PHYSICAL REVIEW B VOLUME 48, NUMBER 20 15 NOVEMBER 1993-II

Spin-dependent multiplet average energies for $3d^N$ impurities in tetrahedral semiconductors and a comparison with spin-polarized mean-field calculations

J. Dreyhsig and H.-E. Gumlich
Institut für Festkörperphysik, Technische Universität Berlin, Sekretariat PN 4-1, Hardenbergstrasse 36, D-10623 Berlin, Germany

J. W. Allen
Department of Physics and Astronomy, University of St. Andrews, St. Andrews, Fife, KY16 9SS Scotland, United Kingdom

(Received 19 March 1993)

We present calculated average multiplet energies for spin-dependent strong-field $e^m t_2^n$ configurations of d^N ions in T_d or O_h point symmetry in terms of the Griffith parameters $a,b,\ldots,j$. The calculations have analogies with the effective-crystal-field approach of Fazzio, Caldas, and Zunger for the spin-independent case [Phys. Rev. B **30**, 3430 (1984)]. By using empirically determined parameters from the observed multiplet splittings the total-energy separations of the spin-dependent configurations can be derived. The expressions for the average energies are compared with those from a mean-field spin-polarized model, similar to the way in which Slater compared spin-dependent average multiplet energies of the free ion with spin-polarized hyper-Hartree-Fock values [Phys. Rev. **165**, 655 (1968); **165**, 658 (1968)]. Hence the relation of the single-electron and total energies derived in the mean-field model to the strong-field multiplet average energies is found. The results are also compared with other models found in the literature. As an example we discuss ZnS:Co and the chemical trends in the exchange splittings of the $3d$ orbitals in ZnS doped with transition metals. We also show how a consistent spin-dependent modification of the crystal-field multiplet theory can be introduced. However, the large number of disposable parameters to be determined in a semiempirical approach is a limitation of the procedure.

I. INTRODUCTION

Transition-metal impurities in semiconductors have been the subject of manifold investigations, both experimental and theoretical. These impurities occur either as unwanted dopants in semiconductors, sometimes with deleterious effects, or as deliberately added dopants so use can be made of their special properties. Examples of the latter are ZnS:Mn in electroluminescent flat-panel displays, where the emission is due to an internal $3d$ transition, or InP:Fe, where a mid-band-gap charge state allows the material to be semi-insulating and hence usable as a substrate for electronic or optoelectronic devices. Effects caused by sp-d exchange, for example giant exciton spin splittings or large Faraday rotations observed in dilute magnetic semiconductors are likely to be the basis of applications in the medium-term future.[1]

A central property of the d electrons is that, in the solid, they retain much of their atomic character as far as internal excitations are concerned. The multiplet structure of the internal excitations is clearly linked to the localization of the wave function. On the other hand, charge-state transitions require the long-range parts of the wave function, extending outside the atomic d-shell radius, to be taken into account. There have been many studies aimed at obtaining information on the d wave function: these have been extensively reviewed by Zunger.[2] The ground-state properties are understood best as some of the experimental [e.g., electron paramagnetic resonance (EPR)] and theoretical (e.g., density-functional) methods are mainly restricted to the description of the ground state. It is worth noting that as far as the excited states are concerned usually only a few transitions within the multiplet manifold are known from experiment, these being mainly the spin-allowed ones. This should be borne in mind when any theoretical model for excited states is compared with experimental data.

There is as yet no theory which can claim to describe all the experimental observations in detail. Many approaches use an effective single-electron Hamiltonian. It is then assumed that the resultant eigenenergies have some relation to observable energies: in fact it is often assumed, without justification, that Koopmans' theorem can be extended to these schemes. A rather different approach is that of density-functional theory. Again the total Hamiltonian is split into single-particle Hamiltonians, but no physical significance is attributed to the individual eigenenergies: only the calculated total energy is to be compared with actual total energies. Strictly it only gives ground-state properties, which in principle are given exactly. The single-particle approaches do not describe multiplet excitations. Usually multiplet theory is employed in a semiempirical manner in various modifications. Several proposals have been made to link single-particle calculations with multiplet theory.[3-10] These have in common the concept that a mean-field single-particle approach already includes an average effect of the multiplet structure. This is not always exactly correct. It was shown that the free-electron $\rho^{1/3}$ exchange approximation as employed in the MS$X\alpha$ (where

0163-1829/93/48(20)/15002(14)/$06.00

MS denotes multiple scattering) method[11] or in the local-density approximation of the Hohenberg-Kohn-Sham theory[12] is only consistent with calculating the energy of single-determinantal wave functions.[13–16] Multiplet splittings are often described by sums of determinantal wave functions, and one has to take this into account when the common average multiplet effect is defined.

The wave functions of the single-particle methods are molecular orbitals, and it is their interaction which has to be considered in calculating multiplet structure. A different approach is that of configuration interaction (CI), which Hubbard, Rimmer, and Hopgood[17] extended to the case of ions in crystals. Though the method was overlooked for many years, it has been used recently by a number of authors for transition-metal compounds[18–20] and doped semiconductors.[10,21,22] It is not yet clear whether this approach is quantitatively superior to conventional crystal-field theory and its modifications, at least as far as internal transitions are concerned. On the other hand, the theory has been successful in describing photoionization phenomena.[10,18,21]

A possible way to include electron exchange and correlation more explicitly and to maintain the computational simplicity of single-particle calculations is to use spin-polarized wave functions.[23–25] One still has the problem that the single-particle eigenenergies are not the same quantities as the differences in total energies which are obtained by experiment, so some method has to be found to link them. Less attention has been paid to this aspect.[9,26–28] It is the aim of the present paper to provide this link for spin-polarized strong-field $e^m t_2^n$ configurations of crystal-field split d^N configurations $(m+n=N)$. This is of special significance as spin-polarized calculations are carried out in order to improve the accuracy of first-principles approaches to $3d$ centers in semiconductors. Their interpretation compared with the complete multiplet manifold is nontrivial, however. In spin-unpolarized calculations the strong-field $e^m t_2^n$ configurations can always be taken to represent an extreme limit of the physical situation: when the Coulomb intracenter interaction can be neglected compared with the crystal-field strength, the form of the wave functions approaches that of pure $e^m t_2^n$ configurations. For spin-polarized calculations there is no such limiting case for isolated, strongly correlated systems such as the d electrons of $3d$ impurities in semiconductors or in any other solid. The possibility of spin polarization arises from the existence of multiplets caused by the Coulomb interaction: in the limit of no Coulomb interaction there is no spin polarization. Spin-polarized calculations can only be interpreted in terms of average energies in this case. This paper shows how these averages can be defined from crystal-field multiplet perturbation theory in analogy to the results of Fazzio, Caldas, and Zunger[6] for the spin-independent case. Next we discuss the relation of these averages to results of a simple spin-polarized model Hamiltonian and to other spin-polarized calculations. Hence it is possible to decide to what extent spin-polarized calculations include average multiplet effects.

To pursue our aim we follow Slater's work on the comparison of spin-polarized calculations of free ions with their multiplet manifold.[29,30] As an example of the procedure we consider a free ion with a d^2 configuration (Fig. 1). The average energy $\hat{E}(N)$, with $N=2$, is defined as the average of all multiplet energies $E({}^{2S+1}L)$ arising from the configuration. This is extended to the spin-dependent case by defining average energies $\hat{E}(S)$, i.e., averaging singlets and triplets separately. Whenever we refer to averages with respect to the total spin of shells or subshells, we shall use the terminology "spin-dependent" average energies, in contrast to the term "spin polarization," which we use in context with single-electron Hamiltonians. For clarity purposes we introduce the nomenclature $\hat{E}(N\uparrow,N\downarrow)\equiv\hat{E}(S)$, with $N\uparrow+N\downarrow=N$, and the total spin quantum number is derived by $S=\frac{1}{2}(N\uparrow-N\downarrow)$. $N\uparrow$ and $N\downarrow$ refer to the occupation numbers of relative spin. They must not be mixed up with the occupation numbers with respect to a quantization axis. Whereas the wave functions with the quantum numbers $M_S=0$ and 1 of a triplet, i.e., $S=1$, contain different contributions from single-electron orbitals with either spin orientation, the total wave function still has the total spin quantum number $S=1$. In a triplet one has two parallel spins, no matter how the actual quantization axis is defined. The Hamiltonian commutes with the squared total spin operator but not with the single-electron-spin operators. The differences of the energies $\hat{E}(N\uparrow,N\downarrow)$, here the difference of the average singlet energy $\hat{E}(1,1)$ and the average triplet energy $\hat{E}(2,0)$, represent average spin-flip energies which can now serve to interpret the results of spin-polarized single-electron calculations. Intuitively one tends to assume that the spin-flip energies which are derived from averages of multiplet energies will be represented by total-energy differences of single-electron calculations or even differences of single-electron energies. The comparison of the results of the two methods is by no means obvious, however, and in the present paper we shall look at this for the case of $3d$ impurities in semiconductors.

