impurities in Rb (in Ry).

| Impurity | Configuration | $\tilde{\Delta}$ |
|---|---|---|
| Mn | $d^5$ | 0.0004 |
| Mn | $d^6$ | 0.0013 |
| Tc | $d^5$ | 0.0012 |
| Tc | $d^6$ | 0.0022 |
| Re | $d^5$ | 0.0019 |
| Re | $d^6$ | 0.0032 |

the impurity site and all other electronic states and allow only the charge transfer between these two subsystems.

We will stick to this approximation in the following. Moreover, we assume the following order for the occupation of the one-electron states: first $m = -2, -1, 0, 1, 2$ for spin $up$ and then $m = 2, 1, 0, -1, -2$ for spin $down$, which corresponds to the Hund's first and second rules. Since in this work we restrict ourselves to the atomic-sphere approximation in which the LDA part of potential is spherically symmetric at the impurity site, the condition (25) is automatically satisfied for complex harmonics and this choice of basis set is quite appropriate for the construction of corrections in the LDA+$U$ formalism (22).

All calculations were performed in accordance with the following scheme. We assumed first some set of single-particle levels to be occupied for a given configuration ($input$). Then, using the single-particle LDA energies for the $d$ states and the calculated $U$ and $J$ values for this configuration, the positions of occupied and empty states in LDA+$U$ with respect to Fermi level can be found ($output$). Since the single-particle eigenvalues in the LDA+$U$ formalism are directly connected with ionization potential and electron affinity, only knowledge of the single-particle energies is quite sufficient to determine the stability of the given configuration. The condition for charge equilibrium between the localized states and the host (which appears here as a reservoir) can be expressed in the simple form:

$$\varepsilon_{\max}(n_d) < E_F(n_d) < \varepsilon_{\min}(n_d), \qquad (29)$$

where $\varepsilon_{\max}$ ($\varepsilon_{\min}$) is the highest (lowest) occupied (empty) one-electron level in LDA+$U$ and $E_F$ is the Fermi level. Therefore, the considered configuration is only stable, if the output eigenvalues are consistent with the assumed input configuration. Otherwise, occupied (empty) states are situated above (below) the Fermi level and the considered trial configuration is evidently not stable since removal (addition) of one electron would lower the total energy.

Positions of single-particle $d$ levels of all transition-metal impurities are presented in Fig. 4 for both configurations. One can see that most $d$ impurities in Rb have the configuration $d^{n+1}$ in the ground state (valence state $T^{1+}$). Two exceptions to this rule are Mn and Re having the configuration $d^5$. Moreover, we also find that for the Pd impurity in Rb neither the $d^8$ nor the $d^9$ configuration is stable since in the ground-state it has a fully-occupied $d$ shell ($d^{10}$). One comment illustrating the need for an accurate choice of the $U$ and $J$ parameters in LDA+$U$ calculations should be added here. As it was mentioned in the previous section, the $U$ and $J$ parameters for $3d$ impurities in Rb strongly depend on the configuration. For example, for the Mn impurity in Rb the Coulomb interaction parameter is 0.39 and 0.29 Ry for configurations $d^5$ and $d^6$, respectively. If we tried to apply LDA+$U$ scheme for this case but with the same values of $U$ and $J$ (equal, for example, those for configuration $d^6$) we would get the paradoxical result that neither the $d^5$ nor the $d^6$ configuration of Mn is stable and that the addition of one electron to $d^5$ and removal of one electron from $d^6$

would lower the total energy. This example shows that the values of the electron-electron interaction parameters for different configurations should always be consistent with the shift of LDA single-electron energies which takes place during such a transition.

On the other hand, one can also look at the configurational stability using a total energy analysis. It would be interesting to see if in LDA+$U$ this leads to the same result as the above discussion of the single-particle energies. The differences of total energies between both configurations of $d$ impurities in Rb, $\Delta E = E(d^{n+1}) - E(d^n)$ are shown in Fig. 5. We can see that only two impurities are characterized by a positive difference $\Delta E$, i.e., Mn and Re. All other impurities have a $d^{n+1}$ ground-state configuration. Thus, in LDA+$U$ both schemes, the single-electron levels and the total energy analysis, are completely consistent and give an identical description of the configurational stability.

