PHYSICAL REVIEW B VOLUME 40, NUMBER 15 15 NOVEMBER 1989-II

Density-functional calculation of effective Coulomb interactions in nonmetallic systems: Application to Mn in CdTe, CdS, and ZnO

O. Gunnarsson, A. V. Postnikov,* and O. K. Andersen
Max-Planck-Institut für Festkörperforschung, Postfach 80 06 65, D-7000 Stuttgart 80, West Germany

(Received 6 June 1989)

The effective Coulomb interaction U between the $3d$ electrons of Mn impurities in CdTe, CdS, and ZnO is calculated. The influence of the host on the renormalization of U is studied. It is shown that the screening due to charge transfer to the Mn atom is very efficient for Mn in CdTe, less efficient for Mn in CdS, and rather inefficient for ZnO. This is related to the increasing ionic character, which makes charge transfer to Mn increasingly difficult. The total effect of all charge-transfer processes, including charge transfer to the ligand atoms, is nevertheless substantial even for Mn in ZnO.

I. INTRODUCTION

The eigenvalue spectrum in the local density (LD) approximation to the density-functional (DF) formalism[1] often gives an accurate description of the excitation spectrum of weakly or moderately strongly correlated systems. For strongly correlated systems, such as $4f$, $5f$, and many $3d$ compounds, however, the eigenvalue spectrum often disagrees qualitatively with experiment.[2] For many of these systems the Anderson impurity model has been shown to give a satisfactory description of excitations of the system.[3-9] It is then interesting to ask if the DF formalism can be used to calculate the parameters of the Anderson model. Recently, there have been a number of such calculations, in most cases with encouraging agreement with experiment.[5,10-17]

Here we will focus on the calculation of the on-site Coulomb integral U in the Anderson model. For rare earth or actinide compounds, U refers to the Coulomb interaction between the f electrons and for a transition metal compound between the $3d$ electrons. As discussed by Herring,[18] U is a renormalized quantity, which includes effects neglected explicitly in the Hamiltonian. If, for instance, an extra $3d$ electron is put on a transition metal atom in a compound, the number of $4s$ and $4p$ electrons on that atom is reduced so that the energy cost of adding the $3d$ electron is decreased. Since this screening effect by the $4s$ and $4p$ electrons, due to the Coulomb interaction between these electrons and the $3d$ electrons, is not included explicitly in the Anderson model, it is included implicitly as a reduction of U. Herbst *et al.*[10] have calculated U for the rare earth and actinide metals, by assuming that the change in the number of f electrons is completely screened within the Wigner-Seitz sphere by the conduction electrons. While this appears to be a good assumption for metallic systems, it is not in general true for other systems. For nonmetallic systems one therefore has to calculate the screening charge for the system of interest to obtain U. In a recent paper, such a calculation has been performed for Mn in CdTe and different screening mechanisms have been analyzed in detail.[15] Here we want to discuss how the screening changes when the system becomes more ionic. We consider in order of increasing ionicity a Mn impurity in CdTe, CdS, and ZnO, which have band gaps of 1.6, 2.6, and 3.4 eV, respectively. We expect to find similar trends for $4f$ and $5f$ impurities as are found here for the $3d$ impurity Mn.

II. GENERAL CONSIDERATIONS ABOUT SCREENING DUE TO CHARGE TRANSFER

As in the earlier work[15] we obtain the definition of U ($\equiv U^{\text{eff}}_{3d,3d}$) by considering the Coulomb contribution to the total energy $\frac{1}{2}Un_{3d}(n_{3d}-1)$ in the Anderson impurity model. Mapping the results in the LD calculation onto the model, we find

$$U=\frac{\partial^2 E}{\partial n_{3d}^2}=\frac{\partial \varepsilon_{3d}}{\partial n_{3d}} , \tag{1}$$

where E is the total energy and ε_{3d} is the $3d$ eigenvalue. We have used the relation[19] $\partial E/\partial n_{3d}=\varepsilon_{3d}$. In the calculation of E the hopping between the $3d$ level and the other levels of the system is suppressed, since this hopping is included explicitly in the Hamiltonian.[15] Including the hopping also in the LD calculation of E would lead to double counting of the hybridization.