For the spin-dependent configurations we use a similar

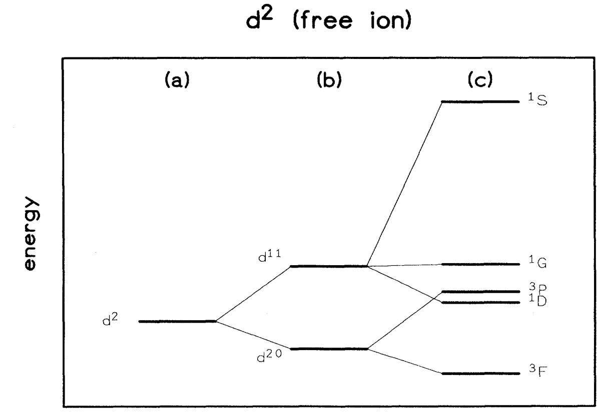

FIG. 1. Average energy levels of a free ion d^2 configuration: (a) spin-independent average $\hat{E}(N)$; (b) spin-dependent averages $\hat{E}(N\uparrow,N\downarrow)$, i.e., for d^{20} and d^{11} defined as averages of triplets and singlets, respectively; (c) multiplet levels $E({}^{2S+1}L)$.

notation to that for spin-polarized calculations: $d^{N\uparrow N\downarrow}$, in our example d^{20} and d^{11}. Slater has given analytical expressions for $\hat{E}(N)$ and $\hat{E}(N\uparrow,N\downarrow)$.[29] He also showed how these energies are related to single-electron parameters such as the exchange splitting $\Delta^{\uparrow\downarrow}$ between the single-electron energies of spin-up and spin-down electrons (Fig. 2) as derived from the spin-polarized hyper-Hartree-Fock method.[30]

Next, if the $3d^N$ ion occupies a site of T_d or O_h point symmetry in a crystal, the d orbitals split into orbitals of $e_{(g)}$ and $t_{2(g)}$ symmetries. [We shall drop the index (g) appropriate to O_h symmetry since the correspondence with T_d symmetry concerns only the sign of the crystal-field splitting.] Spin-polarized single-electron calculations now yield energy levels specified by the crystal-field splitting parameter Δ and the exchange splittings $\Delta_e^{\uparrow\downarrow}$ and $\Delta_{t2}^{\uparrow\downarrow}$ (Fig. 2). If a d^2 impurity system like ZnS:Ti is considered one may ask again how the multiplet energies $E(^{2S+1}\Gamma)$ as shown in Fig. 3(c) can be averaged for strong-field configurations. Fazzio, Caldas, and Zunger showed how the average energies $\hat{E}(m,n)$ for a spin-independent $e^m t_2^n$ [Fig. 3(a)] configuration can be calculated.[6] We generalize this to the spin-dependent case.

In Sec. II of this paper we show how the corresponding average energies $\hat{E}(S_e,S_{t2},S)$, with $S_e=\frac{1}{2}(m\uparrow-m\downarrow)$, and $S_{t2}=\frac{1}{2}(n\uparrow-n\downarrow)$, $m\uparrow+m\downarrow=m$, and $n\uparrow+n\downarrow=n$, are derived. The more general parameter scheme of Griffith is used to describe electron-electron interactions.[31] Since for almost all configurations the spins S_e and S_{t2} are either parallel or antiparallel to each other, we can use the nomenclature $\hat{E}(m\uparrow,m\downarrow;n\uparrow,n\downarrow)\equiv\hat{E}(S_e,S_{t2},S)$. Thus the averaging is over states of particular spin, just as in the free ion case for d^2 the averaging was over singlets and triplets separately. The corresponding configurations are denoted as in spin-polarized single-electron approaches: $e^{m\uparrow m\downarrow}t_2^{n\uparrow n\downarrow}$. Numerical results for ZnS:Ti are shown in Fig. 3(b). In Sec. III we set up a model similar to Slater's spin-polarized hyper-Hartree-Fock model in order to obtain relations between the average energies $\hat{E}(m\uparrow,m\downarrow;n\uparrow,n\downarrow)$, the total energies of the single-particle Hamiltonian and the single-particle quantities as illustrated in Fig. 2. A comparison with other calculations is given in Sec. IV, together with some examples for ZnS doped with transition-metal impurities. Finally we report in Sec. V on the possibility of introducing a spin-polarized modification of crystal-field theory which is consistent with multiplet perturbation theory. This work has been motivated by our observation that, in describing internal excitation energies of $3d^N$ impurities, and compared with the simple Tanabe-Sugano approach[32] where e and t_2 orbitals have the same radial form, attempts to include hybridization in some manner[4,6,33–38] do not give any improvement for low-spin levels. This may have its reason in the approaches themselves or in the nature of spin polarization. We compare our procedure to a scheme introduced by Biernacki,[39] and discuss its merits in view of its applicability.

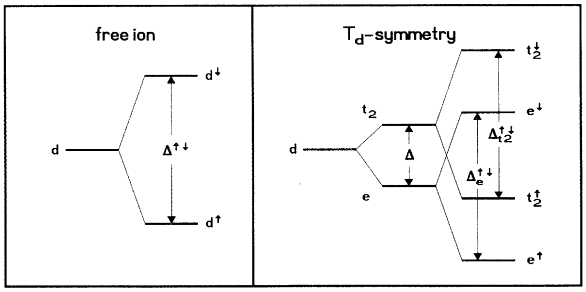

FIG. 2. Single-electron picture of d electrons in the free ion case and for a site of tetrahedral symmetry. The introduced parameters are the exchange splittings $\Delta^{\uparrow\downarrow}$, $\Delta_e^{\uparrow\downarrow}$, and $\Delta_{t2}^{\uparrow\downarrow}$, and the crystal-field splitting Δ.

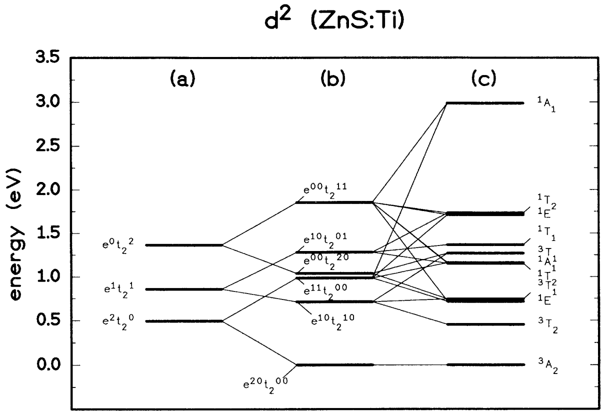

FIG. 3. Average energy levels of a Ti(d^2) impurity in ZnS (parameters from Ref. 57): (a) spin-independent averages $\hat{E}(m,n)$ of strong-field $e^m t_2^n$ configurations; (b) spin-dependent averages $\hat{E}(m\uparrow,m\downarrow;n\uparrow,n\downarrow)$ of strong-field $e^{m\uparrow m\downarrow}t_2^{n\uparrow n\downarrow}$ configurations (also see text for definition of notation); (c) multiplet levels $E(^{2S+1}\Gamma)$.

II. SPIN-DEPENDENT AVERAGES OF *d*-MULTIPLET ENERGIES

Slater pointed out that significant exchange splittings occur in single-electron approaches even if the spatial orbitals for the two spin directions of an electron are taken to be the same.[30] We also make this approximation using the same spatial orbital for both spins. In fact there is at present no straightforward method available for performing perturbation calculations of multiplet structure using spin-polarized orbitals with different spatial wave functions. An attempt was made by Biernacki[39] but we feel it is inadequate, as discussed below. Dropping this approximation would require the introduction of further parameters, which would not improve our basic insight into the problem.