Thus, in the $3d$ and $5d$ series both Cr and Mn, W, and Re, respectively, have a $d^5$ configuration. This a consequence of the exchange interaction which favors a half-filled $d$ band. For both $d^5$ and $d^6$ configurations the total energy in LDA+$U$ can be rewritten as

$$E = E^{\text{LDA}} - \frac{1}{4}Jm_d^2 \qquad (30)$$

since in these cases the orbital polarization effect gives no contribution to the total energy. This is quite obvious for the configuration $d^5$ where all spin $up$ states are occupied and all spin $down$ ones are empty, but it is also true for the configuration $d^6$ since it has only one electron with spin $down$ interacting with a spherically symmetric shell of spin $up$ electrons so that the total energy does not depend on the orbital quantum number of the spin $down$ electron. The last term in Eq. (30), the intra-atomic exchange term being responsible for the Hund's first rule, evidently prefers the configuration with the highest spin magnetic moment and takes its minimal value for the configuration $d^5$ ($m_d = 5$). This is the driving force which can stabilize the configuration $d^5$ instead of $d^6$. In Table III, we have plotted the above two contributions, i.e., LDA and intra-atomic exchange, to the total energy difference $\Delta E$ between the two configurations $d^6$ and $d^5$ for the isoelectronic impurities Mn, Tc, and Re. The exchange part $\Delta E^J$ is always positive since both the moment and the $J$ value are larger for configuration $d^5$ (see Fig. 3). The continuous decrease between the third and fifth series reflects the decreasing $J$ values of Fig. 3. On the other hand, the LDA contributions favor the $d^6$ configuration, signalizing the usual tendency of larger band fillings with increasing valence. The large value obtained for Tc is an atomic effect. In the $4d$ series the $5s$ level is shifted to higher energies with respect to the $4d$ levels, favoring a somewhat larger $d$ population. Therefore, for Tc the $d^6$ configuration is more stable. For Re one expects the same effect to occur but in the $5d$ series relativistic effects become important in addition and favor smaller $d$ occupancies so that in the end the $d^5$ configuration wins for Re.

In all our calculations, we have neglected the lattice

relaxation around the impurities. However, due to the large volume differences between the alkali metals and the transition metals, large relaxations are expected to occur around the impurities. In order to illustrate possible relaxation effects, we have performed calculations for homogeneously compressed MnRb$_3$ supercells, assuming equal Wigner-Seitz spheres for both the Mn and Rb atoms (see Fig. 6). The theoretical values for the equilibrium volume of the MnRb$_3$ supercell differ drastically from that of pure Rb metal: corresponding Wigner-Seitz radii are 4.5 for the MnRb$_3$ supercell and 5.04 for pure Rb with a difference of more than 10%. We also note