In this section we obtain a simple estimate of the effectiveness of the screening due to charge transfer to the atom with the $3d$ orbital. We first calculate the hopping integrals between the high-lying Mn $4s$ and $4p$ orbitals and the valence states of the system:

$$V_{4l}^2\equiv\sum_k |V_{k,4l}|^2, \quad l=s,p , \tag{2}$$

where the sum is over states k belonging to the valence band and $V_{k,4l}$ is a hopping matrix element between the Mn $4l$ state and a valence-band state k.[20] This type of calculation was described in Ref. 15. Perturbation theory then gives the occupancy n_{4l} of the Mn $4l$ orbital due to the mixing into the valence band:

$$n_{4l}=2(2l+1)\frac{|V_{4l}|^2}{(\varepsilon_{4l}-\varepsilon_v)^2} , \tag{3}$$

©1989 The American Physical Society

where ε_{4l} is the energy of the Mn $4l$ orbital and ε_v is a typical energy of the valence band. To calculate the derivative $\partial\varepsilon_{3d}/\partial n_{3d}$, we now change the number of $3d$ electrons by ∂n_{3d}. This leads to a change of the $4l$ orbital energy by

$$\begin{aligned}\partial\varepsilon_{4l} &= U_{4l,3d}\partial n_{3d} + \sum_{l'=s,p} U_{4l',4l}\partial n_{4l'} \\ &\equiv U^{\text{eff}}_{4l,3d}\partial n_{3d}\ ,\end{aligned} \tag{4}$$

where $U_{4l,3d}$ is the Coulomb interaction between the $3d$ and $4l$ orbitals, and $U_{4l',4l}$ is the Coulomb interaction between the $4l$ and $4l'$ electrons. The second term results from the charge transfer to the Mn atom, and it tends to limit the amount of charge transfer in a self-consistent way. The change in the number of $4l$ electrons is then[21]

$$\frac{\partial n_{4l}}{\partial n_{3d}} = -4(2l+1)U^{\text{eff}}_{4l,3d}\frac{|V_{4l}|^2}{(\varepsilon_{4l}-\varepsilon_v)^3}\ . \tag{5}$$

This leads to a change in the $3d$ orbital energy and hence to a reduction of U by

$$\begin{aligned}\delta U &= \sum_{l=s,p} U_{4l,3d}\frac{\partial n_{4l}}{\partial n_{3d}} \\ &= -4\sum_{l=s,p}(2l+1)U_{4l,3d}U^{\text{eff}}_{4l,3d}\frac{|V_{4l}|^2}{(\varepsilon_{4l}-\varepsilon_v)^3}\ .\end{aligned} \tag{6}$$

We can see that $|V_{4l}|^2/(\varepsilon_{4l}-\varepsilon_v)^3$ provides a crude measure for the importance of the screening of U due to charge transfer to the atom with the $3d$ orbital.

For the systems of interest here, the $4s$ level is too close to the valence band for perturbation theory to be valid and we therefore concentrate on the $4p$ level in our simple estimates. The results of the full calculations, to be discussed in the following sections, show that the $4s$ and $4p$ contributions to screening are comparable for these systems (see Table III). For the simple estimates we deduce ε_v from $V_{4p}^2/(\varepsilon_{4p}-\varepsilon_v)^2 \equiv \sum_k^{occ}|V_{k,4p}|^2/(\varepsilon_{4p}-\varepsilon_k)^2$. For the orbitals we use orthogonal linear muffin-tin orbitals,[22] as in our previous work.[15]