We restrict ourselves to the case of two open shells: the doubly degenerate e and the triply degenerate t_2 orbitals (space degeneracy). It is common to denote these as ε, Θ (e) and η, ξ, ζ (t_2). To maintain generality the calculation is performed in terms of the Griffith parameters $a, b, c, \ldots, i, j$,[31] for which only a constraint exists on the angular part of the orbitals which are restricted to the spherical harmonics $Y_2^m(\Theta,\vartheta)$. The same wave functions are used for all configurations (i.e., there is no electronic relaxation with change of state). The ten independent Griffith parameters are given in Table I in terms of the Coulomb matrix elements. When the e and t_2 radial functions are the same, the Griffith parameters reduce to linear combinations of the Racah parameters A, B, and C.[31,32] To allow for a certain degree of difference in the e and t_2 radial wave functions several authors[4,6,33,34,37,38] took up a proposal by Koide and Pryce[35] to scale the different repulsion integrals by a factor ε^4 for those involving only e orbitals, a factor τ^4 for those involving only t_2 orbitals, and to make the approximation of scaling the mixed integrals by the factors shown in Table I. The integrals are then expressed in terms of ε, τ, and the Racah parameters A, B, and C. (Equal radial wave functions corresponds with $\varepsilon=\tau=1$). Richardson *et al.* introduced a different set of independent parameters[5] which are also listed in Table I.

The diagonal elements of the Coulomb interaction in the strong-field scheme in terms of Griffith parameters were derived by Richardson *et al.*,[5] Bird *et al.*,[40] and Sharma, DeViccaro, and Sundermann[36] (the latter two references also gave the nondiagonal matrix elements). Because of the diagonal sum rule, only the diagonal matrix elements are needed for the determination of the average energies of multiplets in terms of strong-field configurations. The average energy $\hat{E}(m\uparrow,m\downarrow;n\uparrow,n\downarrow)$ of an $e^{m\uparrow m\downarrow}t_2^{n\uparrow n\downarrow}$ configuration averaged over the different multiplets ${}^{2S+1}\Gamma$ is thus given by

$$\hat{E}(m\uparrow,m\downarrow;n\uparrow,n\downarrow)$$

$$=\frac{\sum\limits_{{}^{2S+1}\Gamma}(2S+1)g_\Gamma\langle e^{m\uparrow m\downarrow}t_2^{n\uparrow n\downarrow}\|e^{m\uparrow m\downarrow}t_2^{n\uparrow n\downarrow}\rangle}{\sum\limits_{{}^{2S+1}\Gamma}(2S+1)g_\Gamma}\ , \tag{1}$$

where Γ is the irreducible representation of the point group [in our calculations: T_d (for O_h the sign of the crystal-field splitting is reversed)], and g_Γ is the orbital degeneracy. The sum runs over the different multiplets ${}^{2S+1}\Gamma$. To determine the occupation numbers $m\uparrow$, $m\downarrow$, $n\uparrow$, $n\downarrow$ it is useful to set up correlation diagrams of the kind shown in Fig. 3 for a d^2 configuration. Because of the nature of spin coupling it is straightforward in most cases to find the parental $e^{m\uparrow m\downarrow}t_2^{n\uparrow n\downarrow}$ configuration. The strong-field starting wave functions for a multiplet calculation are suitable combinations of coupled e^m and t_2^n wave functions:

$$|{}^{2S+1}\Gamma,M_S,\gamma\rangle=\sum_{\substack{M_S^e,M_S^{t2}\\ \gamma_e,\gamma_{t2}}}|e^m({}^{2S_e+1}\Gamma_e,M_S^e,\gamma_e)\,,t_2^n({}^{2S_{t2}+1}\Gamma_{t2},M_S^{t2},\gamma_{t2})\rangle\langle S_eM_S^eS_{t2}M_S^{t2}|SM_s\rangle\langle\Gamma_e\gamma_e\Gamma_{t2}\gamma_{t2}|\Gamma\gamma\rangle\ , \tag{2}$$

where ${}^{2S_e+1}\Gamma_e$ and ${}^{2S_{t2}+1}\Gamma_{t2}$ are the multiplets of e^m and t_2^n to be coupled to give ${}^{2S+1}\Gamma$. (M_S^e, M_S^{t2}, M_S, γ_e, γ_{t2}, and γ label the spin and orbital components of a multiplet level.) The spin coupling and hence the corresponding occupation numbers $m\uparrow$, $m\downarrow$, $n\uparrow$, and $n\downarrow$ may be deduced from S_e, S_{t2}, and S.

However, there are two special cases which have to be treated separately because the spin coupling of the inequivalent e and t_2 spins is not necessarily parallel and antiparallel. For one case in d^4 and another in d^5 it is thus not possible to maintain the similarity to spin-polarized strong-field configurations of single-electron approaches as defined in Sec. I, since this implies parallel or antiparallel coupling. These are [suppressing the sum in Eq. (2)]:

$$\begin{aligned} d^4\!:&\quad |{}^3T_2\rangle=|e^2({}^3A_2),t_2^2({}^3T_2)\rangle\ ,\\ d^5\!:&\quad |{}^4A_1\rangle=|e^2({}^3A_2),t_2^3({}^4A_2)\rangle\ . \end{aligned} \tag{3}$$

These cases are listed separately in Table II, where the resultant average energies $\hat{E}(m\uparrow,m\downarrow;n\uparrow,n\downarrow)$ are given in a reduced notation. As in the spin-independent case for $\hat{E}(m,n)$ (Ref. 6) the expressions for

TABLE I. Independent Coulomb repulsion parameters.

Griffith	Integral	Richardson	Koide/Pryce approximation
a	$\langle\xi\xi\|\xi\xi\rangle$	$3\bar{K}(tt)-2K(t\zeta,t\zeta)$	$\tau^4(A+4B+3C)$
b	$\langle\xi\eta\|\xi\eta\rangle$	$\frac{3}{2}[\bar{J}(tt)-\bar{K}(tt)]+K(t\zeta,t\zeta)$	$\tau^4(A-2B+C)$
c	$\langle\Theta\xi\|\varepsilon\xi\rangle$	$\frac{\sqrt{3}}{2}[\bar{J}(et)-J(e\Theta,t\zeta)]$	$\varepsilon^2\tau^2 2\sqrt{3}B$
d	$\langle\varepsilon\xi\|\varepsilon\xi\rangle$	$\frac{1}{2}[\bar{J}(et)+J(e\Theta,t\zeta)]$	$\varepsilon^2\tau^2(A-2B+C)$
e	$\langle\Theta\Theta\|\Theta\Theta\rangle$	$\bar{K}(ee)+\frac{1}{2}\bar{J}(ee)$	$\varepsilon^4(A+4B+3C)$
f	$\langle\Theta\Theta\|\varepsilon\varepsilon\rangle$	$\bar{K}(ee)-\frac{1}{2}\bar{J}(ee)$	$\varepsilon^4(4B+C)$
g	$\langle\Theta\Theta\|\eta\eta\rangle$	$\frac{1}{2}[3\bar{K}(et)-K(e\Theta,t\zeta)]$	$\varepsilon^2\tau^2(B+C)$
h	$\langle\Theta\varepsilon\|\eta\eta\rangle$	$\frac{\sqrt{3}}{2}[K(e\Theta,t\zeta)-\bar{K}(et)]$	$\varepsilon^2\tau^2\sqrt{3}B$
i	$\langle\Theta\eta\|\xi\zeta\rangle$	i	$\varepsilon\tau^3\sqrt{3}B$
j	$\langle\xi\xi\|\eta\eta\rangle$	$K(t\zeta,t\zeta)$	$\tau^4(3B+C)$

TABLE II. Average strong-field multiplet energies $\hat{E}(m\uparrow,m\downarrow;n\uparrow,n\downarrow)$ in terms of Griffith parameters a, b, $c,\ldots,h$, j. The energy differences $\Delta\hat{E}$ are defined relative to the spin-dependent $e^{m\uparrow m\downarrow}t_2^{n\uparrow n\downarrow}$ configuration having the highest total spin quantum number S for a given spin-independent $e^m t_2^n$ configuration, $m=m\uparrow+m\downarrow$, $n=n\uparrow+n\downarrow$. $\Delta\hat{E}=x(a-b+3j)+y[g+(1/\sqrt{3})h]+zf$. $S_e=\frac{1}{2}(m\uparrow-m\downarrow)$, $S_{t2}=\frac{1}{2}(n\uparrow-n\downarrow)$. For one case of d^4 and one case of d^5 there is no single-electron analog, i.e., the occupation numbers $m\uparrow,m\downarrow,n\uparrow,n\downarrow$ cannot be given as S_e and S_{t2} couple neither parallel nor antiparallel to one another.