that both configurations have about the same equilibrium volumes. Due to the relaxation the one-electron, $d$ levels drop approximately by 10 mRy with respect to the Fermi level. Thus, we suspect that for several $d$ impurities in Rb the relaxation effects could change the ground-state configurations. As an example, we might consider the Re-impurity in Rb where the highest occupied state for the configuration $d^6$ is located at 6.6 mRy above the Fermi level. Therefore, we have found this configuration to be unstable for the lattice parameter of pure Rb, but it might be stabilized by the relaxation. Other candidates are Rh and Pt impurities in Rb host which could
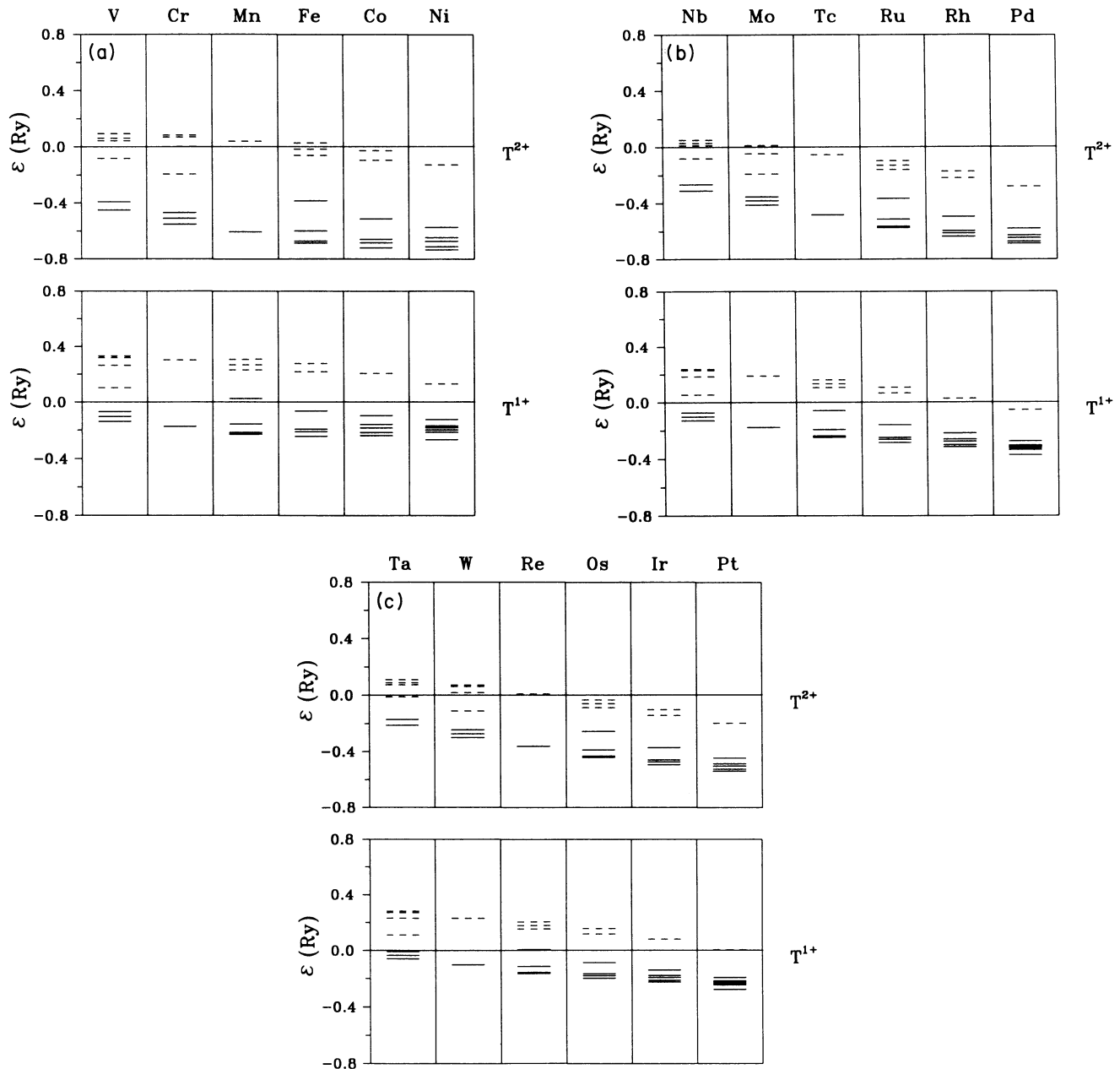