In Table I we give the estimates of $\varepsilon_{4p}-\varepsilon_v$ and V_{4p}^2. We can see that V_{4p}^2 is substantially larger for Mn in ZnO than for Mn in CdTe. The reason is that the atoms are much closer together in ZnO, leading to larger hopping integrals. This tends to make the screening of Mn in ZnO more efficient. The dominating effect is, however, the energy separation of the $4p$ level from the valence band. Because the difference in electronegativity[23] between Mn (1.6) and O (3.5) is much larger than the difference between Mn (1.6) and Te (2.1), the $4p$ level is much higher above the valence band for Mn in ZnO than in CdTe. Thus we expect the screening to be much less effective for the very ionic system Mn in ZnO. The ratio $V_{4p}^2/(\varepsilon_{4p}-\varepsilon_v)^3$, however, overestimates the efficiency for Mn in CdTe compared with the other systems. The reason is that the self-consistency condition (4) strongly reduces $U^{\text{eff}}_{4p,3d}$ for Mn in CdTe. Thus we find that $U_{4p,3d}\sim 0.8$ Ry, $U_{4l',4l}\sim 0.7$ Ry, and $(\Delta n_{4s}+\Delta n_{4p})/\Delta n_{3d}\ \sim 0.7$ (see Table III). Therefore $U^{\text{eff}}_{4p,3d}\sim 0.35$ Ry, while the corresponding reduction for Mn in CdS and ZnO is much smaller because of the smaller charge transfer for these systems (see Table III).

TABLE I. The parameters $\varepsilon_{4p}-\varepsilon_v$ and V_{4p}^2, as well as the quantity $V_{4p}^2/(\varepsilon_{4p}-\varepsilon_v)^3$ entering in (6) for Mn in the hosts CdTe, CdS, and ZnO. All energies are in Ry.

Host	V_{4p}^2	$\varepsilon_{4p}-\varepsilon_v$	$\dfrac{V_{4p}^2}{(\varepsilon_{4p}-\varepsilon_v)^3}$
CdTe	0.15	1.1	0.11
CdS	0.31	2.0	0.04
ZnO	0.61	4.7	0.006

III. RESULTS

We have performed calculations for a Mn impurity in CdTe, CdS, and ZnO, where Mn replaces Cd, Cd, and Zn, respectively. We have assumed that the host has a zinc-blende lattice structure, although ZnO exists only in the wurtzite structure. For CdTe and CdS we have used the experimental lattice parameter, and for ZnO we used a lattice parameter which gives the same atomic volume as the experimental atomic volume in the wurtzite lattice. This gives us a possibility to study the properties which are related to the different ionicity of the atoms involved, without having competing effects due to different lattice structures. Based on the atomic radii, we expect the ligand atoms to relax towards the Mn atom in CdTe and away from the Mn atom in ZnO. This relaxation has been neglected in our calculations. Such a relaxation could be quite important for a quantitative comparison with experiment, but it would not remove the large differences due to the different ionic character of the systems studied here. In the following we therefore consider Mn in unrelaxed CdTe, CdS, or ZnO in the zinc-blende structure as model problems.

This impurity problem was solved using a formalism[24] based on the linear muffin-tin orbital (LMTO) method in the atomic sphere approximation.[25,22] In this approach, space is divided into spheres, and the potential and charge density are assumed to be spherically symmetric inside each sphere. For the hosts considered here, we use four equally large spheres per unit cell. For, e.g., CdTe, there is one sphere centered at Cd and one at Te and two so-called empty spheres in the large interstitial spaces. We use space-filling spheres, i.e., the volume of the four spheres is equal to the unit cell volume. The sphere radii are then $s=3.015$ (CdTe), 2.710 (CdS), and 2.126 a.u. (ZnO). Because of the localized character of the Mn $3d$ orbital, the different Mn sphere sizes have a rather small influence on this orbital. For instance, a normalized Mn atomic orbital integrates to 0.98, 0.97, and 0.91 over spheres with the radii 3.015, 2.710, and 2.126, respectively. As discussed below, the different Mn sphere sizes are part of the reason for the rather small variations of F^0 in the first column of Table II. For each sphere we include *s*-, *p*-, and *d*-partial waves. To compensate for the underestimate of the gap in the local-spin-density (LSD) approximation, we have used the so-called scissor operator.[26] The calculation of the derivative of ε_{3d} in (1) is

TABLE II. The Coulomb integral U for the Mn $3d$ orbital including different screening mechanisms. The unrenormalized value is given by the Slater integral F^0 (7) calculated from atomic orbitals (see text). The column "Mn orbital" shows results when the Mn orbitals are allowed to relax, but no charge transfer is allowed. The column "Mn charge" shows results when in addition charge transfer to the Mn atom is included, and the column "Ligand charge" when also charge transfer to the nearest-neighbor ligand and empty spheres is allowed. The column "Polarization" finally shows results when the ligand atoms in addition are assumed to be polarizable. This column give an upper limit to the effects of the polarizability. All energies are in Ry.