							$\Delta\hat{E}$	
d^N	$e^{m\uparrow m\downarrow}t_2^{n\uparrow n\downarrow}$	S	S_e	S_{t2}	$\hat{E}(m\uparrow,m\downarrow;n\uparrow,n\downarrow)$	x	y	z
d^2	$e^{20}t_2^{00}$	1	1		$e-3f$			
	$e^{11}t_2^{00}$	0	0					$\frac{8}{3}$
	$e^{10}t_2^{10}$	1	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{\sqrt{3}}c+d-g-\frac{1}{\sqrt{3}}h+\Delta$			
	$e^{10}t_2^{01}$	0	$\frac{1}{2}$	$\frac{1}{2}$			2	
	$e^{00}t_2^{20}$	1		1	$b-j+2\Delta$			
	$e^{00}t_2^{11}$	0		0		$\frac{1}{2}$		
d^3	$e^{21}t_2^{00}$	$\frac{1}{2}$		$\frac{1}{2}$	$3e-5f$			
	$e^{20}t_2^{10}$	$\frac{3}{2}$	1	$\frac{1}{2}$	$\frac{2}{\sqrt{3}}c+2d+e-3f-2g-\frac{2}{\sqrt{3}}h+\Delta$			
	$e^{20}t_2^{01}$	$\frac{1}{2}$	1	$\frac{1}{2}$			3	
	$e^{11}t_2^{10}$	$\frac{1}{2}$	0	$\frac{1}{2}$			1	$\frac{8}{3}$
	$e^{10}t_2^{20}$	$\frac{3}{2}$	$\frac{1}{2}$	1	$b+\frac{2}{\sqrt{3}}c+2d-2g-\frac{2}{\sqrt{3}}h-j+2\Delta$			
	$e^{10}t_2^{11}$	$\frac{1}{2}$	$\frac{1}{2}$	0		$\frac{1}{2}$	1	
	$e^{01}t_2^{20}$	$\frac{1}{2}$	$\frac{1}{2}$	1			3	
	$e^{00}t_2^{30}$	$\frac{3}{2}$		$\frac{3}{2}$	$3b-3j+3\Delta$			
	$e^{00}t_2^{21}$	$\frac{1}{2}$		$\frac{1}{2}$		$\frac{3}{4}$		
d^4	$e^{22}t_2^{00}$	0	0		$6e-10f$			
	$e^{21}t_2^{10}$	1	$\frac{1}{2}$	$\frac{1}{2}$	$\sqrt{3}c+3d+3e-5f-2g-\frac{2}{\sqrt{3}}h+\Delta$			
	$e^{21}t_2^{01}$	0	$\frac{1}{2}$	$\frac{1}{2}$			2	
	$e^{20}t_2^{20}$	2	1	1	$b+\frac{4}{\sqrt{3}}c+4d+e-3f-4g-\frac{4}{\sqrt{3}}h-j+2\Delta$			
	$e^{11}t_2^{20}$	1	0	1			2	$\frac{8}{3}$
	$e^{20}t_2^{11}$	1	1	0		$\frac{1}{2}$	2	
	- - -	1	1	1			4	
	$e^{11}t_2^{11}$	0	0	0		$\frac{1}{2}$	2	$\frac{8}{3}$
	$e^{20}t_2^{02}$	0	1	1			6	
	$e^{10}t_2^{30}$	2	$\frac{1}{2}$	$\frac{3}{2}$	$b+\sqrt{3}c+3d-3g-\sqrt{3}h-3j+3\Delta$			
	$e^{01}t_2^{30}$	1	$\frac{1}{2}$	$\frac{3}{2}$			4	
	$e^{10}t_2^{21}$	1	$\frac{1}{2}$	$\frac{1}{2}$		$\frac{3}{4}$	1	
	$e^{10}t_2^{12}$	0	$\frac{1}{2}$	$\frac{1}{2}$		$\frac{3}{4}$	3	
	$e^{00}t_2^{31}$	1		1	$a+5b-3j+4\Delta$			
	$e^{00}t_2^{22}$	0		0		$\frac{1}{2}$		
d^5	$e^{22}t_2^{10}$	$\frac{1}{2}$	0	$\frac{1}{2}$	$\frac{4}{\sqrt{3}}c+4d+6e-10f-2g-\frac{2}{\sqrt{3}}h$			
	$e^{21}t_2^{20}$	$\frac{3}{2}$	$\frac{1}{2}$	1	$b+2\sqrt{3}c+6d+3e-5f-4g-\frac{4}{\sqrt{3}}h-j+\Delta$			
	$e^{12}t_2^{20}$	$\frac{1}{2}$	$\frac{1}{2}$	1			3	
	$e^{21}t_2^{11}$	$\frac{1}{2}$	$\frac{1}{2}$	0		$\frac{1}{2}$	1	
	$e^{20}t_2^{30}$	$\frac{5}{2}$	1	$\frac{3}{2}$	$3b+2\sqrt{3}c+6d+e-3f-6g-2\sqrt{3}h-3j+2\Delta$			
	$e^{11}t_2^{30}$	$\frac{3}{2}$	0	$\frac{3}{2}$			3	$\frac{8}{3}$
	$e^{20}t_2^{21}$	$\frac{3}{2}$	1	$\frac{1}{2}$		$\frac{3}{4}$	2	

TABLE II. (*Continued*).

							$\Delta\hat{E}$	
d^N	$e^{m\uparrow m\downarrow}t_2^{n\uparrow n\downarrow}$	S	S_e	S_{t2}	$\hat{E}(m\uparrow,m\downarrow;n\uparrow,n\downarrow)$	x	y	z
	- - -	$\frac{3}{2}$	1	$\frac{3}{2}$			5	
	$e^{11}t_2^{21}$	$\frac{1}{2}$	0	$\frac{1}{2}$		$\frac{3}{4}$	3	$\frac{8}{3}$
	$e^{02}t_2^{30}$	$\frac{1}{2}$	1	$\frac{3}{2}$			8	
	$e^{20}t_2^{12}$	$\frac{1}{2}$	1	$\frac{1}{2}$		$\frac{3}{4}$	5	
	$e^{10}t_2^{31}$	$\frac{3}{2}$	$\frac{1}{2}$	1	$a+5b+\frac{4}{\sqrt{3}}c+4d-3g-\sqrt{3}h-3j+3\Delta$			
	$e^{01}t_2^{31}$	$\frac{1}{2}$	$\frac{1}{2}$	1			3	
	$e^{10}t_2^{22}$	$\frac{1}{2}$	$\frac{1}{2}$	0		$\frac{1}{2}$	1	
	$e^{00}t_2^{32}$	$\frac{1}{2}$		$\frac{1}{2}$	$2a+8b-4j+4\Delta$			

$\hat{E}(m\uparrow,m\downarrow;n\uparrow,n\downarrow)$ turn out to have a systematic form. In Table II, for simplicity, only the average energy for the maximum total spin for each $e^m t_2^n$ configuration is given explicitly. The energies are linear combinations of nine Griffith parameters, since the parameter i only appears in off-diagonal elements. For the other configurations which result from the maximum spin ones by spin-flip transitions in the single-electron picture only the differences $\Delta\hat{E}$ from the maximum spin states are given in Table II. These differences are expressed in terms of three parameters x, y, and z as follows:

$$\Delta\hat{E}=x(a-b+3j)+y\left[g+\frac{1}{\sqrt{3}}h\right]+zf\ . \qquad (4)$$

The reason for this simplification is obvious when the corresponding occupation numbers $m\uparrow$, $m\downarrow$, $n\uparrow$, and $n\downarrow$ are examined. Two of the terms on the right-hand side of Eq. (4) cover the influence of a spin flip in one subshell on itself. A flip of an e spin changes $\hat{E}(m\uparrow,m\downarrow;n\uparrow n\downarrow)$ by $\frac{8}{3}f$. For t_2 electrons two cases have to be distinguished: a flip starting from $e^{m\uparrow m\downarrow}t_2^{20}$ (or $e^{m\uparrow m\downarrow}t_2^{31}$) gives a change of energy $\frac{1}{2}(a-b+3j)$ while a flip from $e^{m\uparrow m\downarrow}t_2^{30}$ gives a change $\frac{3}{4}(a-b+3j)$. The term $g+(1/\sqrt{3})h$ arises from the influence of a spin flip in one subshell on the electrons in the other subshell, the factor y being dependent on the set (S_e,S_{t2},S) before and after the transition. For example, a flip of an e electron giving a transition from $(\frac{1}{2},1,\frac{3}{2})$ to $(\frac{1}{2},1,\frac{1}{2})$, or that of a t_2 electron giving a transition from $(1,\frac{1}{2},\frac{3}{2})$ to $(1,\frac{1}{2},\frac{1}{2})$, gives a change of $\hat{E}(m\uparrow,m\downarrow;n\uparrow,n\downarrow)$ of $3[g+(1/\sqrt{3})h]$.