FIG. 4. Positions of the one-electron levels with respect to the Fermi energy obtained in the framework of LDA+$U$ for two valence states ($T^{2+}$ and $T^{1+}$) of $3d$ (a), $4d$ (b), and $5d$ impurities (c) in Rb. The solid (dashed) lines were used for the states which were supposed to be occupied (empty).
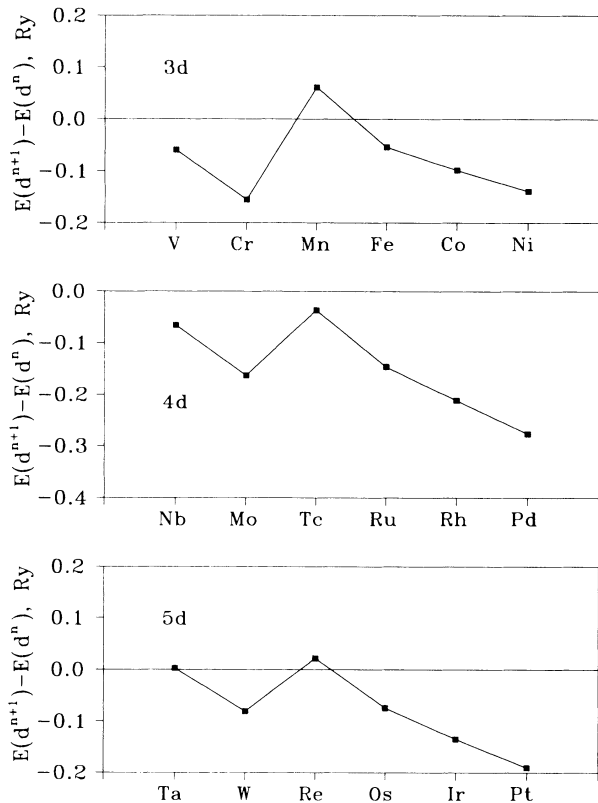
FIG. 5. Total energy differences between the two valence states ($T^{2+}$ and $T^{1+}$) obtained in the framework of the LDA+$U$ formalism for 3$d$, 4$d$, and 5$d$ impurities in Rb.
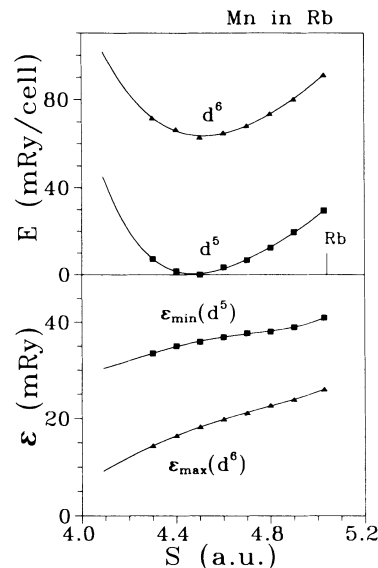
FIG. 6. The total energies and positions of one-electron $d$ levels with respect to the Fermi level for the supercell MnRb$_3$ as a function of the Wigner-Seitz sphere radii. The equilibrium Wigner-Seitz sphere radius for pure Rb is indicated by an arrow.

transform to the configurations $d^9$ and $d^{10}$, respectively.

In addition to lattice relaxations, also, relativistic effects can become very important, especially for 5$d$ impurities. In this work, we used the scalar-relativistic formalism which includes the Darwin and mass-velocity terms but completely neglects the spin-orbit coupling. The importance of spin-orbit coupling for 5$d$ impurities can be illustrated by the following example. For a Re impurity in Rb, we estimated the spin-orbit coupling constant ($\xi$) as 13.3 and 11.9 mRy for the configurations $d^5$ and $d^6$, respectively. In the first order of the perturbation theory the spin-orbit interaction shifts the one-electron levels by $\xi \ell_z s_z$. Thus, for the $d^6$ configuration of Re the highest occupied state will be located at $6.6 - 11.9 \times 2 \times 1/2 = -5.3$ mRy with respect to the Fermi level and this configuration will be already stable. Correspondingly, for the first empty state of $d^5$ configu-

ration, we would get $11.2 - 13.3 \times 2 \times 1/2 = -2.1$ mRy and, therefore, the spin-orbit interaction makes this configuration unstable.