			Relaxation mechanism solid		
Host	Atom F^0	Mn orbital	Mn charge	Ligand charge	Polarization
CdTe	1.63	1.18	0.60	0.57	≥ 0.44
CdS	1.66	1.27	0.78	0.68	≥ 0.49
ZnO	1.76	1.45	1.24	0.95	≥ 0.67

performed at $n_{3d}=5$. We perform non-spin-polarized calculations, and the resulting U should be associated with a Slater F^0 Coulomb integral.[27] Information about the integrals F^2 and F^4 needed to include multiplet effects can be obtained from spin-polarized calculations or atomic data.[15]

The results for the Coulomb interaction are shown in Table II. First we show results for the Slater integral[27]

$$F^0=\frac{e^2}{2}\int_0^s r^2 dr\int_0^s (r')^2 dr'\frac{\phi(r)^2\phi(r')^2}{r_>}\ , \tag{7}$$

where $r_>$ is the larger of r and r', and ϕ is an atomic $3d$ orbital calculated with the occupancies of the $4s$ and $4p$ orbitals in the different hosts. The $3d$ orbital is normalized to the various atomic spheres of Mn, which is the reason why the result for Mn in CdTe is slightly larger than our earlier result.[15] These are the unrenormalized results for U. F^0 is larger for Mn in ZnO than for Mn in CdTe for several reasons. In ZnO the number of $4s$ and $4p$ electrons is smaller than in CdTe. The potential for Mn in ZnO is therefore more attractive and the $3d$ orbital is more contracted, which increases F^0. In addition the smaller atomic sphere for Mn in ZnO compared with Mn in CdTe also leads to a somewhat more compact $3d$ orbital for Mn in ZnO, since the orbital is renormalized to a smaller atomic sphere.

The column "Mn orbital" shows results of calculations where no charge transfer to the Mn atom is allowed and the charge density in the host is unchanged. Only the orbitals inside the Mn atomic sphere are allowed to readjust when the number of $3d$ electrons is changed. The results for Mn in CdTe differ slightly from the earlier results,[15] due to the use of a slightly different reference configuration ($n_{3d}=5$ instead of $n_{3d\uparrow}=5.0$ and $n_{3d\downarrow}=0.1$) and the use of a spin-compensated calculation instead of the average of the spin-up and spin-down results in a spin-polarized calculation. The table illustrates that there is a substantial renormalization of U due to the relaxation of the Mn orbitals. When an electron is added to the $3d$ orbital, all Mn orbitals expand to reduce the energy cost of adding a $3d$ electron. In particular, this relaxation of the $3d$ and to a lesser extent the $4s$ and $4p$ orbitals is very important.[15] For Mn in ZnO,where the occupancies of the $4s$ and $4p$ orbitals is smaller, this screening is less efficient and the reduction relative to F^0 is smaller. The smaller atomic sphere used for Mn in ZnO should also reduce the screening.

In the column "Mn charge" we show results when charge transfer to the Mn atomic sphere is allowed. As expected from the general arguments in Sec. II this mechanism is much more efficient for Mn in CdTe than for Mn in ZnO. Thus the reduction of U due to this mechanism is about 0.6 Ry in CdTe but only about 0.2 Ry in ZnO. This is also illustrated in Table III, which shows the screening charge in different channels per unit change of the number of $3d$ electrons. We can see that the change in the $3d$ charge is screened to about 70% for Mn in CdTe but only to about 20% for Mn in ZnO. For metals this screening is traditionally assumed to be 100%,[18,10] and the screening is therefore less efficient for Mn in the

TABLE III. The change in the charge on the central Mn site, partitioned in l components, and on the neighboring four ligand and four empty sites, per unit change of the number of Mn $3d$ electrons. For each host the upper row shows a calculation when no change on the neighboring atoms was allowed.