The values for d^{10-N} configurations are easily obtained from Table II by reversing the sign of the crystal-field splitting and adding a shift which depends only on $m=m\uparrow+m\downarrow$ and $n=n\uparrow+n\downarrow$:

$$\begin{aligned}\langle e^{4-m}t_2^{6-n}\|e^{4-m}t_2^{6-n}\rangle-\langle e^m t_2^n\|e^m t_2^n\rangle\\ =(3-n)a+(12-3n)b+(24-4n-6m)\left[\frac{1}{\sqrt{3}}c+d\right]\\ +(6-3m)e+(5m-10)f\\ +(3m+2n-12)\left[g+\frac{1}{\sqrt{3}}h\right]-(6-2n)j\ . \qquad (5)\end{aligned}$$

As a check on our results, by going to the spin-independent case we reproduce the results of Fazzio, Caldas, and Zunger.[6,41] Additionally, we evaluated the average energy for states of a total spin S for a given number of electrons $N=m+n$, thereby reproducing Slater's result for the free ion:[29]

$$\begin{aligned}\hat{E}(S-1)-\hat{E}(S)=\hat{E}(N\uparrow-1,N\downarrow+1)-\hat{E}(N\uparrow,N\downarrow)\\ =\tfrac{7}{6}S(5B+2C)\ . \qquad (6)\end{aligned}$$

The crystal-field parameter Δ appearing in Table II is the difference in energy of single-particle t_2 and e states. In the many-electron system the difference in total energy of $e^m t_2^n$ and $e^{m-1}t_2^{n+1}$ depends on the particular configuration. Elementary treatments ignore this dependence and use the value Δ for all the differences in energy. The approximation may be too crude. De Leo, Watkins, and Fowler calculated the total-energy separations of $e^m t_2^n$ and $e^{m-1}t_2^{n+1}$ configurations of interstitial $3d$ impurities in silicon within the MS$X\alpha$ mean-field approach,[3] clearly demonstrating inequivalent spacings between adjacent strong-field configurations. Fazzio, Caldas, and Zunger[6] approached the problem using multiplet theory. They took weighted averages over the multiplets to find an average energy $\hat{E}(m,n)$ for the $e^m t_2^n$ states and then defined effective crystal-field parameters as differences in these averaged energies, and they even allowed for some configurational dependence of the interaction parameters. Their calculations were for the spin-independent case. With the expressions given in Table II one could do the same for the spin-dependent case. A practical difficulty arises with the number of available parameters. Fazzio, Caldas, and Zunger obtained their effective-crystal-field splittings by fitting to experimental energy spectra but already had too many disposable parameters and had to replace various values by a single averaged one. The spin-dependent calculation gives even more disposable parameters when parameters dependent on the values of $m\uparrow$, $m\downarrow$, $n\uparrow$, and $n\downarrow$ (or better S, S_e, and S_{t2}) are introduced. One would like to calculate the multiplet energies and hence the effective-crystal-field values by using single-electron wave functions obtained by mean-field theory to evaluate the matrix elements, but this has hardly been done.[8] Therefore,

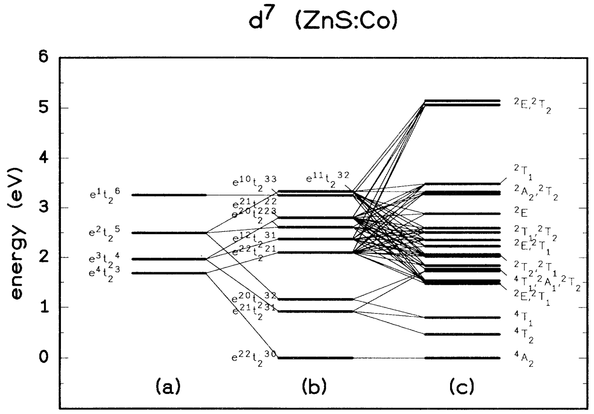

FIG. 4. Average energy levels of a Co(d^7) impurity in ZnS (parameters from Ref. 42): (a) spin-independent averages $\hat{E}(m,n)$ of strong-field $e^m t_2^n$ configurations; (b) spin-dependent averages $\hat{E}(m\uparrow,m\downarrow;n\uparrow,n\downarrow)$ of strong-field $e^{m\uparrow m\downarrow}t_2^{n\uparrow n\downarrow}$ configurations (see also text for definition of notation); (c) multiplet levels $E(^{2S+1}\Gamma)$.

we do not consider configurational dependent parameters in this part of the present work (the treatment of this problem is postponed to Sec. V). Here we want to derive average spin-flip energies from multiplet theory so that we can compare this with single-electron approaches. For numerical examples we therefore take parameters obtained by fitting crystal-field spectra to a Tanabe-Sugano scheme, e.g., the e and t_2 radial functions are the same and the angular functions are $Y_2^m(\Theta,\vartheta)$, so the Griffith parameters reduce to the Racah parameters. Our procedure could always be applied to the more general case of different radial e and t_2 orbitals if these are known from mean-field theory.

As an illustration, Fig. 4 is an energy-level scheme for ZnS:Co d^7, similar to Fig. 3 for ZnS:Ti d^2. Weakliem measured the optical-absorption spectrum and fitted the peak positions to a Tanabe-Sugano scheme, thereby obtaining values for the empirical parameters B, C, and Δ.[42] The multiplet energies in Fig. 4(c) were calculated using these values, and because Weakliem obtained a good fit these energies are close to the experimental ones. Using the same values of B, C, and Δ the average energies $\hat{E}(m\uparrow,m\downarrow;n\uparrow,n\downarrow)$ and $\hat{E}(m,n)$ were calculated and are shown in Figs. 4(b) and 4(a), respectively. It is clear from Figs. 3 and 4 that the spin-dependent average energies are only a rough approximation of the actual energies, although they are much better than the spin-independent average energies. It should be noted, however, that for the following high-spin ground states $\hat{E}(m\uparrow,m\downarrow;n\uparrow,n\downarrow)$ gives the correct energy: $^3A_2$ of d^2 (e^{20},t_2^{00}), $^5T_2$ of $d^4(e^{20}t_2^{20})$, $^6A_1$ of d^5 $(e^{20}t_2^{30})$, ^5E of d^6 $(e^{21}t_2^{30})$, and $^4A_2$ of d^7 $(e^{22}t_2^{30})$. For the spin-independent values $\hat{E}(m,n)$ there is no case for which this holds (not considering the trivial cases of d^1 and d^9 configurations).

III. COMPARISON WITH SINGLE-ELECTRON MEAN-FIELD ENERGIES

In order to compare our results for the weighted average multiplet energies with energies obtained from mean-field calculations, we follow Slater's hyper-Hartree-Fock model of the free ion.[30,43] First we consider the spin-unpolarized case: Taking into account explicitly only the electron-electron interaction among the e and t_2 electrons and summarizing all other contributions in single-electron energies ε_{oe} and ε_{ot}, the total energy of a transition-metal impurity may be written as combinations of average Coulomb and exchange integrals for the relevant shells:

$$\begin{aligned}
E_{\text{av}}(m,n) &\equiv \langle \Psi | H | \Psi \rangle \\
&= \varepsilon_{oe} m + \varepsilon_{ot} n + \tfrac{1}{2} m(m-1)(J_{ee}-K_{ee})_{\text{av}} \\
&\quad + \tfrac{1}{2} n(n-1)(J_{tt}-K_{tt})_{\text{av}} + mn(J_{et}-K_{et})_{\text{av}} , \\
(J_{ee}-K_{ee})_{\text{av}} &= e - \tfrac{5}{3} f , \qquad (7)\\
(J_{tt}-K_{tt})_{\text{av}} &= \tfrac{1}{5}(a+4b-2j) , \\
(J_{et}-K_{et})_{\text{av}} &= \frac{1}{\sqrt{3}} c + d - \tfrac{1}{2}\left[g + \frac{1}{\sqrt{3}} h \right] ,
\end{aligned}$$

where we have deduced the average integrals in terms of Griffith parameters from all possible combinations of wave functions. Since Eq. (7) is equivalent to evaluating the average energy of all single determinantal wave functions arising from an $e^m t_2^n$ configuration, $E_{\text{av}}(m,n)$ is equivalent to Fazzio, Caldas, and Zunger's average multiplet energies,[6] i.e., $E_{\text{av}}(m,n)=\hat{E}(m,n)$.