Finally, we note that in all our calculations, we have neglected the hybridization between the localized $d$ states of the impurity and the $sp$ states of the Rb host. Within the LDA+$U$ approach hybridization leads to a resonance broadening of the $d$ levels. This has basically two consequences. States close to the Fermi-energy can become partially occupied. In addition, states well below the Fermi energy, which are practically fully occupied, also do not have an integer local occupation number since part of the weight resides on the neighboring sites. Previous calculations[28] based on an "older" LDA+$U$ scheme, but including hybridization clearly showed, that even for relatively narrow resonances the local $d$ charges and moments show significant deviations from integer values. We also expect similar modifications for our present results, once hybridization is included.

Due to these approximations, i.e., the neglect of lattice relaxation, hybridization, and spin-orbit coupling, our present results have a more qualitative character and cannot make reliable predictions for the ionic configurations of the impurities. But, nevertheless some qualitative comparisons with available experimental data can be done. From the ionic-type analysis applied to the experimental results obtained with the time-differential perturbed $\gamma$-ray distribution method,[22–26] Ni impurities in Rb host were reported to have a $d^9$ configuration (spin, orbital, and total moments are correspondingly $S = 1/2$, $L = 2$, and $J = 5/2$) which is in good agreement with our estimations. Experimental results for Fe impurities in Rb can be well understood assuming the Fe($d^6$) configuration with $S = 2$, whereas we found it to be Fe($d^7$). These discrepancies probably arise from the approximations used

TABLE III. The LDA ($\Delta E^{\text{LDA}}$) and intra-atomic exchange ($\Delta E^J$) contributions to the total energy differences ($\Delta E$) between the configurations $d^6$ and $d^5$ for Mn, Tc, and Re impurities in Rb (in Ry).

| Impurity | $\Delta E^{\text{LDA}}$ | $\Delta E^J$ | $\Delta E$ |
|---|---|---|---|
| Mn | −0.112 | 0.174 | 0.061 |
| Tc | −0.153 | 0.117 | −0.036 |
| Re | −0.080 | 0.101 | 0.022 |

in our calculations as already mentioned above. On the other hand, interpretation of the experimental results is often rather ambiguous and strongly depends on the choice of used model parameters. Both more realistic calculations of the electronic structure and more careful analysis of experimental data are needed to clarify the ground-state configuration of Fe impurities in Rb. The magnetic behavior of Mo and Ru impurities in Rb and Cs has been explained by assuming predominant $d^5$ and $d^7$ ($S = 5/2$ and $S = 3/2$, respectively) configurations for them[24-26] which is in good agreement with our findings. Pd ions in Rb and Cs were predicted to be nonmagnetic.[26] It is consistent with the fully-occupied $d^{10}$ configuration of Pd impurities obtained in present work. Tc impurities in Rb were reported in Ref. 26 as an example of $d$ system with mixed-valence behavior. In our calculations, we found that Tc has the electronic configuration $d^6$ in the ground-state but the energy difference between the $d^5$ and $d^6$ configurations for Tc impurity in Rb is relatively small (0.036 Ry/impurity site). Other candidates for mixed-valence behavior in accordance with our calculations could be some impurities from the $5d$ row (which were not investigated experimentally yet): Re ($\Delta E = 0.022$ Ry/impurity site) and Ta (which has practically the same total energies for the configurations $d^3$ and $d^4$).

## IV. SUMMARY

In conclusion, we have derived a version of the LDA+$U$ formalism which allows us to reproduce the "atomic limit" in band structure calculations and is suitable for the description of systems with strongly localized electrons. We have shown that it can be considered as a constrained LDA with additional corrections describing the spin- and orbital-polarization effects. The discontinuity of the one-electron potential known for an "exact" density functional is also incorporated in this formalism. The method has been applied to the analysis of the electronic structure and configurational stability of $d$ impurities in Rb. We have shown that in this formulation of the LDA+$U$ method the single-electron levels and the total energy analysis are completely consistent and give an identical description of the configurational stability.

## ACKNOWLEDGMENTS

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Computations performed with hydrogenlike functions give the following ratios between $F^2$, $F^4$, and $F^6$ integrals: $F^4/F^2 = 451/675$, $F^6/F^2 = 1001/2025$ [E.I. Zabolotskii (private communication)].

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