Host	Mn $4s$	Mn $4p$	Mn $3d$	Ligand	Empty
CdTe	−0.33	−0.36	1.00	0	0
CdTe	−0.27	−0.30	1.00	−0.17	−0.18
CdS	−0.27	−0.25	1.00	0	0
CdS	−0.18	−0.16	1.00	−0.47	−0.13
ZnO	−0.11	−0.08	1.00	0	0
ZnO	−0.08	−0.06	1.00	−0.42	−0.27

semiconductor CdTe. Still this screening is very essential for Mn in CdTe. For Mn in ZnO; on the other hand, we are much closer to the limit where this type of screening is ineffective. Even in this case, though, the charge transfer to the Mn atomic sphere cannot be neglected, as illustrated by the reduction of U by about 0.2 Ry.

In the column "Ligand charge" we have also allowed the charge in the nearest-neighbor ligand atoms and empty spheres to relax. This leads to a rather small effect on U for Mn in CdTe. This is primarily due to the rather efficient screening already achieved by the charge transfer to the Mn sphere. But also the relatively large distance between the Mn and Te atoms makes this screening rather inefficient.[15] For Mn in ZnO, on the other hand, U is reduced substantially due to this relaxation mechanism, both because of the small on-site screening and because of the short Mn-O separation. This is further illustrated in Table III. Thus about 70% of the change in the $3d$ charge is screened in the neighboring spheres, while the corresponding number for Mn in CdTe is only 35%. The screening in the Mn sphere is now somewhat reduced so that the total screening charge is more than 90% for Mn in CdTe and more than 80% for Mn in ZnO. In linear response the screening charge should integrate to $1-1/\epsilon$ over a large volume surrounding the impurity, where ϵ is the electronic contribution to the dielectric constant. This formula predicts about 86% screening for CdTe and 73–75 % screening for ZnO.

As mentioned above, we use the atomic sphere approximation (ASA), which means that only the spherical averages of the potentials and charge densities inside the spheres are considered. We have therefore neglected possible polarization effects inside the atomic spheres in the calculations. The use of empty spheres, however, means that some effects are included, which would normally be defined as polarization effects. To estimate an upper limit to the effects of the ASA, we have used empirical polarizabilities.[28] These atomic polarizabilities were estimated by assuming that the polarizability of a solid can be written as a sum of atomic polarizabilities. Such empirical polarizabilities should therefore ideally describe effects both due to charge transfer between the atomic spheres and polarization inside the spheres. Adding these polarizabilities to our ASA calculations, which already include charge transfer effects, therefore leads to double counting of charge transfer effects, which effectively makes the polarization inside the spheres appear more important than it is. Nevertheless, these polarizabilities provide an upper limit for the errors due to the ASA. We have performed calculations where we calculate the electric field acting on the nearest-neighbor ligand atoms due to the charges obtained in an ASA calculation. From the empirical polarizabilities we then obtain the induced dipoles. These give rise to an electric field which is included in the ASA calculation and in the calculations of the dipoles in a self-consistent way. The result of these calculations are shown in the column "Polarization." For Mn in CdTe we find a rather small effect and U is reduced by about 0.1 Ry. Since the empirical polarizabilities in this case probably give a substantial overestimate of the errors in the ASA, we believe that the ASA result is rather close to the correct value. The rather small effect for Mn in CdTe is due to the fact that the charge transfer screening is quite effective. Adding the empirical polarizability, although alone an efficient screening mechanism, therefore leads to a small further reduction of U. For Mn in ZnO we find a substantially larger effect, namely 0.3 Ry. This reduction makes the ASA result for Mn in ZnO much more questionable, as one might also have expected from the less efficient charge transfer screening. As mentioned above, the empirically polarizabilities should ideally describe both charge transfer between the spheres and polarization inside the spheres.[29] It is therefore not surprising that we find that a somewhat larger reduction of U from using the empirical polarizabilities alone than from using the charge transfer mechanism alone.