For the spin-polarized case one requires spin-polarized parameters. Hence Eq. (7) now reads

$$\begin{aligned}
E_{\text{av}}(m\uparrow,m\downarrow;n\uparrow,n\downarrow) \equiv{}& \varepsilon_{oe}^{\uparrow} m\uparrow + \varepsilon_{oe}^{\downarrow} m\downarrow + \varepsilon_{ot}^{\uparrow} n\uparrow + \varepsilon_{ot}^{\downarrow} n\downarrow + m\uparrow m\downarrow \hat{J}_{ee}^{\uparrow\downarrow} + \tfrac{1}{2} m\uparrow(m\uparrow-1)(\hat{J}_{ee}^{\uparrow\uparrow}-\hat{K}_{ee}^{\uparrow\uparrow}) \\
&+ \tfrac{1}{2} m\downarrow(m\downarrow-1)(\hat{J}_{ee}^{\downarrow\downarrow}-\hat{K}_{ee}^{\downarrow\downarrow}) + n\uparrow n\downarrow \hat{J}_{tt}^{\uparrow\downarrow} + \tfrac{1}{2} n\uparrow(n\uparrow-1)(\hat{J}_{tt}^{\uparrow\uparrow}-\hat{K}_{tt}^{\uparrow\uparrow\uparrow}) \\
&+ \tfrac{1}{2} n\downarrow(n\downarrow-1)(\hat{J}_{tt}^{\downarrow\downarrow}-\hat{K}_{tt}^{\downarrow\downarrow}) + m\uparrow n\downarrow \hat{J}_{et}^{\uparrow\downarrow} + m\downarrow n\uparrow \hat{J}_{et}^{\downarrow\uparrow} + m\uparrow n\uparrow(\hat{J}_{et}^{\uparrow\uparrow}-\hat{K}_{et}^{\uparrow\uparrow}) \\
&+ m\downarrow n\downarrow(\hat{J}_{et}^{\downarrow\downarrow}-\hat{K}_{et}^{\downarrow\downarrow}) . \qquad (8)
\end{aligned}$$

As in Sec. II, the approximation is made that the space orbitals for spin-up and spin-down are the same. (In fact it is only necessary to require that the corresponding integrals are the same.) Then one is left with eight average Coulomb and exchange integrals and two single-electron energies:

$$
\begin{aligned}
&\hat{J}^{\parallel}_{ee}\equiv\hat{J}^{\uparrow\uparrow}_{ee}=\hat{J}^{\downarrow\downarrow}_{ee}\ ,\quad \hat{K}_{ee}\equiv\hat{K}^{\uparrow\uparrow}_{ee}=\hat{K}^{\downarrow\downarrow}_{ee},\hat{J}^{\uparrow\downarrow}_{ee}\ ,\\
&\hat{J}^{\parallel}_{tt}\equiv\hat{J}^{\uparrow\uparrow}_{tt}=\hat{J}^{\downarrow\downarrow}_{tt}\ ,\quad \hat{K}_{tt}\equiv\hat{K}^{\uparrow\uparrow}_{tt}=\hat{K}^{\downarrow\downarrow}_{tt},\hat{J}^{\uparrow\downarrow}_{tt}\ ,\\
&\hat{J}^{\parallel}_{et}\equiv\hat{J}^{\uparrow\uparrow}_{et}=\hat{J}^{\downarrow\downarrow}_{et}=\hat{J}^{\uparrow\downarrow}_{et}=\hat{J}^{\downarrow\uparrow}_{et}\ ,\quad \hat{K}_{et}\equiv\hat{K}^{\uparrow\uparrow}_{et},\hat{K}^{\downarrow\downarrow}_{et}\\
&\varepsilon_{oe}\equiv\varepsilon^{\uparrow}_{oe}=\varepsilon^{\downarrow}_{oe}\ ,\quad \varepsilon_{ot}\equiv\varepsilon^{\uparrow}_{ot}=\varepsilon^{\downarrow}_{ot}\ .
\end{aligned}
\tag{9}
$$

We emphasize at this stage that from the point of view of strong-field configurations one should use different average integrals for e and t_2 orbitals simply because the shells do not have spherical symmetry. (By an extension to Unsöld's theorem a fully occupied e or t_2 shell has A_1 symmetry, i.e., the total symmetry of the site rather than spherical symmetry.) This has to be taken into account if different calculations are compared. Instead of the set of parameters in (9), spherical averages are usually taken.[9,26,44–46] In particular, spherical averages are assumed in MS$X\alpha$ calculations where a muffin-tin potential is employed.

In Table III we give the eight parameters of (9) expressed in terms of the nine Griffith parameters a, b, $c, \ldots, h$, j. They are easily determined by evaluating the average values of all possible orbital combinations for a given integral. Similar parameter sets were used by other authors which are equivalent to our scheme. The relations of the parameter set in (9) to the independent $e-t_2$ parameters of Richardson *et al.*[5] and to the Kanimori parameters[9,44,47] are also given in Table III.

It is useful to recall the different definitions of $\hat{E}(m\uparrow,m\downarrow;n\uparrow,n\downarrow)$ and $E_{\text{av}}(m\uparrow,m\downarrow;n\uparrow,n\downarrow)$, ie Eqs. (1) and (8). Whereas the first energy is obtained by averaging multiplet energies of particular total spin quantum numbers S, S_e, and S_{t2}, the latter represents a model of taking the electrons as belonging to four different subshells where all electrons in one shell share the same interaction with each other, and where all electrons in one subshell interact with the electrons in another subshell by a constant interaction independent of the actual occupation numbers. The interaction integrals are obtained by averaging the interaction of all possible combinations of wave functions which are possible with respect to the considered subshells. These two averaging procedures are not equivalent, as will be discussed below.

TABLE III. Average integrals for d-d Coulomb and exchange integrals.

Integral	Griffith	Richardson	Kanimori
$\hat{J}^{\parallel}_{ee}$	$e-2f$	$\frac{3}{2}\bar{J}(ee)-\bar{K}(ee)$	U'_{ee}
$\hat{K}_{ee}$	f	$\bar{K}(ee)-\frac{1}{2}\bar{J}(ee)$	J_{ee}
$\hat{J}^{\uparrow\downarrow}_{ee}$	$e-f$	$\bar{J}(ee)$	$\frac{1}{2}(U_{ee}+U'_{ee})$
$\hat{J}^{\parallel}_{tt}$	b	$\frac{3}{2}[\bar{J}(tt)-\bar{K}(tt)]+K(t\zeta,t\zeta)$	U'_{tt}
$\hat{K}_{tt}$	j	$K(t\zeta,t\zeta)$	J_{tt}
$\hat{J}^{\uparrow\downarrow}_{tt}$	$\frac{1}{3}(a+2b)$	$\bar{J}(tt)$	$\frac{1}{3}(U_{tt}+2U'_{tt})$
$\hat{J}^{\parallel}_{et}=\hat{J}^{\uparrow\downarrow}_{et}$	$\frac{1}{\sqrt{3}}c+d$	$\bar{J}(et)$	U'_{et}
$\hat{K}_{et}$	$g+\frac{1}{\sqrt{3}}h$	$\bar{K}(et)$	J_{et}

Single-electron energies are defined from Eq. (8) by taking the occupation numbers as continuous variables and taking partial derivatives with respect to these variables, as in the $X\alpha$ method (see also Ref. 48):

$$
\begin{aligned}
\varepsilon^{\uparrow}_{e}=\frac{\partial E_{\text{av}}}{\partial m\uparrow}&=\varepsilon_{oe}+m\downarrow\hat{J}^{\uparrow\downarrow}_{ee}+(m\uparrow-\tfrac{1}{2})(\hat{J}^{\parallel}_{ee}-\hat{K}_{ee})\\
&\quad+n\downarrow\hat{J}^{\uparrow\downarrow}_{et}+n\uparrow(\hat{J}^{\parallel}_{et}-\hat{K}_{et})\ ,
\end{aligned}
\tag{10a}
$$

$$
\begin{aligned}
\varepsilon^{\downarrow}_{e}=\frac{\partial E_{\text{av}}}{\partial m\downarrow}&=\varepsilon_{oe}+m\uparrow\hat{J}^{\uparrow\downarrow}_{ee}+(m\downarrow-\tfrac{1}{2})(\hat{J}^{\parallel}_{ee}-\hat{K}_{ee})\\
&\quad+n\uparrow\hat{J}^{\uparrow\downarrow}_{et}+n\downarrow(\hat{J}^{\parallel}_{et}-\hat{K}_{et})\ ,
\end{aligned}
\tag{10b}
$$

$$
\begin{aligned}
\varepsilon^{\uparrow}_{t}=\frac{\partial E_{\text{av}}}{\partial n\uparrow}&=\varepsilon_{ot}+n\downarrow\hat{J}^{\uparrow\downarrow}_{tt}+(n\uparrow-\tfrac{1}{2})(\hat{J}^{\parallel}_{tt}-\hat{K}_{tt})\\
&\quad+m\downarrow\hat{J}^{\uparrow\downarrow}_{et}+m\uparrow(\hat{J}^{\parallel}_{et}-\hat{K}_{et})\ ,
\end{aligned}
\tag{10c}
$$

$$
\begin{aligned}
\varepsilon^{\downarrow}_{t}=\frac{\partial E_{\text{av}}}{\partial n\downarrow}&=\varepsilon_{ot}+n\uparrow\hat{J}^{\uparrow\downarrow}_{tt}+(n\downarrow-\tfrac{1}{2})(\hat{J}^{\parallel}_{tt}-\hat{K}_{tt})\\
&\quad+m\uparrow\hat{J}^{\uparrow\downarrow}_{et}+m\downarrow(\hat{J}^{\parallel}_{et}-\hat{K}_{et})\ .
\end{aligned}
\tag{10d}
$$