IV. CONCLUDING REMARKS

We have calculated the $3d$-$3d$ Coulomb interaction U for Mn in CdTe, CdS, and ZnO, with the emphasis on how the renormalization depends on the host. In particular we have been interested in how the increasing ionicity in the series CdTe, CdS, and ZnO influences the screening of U. An important mechanism for screening is the transfer for charge to the Mn atom when the number of Mn $3d$ electrons is changed. This transfer is favored if hopping integrals between the valence band and the Mn $4s$ and $4p$ levels are large and the energy separations between the valence band and the $4s$ and $4p$ levels are small. We find that the hopping integrals increase in the series CdTe, CdS, and ZnO, due to the decreasing atomic separations. This effect is, however, clearly outweighed by the increasing energy separation of the $4s$ and $4p$ levels to the valence band, related to the increasing ionicity. Thus we find that the charge transfer to the Mn atom reduces U by 0.6 Ry for Mn in CdTe and by 0.2 Ry for Mn in ZnO. We find that the change in the number of $3d$ electrons is screened to about 60–70 % in CdTe and to about 15–20 % in ZnO inside the Mn Wigner-Seitz sphere. This in contrast to metallic hosts, where the screening is normally assumed to be about 100%. Because of this assumption, U can be estimated from renormalized atom calculations for metallic systems,[10] while for nonmetallic systems we have to perform an impurity calculation.

Because of the incomplete screening of the change in the number of $3d$, electrons inside the Mn Wigner-Seitz sphere for these systems, there is also charge transfer to the nearest-neighbor ligand atoms. This has a small effect for Mn in CdTe, but for Mn in ZnO this screening gives a further reduction of U by about 0.3 Ry. Thus we find that charge transfer screening is important even for a very ionic system like Mn in ZnO. Our calculations assumes that the charge density is spherically symmetric inside each atomic sphere. To allow for polarization effects inside the spheres, we have introduced empirical polarizabilities in the calculations. These corrections should give a (possibly substantial) overestimate of the effects of nonspherical charge densities. We conclude that the ASA probably gives rather accurate results for Mn in CdTe because of the efficient charge transfer screening, while corrections to the ASA probably are more important for Mn in ZnO.

[*] Present address: Institute of Metal Physics, Sverdlovsk, Union of Soviet Socialist Republics.

[1] P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964); W. Kohn and L. J. Sham, Phys. Rev. **140**, A1133 (1965).

[2] See, e.g., O. Gunnarsson, O. K. Andersen, and A. Svane, in *Proceedings of the NATO Workshop on Interacting Electrons in Reduced Dimensions,* edited by D. Baerswyl and D. K. Campbell (Plenum, New York, 1989).

[3] O. Gunnarsson and K. Schönhammer, Phys. Rev. Lett. **50**, 604 (1983); Phys. Rev. B **28**, 4315 (1983).

[4] O. Gunnarsson and K. Schönhammer, in *Handbook on the Physics and Chemistry of Rare Earths,* edited by K. Gschneidner, L. Eyring, and S. Hüfner (North-Holland, Amsterdam, 1987), Vol. 10, p.103.

[5] R. Monnier, L. Degiorgi, and D. D. Koelling, Phys. Rev. Lett. **86**, 2744 (1986); L. Degiorigi, T. Greber, F. Hullinger, R. Monnier, L. Schlapbach, and B. T. Thole, Europhys. Lett. **4**, 755 (1987).

[6] O. Gunnarsson, D. D. Sarma, F. U. Hillebrecht, and K. Schönhammer, J. Appl. Phys. **63**, 3676 (1988).

[7] A. Kotani and Y. Toyozawa, J. Phys. Soc. Jpn. **35**, 1073 (1973); **37**, 912 (1974); **46**, 488 (1979).

[8] J. Zaanen, C. Westra, and G. A. Sawatzky, Phys. Rev. B **33**, 8060 (1986); G. van der Laan, J. Zaanen, G. A. Sawatzky, R. Karnatak, and J.-M. Esteva, *ibid.* **33**, 4253 (1986); G. A. Sawatzky and J. W. Allen, Phys. Rev. Lett. **55**, 418 (1985).

[9] A. Fujimori, F. Minami, and S. Sugano, Phys. Rev. B **29**, 5225 (1984).

[10] J. F. Herbst, R. E. Watson, and J. W. Wilkins, Phys. Rev. B **13**, 1439 (1976); **17**, 3089 (1978).

[11] O. Sakai, H. Takahashi, H. Takeshige, and T. Kasuya, Solid State Commun. **52**, 997 (1984).

[12] P. H. Dederichs, S. Blügel, R. Zeller, and H. Akai, Phys. Rev. Lett **53**, 2512 (1984).