In Slater's original work on the spin-polarized hyper-Hartree-Fock approach, the single-electron equations are derived by the variational principle.[30] When being solved self-consistently, the calculated single-electron orbitals enable one to calculate the average interaction integrals and thus the total energy of the system. Here the situation is different: we already assume that the interaction integrals are known from experiment. In this case we are only interested in the way the total energies and the single-electron energies are mathematically connected. As the reader may readily verify from Ref. 30, the partial derivatives in Eqs. (10a)–(10d) simply give this connection. From Eqs. (10a)–(10d) the exchange splittings between spin-up and spin-down states for e and t_2 electrons are ($\Delta^{\uparrow\downarrow}_{t}\equiv\Delta^{\uparrow\downarrow}_{t2}$)

$$
\begin{aligned}
\Delta^{\uparrow\downarrow}_{e}&=\varepsilon^{\downarrow}_{e}-\varepsilon^{\uparrow}_{e}\\
&=(m\uparrow-m\downarrow)(\hat{J}^{\uparrow\downarrow}_{ee}-\hat{J}^{\parallel}_{ee}+\hat{K}_{ee})+(n\uparrow-n\downarrow)\hat{K}_{et}\\
&=(m\uparrow-m\downarrow)2f+(n\uparrow-n\downarrow)\left[g+\frac{1}{\sqrt{3}}h\right]\ ,
\end{aligned}
\tag{11a}
$$

$$
\begin{aligned}
\Delta^{\uparrow\downarrow}_{t}&=\varepsilon^{\downarrow}_{t}-\varepsilon^{\uparrow}_{t}\\
&=(n\uparrow-n\downarrow)(\hat{J}^{\uparrow\downarrow}_{tt}-\hat{J}^{\parallel}_{tt}+\hat{K}_{tt})+(m\uparrow-m\downarrow)\hat{K}_{et}\\
&=(n\uparrow-n\downarrow)\tfrac{1}{3}(a-b+3j)+(m\uparrow-m\downarrow)\left[g+\frac{1}{\sqrt{3}}h\right]\ .
\end{aligned}
\tag{11b}
$$

Slater showed that for free d ions one has[30]

$$
\tfrac{5}{6}\Delta^{\uparrow\downarrow}=\hat{E}(S-1)-\hat{E}(S)=\hat{E}(N\uparrow-1,N\downarrow+1)-\hat{E}(N\uparrow,N\downarrow)\ ,
\tag{12}
$$

where now $N\uparrow+N\downarrow=N$. If one combines Eqs. (11a) and (11b) with the results given in Table II, it is possible to obtain similar relations, though the situation is more complicated as here one deals with two open shells. We may divide the splittings of Eqs. (11a) and (11b) into two parts:

$$\Delta_e^{\uparrow\downarrow} = {}^{e}\Delta_e^{\uparrow\downarrow} + {}^{t}\Delta_e^{\uparrow\downarrow} \ , \tag{13a}$$

$$\Delta_t^{\uparrow\downarrow} = {}^{t}\Delta_t^{\uparrow\downarrow} + {}^{e}\Delta_t^{\uparrow\downarrow} \ . \tag{13b}$$

The first term on each right-hand-side of Eqs. (13a) and (13b) corresponds with interactions within a subshell, the second term represents the influence of one subshell on the other subshell. Similarly the average energies $\hat{E}(m\uparrow,m\downarrow;n\uparrow,n\downarrow)$ in Table II are linear combinations of a term in x which involves only interactions within the t_2 shell and which we call $\hat{E}^{t}(m\uparrow,m\downarrow;n\uparrow,n\downarrow)$, a term in z involving only interactions within the e shell which we call $\hat{E}^{e}(m\uparrow,m\downarrow;n\uparrow,n\downarrow)$ and a term in y which involves interactions between subshells. Those quantities involving only one subshell fulfill conditions similar to that for the free atom in Eq. (12), namely

$$\tfrac{2}{3}{}^{e}\Delta_e^{\uparrow\downarrow} = \hat{E}^{e}(m\uparrow-1,m\downarrow+1;n\uparrow,n\downarrow) - \hat{E}^{e}(m\uparrow,m\downarrow;n\uparrow,n\downarrow) \ , \tag{14a}$$

$$\tfrac{3}{4}{}^{t}\Delta_t^{\uparrow\downarrow} = \hat{E}^{t}(m\uparrow,m\downarrow;n\uparrow-1,n\downarrow+1) - \hat{E}^{t}(m\uparrow,m\downarrow;n\uparrow,n\downarrow) \ . \tag{14b}$$

It is not possible to give similar expressions for those quantities representing the influence of a spin flip in one subshell on the other subshell. The terms ${}^{t}\Delta_e^{\uparrow\downarrow}$ and ${}^{e}\Delta_t^{\uparrow\downarrow}$ are clearly linked to the term $y[g+(1/\sqrt{3})h]$ in Table II, but too many cases have to be distinguished so that we cannot give simple expressions as in Eqs. (14a) and (14b). Nevertheless we conclude that the exchange splittings of Eqs. (11a) and (11b), obtained from the single-electron energies defined in Eqs. (10a)–(10d), resemble average energy differences corresponding with a spin flip in analogy with Slater's result for the free ion.

Taking single-electron energies as partial derivatives of the total energy with respect to the occupation number, as in Eqs. (10a)–(10d) is a useful approximation. A better expression for the spin-flip energies is given by differences of total energies. Since we neglect relaxation, these differences are exactly equal to the energies found by Slater's transition state method. The spin-reversal energies $\Delta E_{\text{av}}^{\uparrow\downarrow,e,t}(m\uparrow,m\downarrow;n\uparrow,n\downarrow)$ are then

$$\begin{aligned}\Delta E_{\text{av}}^{\uparrow\downarrow e}(m\uparrow,m\downarrow;n\uparrow,n\downarrow) &\equiv E_{\text{av}}(m\uparrow-1,m\downarrow+1;n\uparrow,n\downarrow) - E_{\text{av}}(m\uparrow,m\downarrow;n\uparrow,n\downarrow)\\ &= (m\uparrow-m\downarrow-1)(\hat{J}_{ee}^{\uparrow\downarrow}-\hat{J}_{ee}^{\parallel}+\hat{K}_{ee}) + (n\uparrow-n\downarrow)\hat{K}_{et}\\ &= (m\uparrow-m\downarrow-1)2f + (n\uparrow-n\downarrow)\left[g+\frac{1}{\sqrt{3}}h\right] \ ,\end{aligned} \tag{15a}$$

$$\begin{aligned}\Delta E_{\text{av}}^{\uparrow\downarrow,t}(m\uparrow,m\downarrow;n\uparrow,n\downarrow) &\equiv E_{\text{av}}(m\uparrow,m\downarrow;n\uparrow-1,n\downarrow+1) - E_{\text{av}}(m\uparrow,m\downarrow;n\uparrow,n\downarrow)\\ &= (n\uparrow-n\downarrow-1)(\hat{J}_{tt}^{\uparrow\downarrow}-\hat{J}_{tt}^{\parallel}+\hat{K}_{tt}) + (m\uparrow-m\downarrow)\hat{K}_{et}\\ &= (n\uparrow-n\downarrow-1)\tfrac{1}{3}(a-b+3j) + (m\uparrow-m\downarrow)\left[g+\frac{1}{\sqrt{3}}h\right] \ .\end{aligned} \tag{15b}$$

Equations (15a) and (15b) differ from Eqs. (11a) and (11b) in the factors involving occupation numbers. This is because the differentiation with respect to the occupation number is performed in Eqs. (10a)–(10d) at the occupation numbers $m\uparrow$, $m\downarrow$, $n\uparrow$, and $n\downarrow$, whereas in effect it is performed in Eqs. (15a) and (15b) at the half-integral values of Slater's transition state.