[13] H. Ehrenreich, Science **235**, 1029 (1987), and references therein.

[14] J. M. Wills and B. R. Cooper, Phys. Rev. B **36**, 3809 (1987); N. Kioussis, B. R. Cooper, and J. M. Wills, J. Appl. Phys. **63**, 3683 (1988).

[15] O. Gunnarsson, O. K. Andersen, O. Jepsen, and J. Zaanen, in *Proceedings of the 10th Taniguchi Symposium on Core Level Spectroscopy in Condensed Systems,* edited by J. Kanamori and A. Kotani (Springer, Heidelberg, 1988), p. 82; Phys. Rev. B **39**, 1708 (1989).

[16] J. Zaanen, O. Jepsen, O. Gunnarsson, A. T. Paxton, O. K. Andersen, and A. Svane, Physica B+C **153-155C**, 1636 (1988).

[17] O. Gunnarsson, N. E. Christensen, and O. K. Andersen, J. Magn. Magn. Mater. **76&77**, 30 (1988).

[18] C. Herring, in *Magnetism,* edited by G. T. Rado and H. Suhl (Academic, New York, 1966).

[19] J. C. Slater, *Quantum Theory of Molecules and Solids* (McGraw-Hill, New York, 1974), Vol. 4; J. F. Janak, Phys. Rev. B **18**, 7165 (1978).

[20] The states k are the solutions of the single-particle Hamiltonian including the conduction and valence states of Mn in the host, but with the $4l$ orbital on Mn removed. The reason is that the hopping including this orbital will later be included in the solution of the model Hamiltonian. Let us consider the case when $4l$ refers to $4p$ and when the host is CdTe. Compared with the unperturbed host, the central Cd $3d$ and $4s$ orbitals have then been replaced by Mn $3d$ and $4s$ orbitals and the central Cd $4p$ orbital has been removed. Since the coupling between the Cd $4p$ orbital and the rest of the host is strong, the removal of this coupling leads to a bound state above the top of the valence band. This bound state is occupied and it has to be included in the valence states k. It contains an essential part of the coupling to the Mn $4p$ state. This type of effect is less important when we calculate the coupling of the Mn $3d$ orbital to the host, because in that case we have removed the coupling to the localized Cd $3d$ orbital.

[21] In the case of Mn in ZnO, there is a substantial change of $|V_{4p}|^2$ when the $3d$ occupancy is changed, which cannot be neglected for quantitiative estimates.

[22] O. K. Andersen and O. Jepsen, Phys. Rev. Lett. **53**, 2571 (1984); O. K. Andersen, O. Jepsen, and D. Glötzel, in *Highlights in Condensed Matter Theory,* edited by F. Bassani, F. Fumi, and M. P. Tosi (North-Holland, Amsterdam, 1985), p. 59; O. K. Andersen, Z. Pawlowska, and O. Jepsen, Phys. Rev. B **34**, 5253 (1986).

[23] L. Pauling, *The Chemical Bond* (Cornell University Press, Ithaca, 1967).

[24] O. Gunnarsson, O. Jepsen, and O. K. Andersen, Phys. Rev. B **27**, 7144 (1983).

[25] O. K. Andersen, Phys. Rev. B **12**, 3060 (1975).

[26] G. Baraff and M. Schlüter, Phys. Rev. B **30**, 3460 (1984).

[27] J. C. Slater, *Quantum Theory of Atomic Structures* (McGraw-Hill, New York, 1960), Vol. 1.

[28] We have used the values 27.5×10^{-25} cm^3 (O^{2-}), 86×10^{-25} cm^3 (S^{2-}), and 157×10^{-25} cm^3 (Te^{2-}); see H. Stuart, in *Molekular refraktion und elektrische Polarisierbarkeit von Atomen und Ionen,* Vol. 1 of *Landolt-Börnstein,* edited by A. Eucken (Springer, Berlin, 1950), p. 399.

[29] It is clear, however, that the empirical polarizations cannot properly describe the charge transfer to the Mn sphere, since the Mn polarizability does not even enter the calculation, as the symmetry of the problem means that there is no induced dipole on the Mn site.