Once the multiplet parameters were deduced from experiment, the results of this and Sec. II enable us to determine an energy-level diagram for the total energies of spin-polarized strong-field configurations according to Eq. (8) or the values of $\hat{E}(m\uparrow,m\downarrow;n\uparrow,n\downarrow)$ as given in Table II. In Fig. 5 we show an example for Co in ZnS, again making the approximation of equal radial functions of e and t_2 orbitals and using Weakliem's values[42] of the Racah parameters B, C, and the crystal-field splitting Δ. Figure 5(a) gives $\hat{E}(m\uparrow,m\downarrow;n\uparrow,n\downarrow)$, thus the level scheme is the same as in Fig. 4(b). The levels in Fig. 5(b) were calculated according to Eq. (8). The following points should be noted: for the high-spin configuration of each $e^{m\uparrow m\downarrow}t_2^{n\uparrow n\downarrow}$ configuration the two approaches yield exactly the same values. This can be shown to hold for

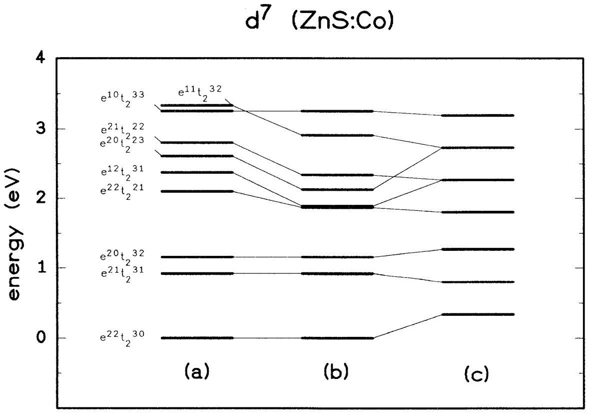

FIG. 5. Total energies of strong-field spin-polarized/spin-dependent $e^{m\uparrow m\downarrow}t_2^{n\uparrow n\downarrow}$ configurations of a Co(d^7) impurity in ZnS (parameters from Ref. 42): (a) averages $\hat{E}(m\uparrow,m\downarrow;n\uparrow,n\downarrow)$ of multiplet levels [i.e., Fig. 4(b)]; (b) $E_{\text{av}}(m\uparrow,m\downarrow;n\uparrow,n\downarrow)$ as calculated from the single-electron Hamiltonian Eq. (8); and (c) $E_{\text{av}}^{\text{isotrop}}(m\uparrow,m\downarrow;n\uparrow,n\downarrow)$, where the Coulomb and exchange integrals are taken to be the same for e and t_2 electrons.

all d^N configurations. The low-spin configurations are shifted to lower energies for Fig. 5(b) compared with Fig. 5(a). The reason for this property of $E_{\mathrm{av}}(m\uparrow,m\downarrow;n\uparrow,n\downarrow)$ is found in the way we defined the parameter set (9): Just as Eq. (7) gives the average energy for an $e^m t_2^n$ configuration, Eq. (8) yields the average energy for all single-determinantal wave functions with the same spin z components M_S^e and M_S^{t2}. Hence Eq. (8) is identical to (1) in the case of the high-spin configurations. Once one spin is flipped, Eq. (8) averages more than one expression of Eq. (1), and the two equations are no longer equivalent. In other words, $E_{\mathrm{av}}(m\uparrow,m\downarrow;n\uparrow,n\downarrow)$ corresponds to an average over single-determinantal wave functions, whereas $\hat{E}(m\uparrow,m\downarrow;n\uparrow,n\downarrow)$ gives a weighted mean of multideterminantal wave functions, which is not necessarily the same. To summarize, when the same orbitals are taken to calculate total energies according to Eqs. (1) and (8), the spin-flip energies as defined from the point of view of single-electron mean-field theory do not strictly correspond to spin flips between states with quantum numbers S_e and S_e-1, or S_{t2} and $S_{t2}-1$, or between different couplings of S_e and S_{t2}. They underestimate the latter energies when they are interpreted in that way.

If the Coulomb and exchange integrals in Eq. (8) are taken to be isotropic, e.g., only three parameters $\hat{J}_{dd}^{\parallel}$, $\hat{K}_{dd}$, and $\hat{J}_{dd}^{\uparrow\downarrow}$ are used as in Refs. 26 and 27, and thus the Coulomb and exchange integrals among the e-e, t_2-t_2, and e-t_2 orbitals are taken to be the same, a level scheme $E_{\mathrm{av}}^{\mathrm{isotrop}}(m\uparrow,m\downarrow;n\uparrow,n\downarrow)$ like that shown in Fig. 5(c) is obtained. Compared with $E_{\mathrm{av}}(m\uparrow,m\downarrow;n\uparrow,n\downarrow)$, the levels of $E_{\mathrm{av}}^{\mathrm{isotrop}}(m\uparrow,m\downarrow;n\uparrow,n\downarrow)$ deviate considerably from $\hat{E}(m\uparrow,m\downarrow;n\uparrow,n\downarrow)$. Additionally, some configurations are taken to be degenerate (e.g., $e^{12}t_2^{31}$ is degenerate with $e^{21}t_2^{22}$, and $e^{20}t_2^{23}$ with $e^{11}t_2^{32}$). We conclude that when a comparison with the experimental average energies of ${}^{2S+1}\Gamma$ levels is sought, the values of $E_{\mathrm{av}}(m\uparrow,m\downarrow;n\uparrow,n\downarrow)$ are a much better choice.

It should be noted that for both $E_{\mathrm{av}}(m\uparrow,m\downarrow;n\uparrow,n\downarrow)$ and $\hat{E}(m\uparrow,m\downarrow;n\uparrow,n\downarrow)$ the free ion case will not be a limiting case for $\Delta\rightarrow 0$. This is due to our averaging procedure, which distinguishes between two shells of electrons rather than taking only one shell as in the atomic limit. Hence the differences of total energies between strong-field configurations do not show a ladder of equally spaced values with spacing equal to Δ, but there are extra contributions to the spacings which arise from the different average repulsion between e electrons, t_2 electrons, and e and t_2 electrons. These contributions to $E_{\mathrm{av}}(m\uparrow,n\downarrow;n\uparrow,n\downarrow)$ and $\hat{E}(m\uparrow,m\downarrow;n\uparrow,n\downarrow)$, or even to $E_{\mathrm{av}}(m,n)=\hat{E}(m,n)$, do not vanish when $\Delta\rightarrow 0$. On the other hand, the average repulsion integrals for $E_{\mathrm{av}}^{\mathrm{isotrop}}(m\uparrow,m\downarrow;n\uparrow,n\downarrow)$ are calculated for the free ion case, depending on the quantum numbers $N\uparrow=m\uparrow+n\uparrow$, $N\downarrow=m\downarrow+n\downarrow$ only. Hence a Δ-spaced ladder is now observed for all configurations with the same set $N\uparrow$, $N\downarrow$ [Fig. 5(c)], thus also explaining the above-mentioned degeneracies. The free ion case is now a limit for $\Delta\rightarrow 0$. However, $E_{\mathrm{av}}^{\mathrm{isotrop}}(m\uparrow,m\downarrow;n\uparrow,n\downarrow)$ should better be compared with $\hat{E}(N\uparrow,N\downarrow)$ than with strong-field averages of multiplet energies. Moreover, the averaging procedure for $E_{\mathrm{av}}^{\mathrm{isotrop}}(m\uparrow,m\downarrow;n\uparrow,n\downarrow)$ is inconsistent: For the Coulomb and exchange integrals all electrons of either spin are taken to be equivalent, whereas for the crystal-field interaction this is not assumed. The same argument holds for the spin-unpolarized case.

IV. COMPARISON WITH OTHER APPROACHES

In Secs. II and III we have shown how averages of strong-field multiplet energies are derived, and how the energy levels of an effective spin-polarized Hamiltonian [i.e., Eq. (8)] are related to these average multiplet energies. Taking experimentally deduced values for the intracenter and crystal-field interaction parameters we may now compare the level scheme as derived from the results of Sec. III [i.e., from the Hamiltonian Eq. (8)] to other spin-polarized single-electron calculations. Thus it is possible to link these calculated single-electron parameters to experimental results. In performing this comparison, however, one has to be cautious. In our approach the parameters describing the internal transitions are supposed to give the level structure for a large range of photon energies, assuming a fixed set of basis wave functions for all configurations. On the other hand, there are mean-field cluster and density-functional calculations. The latter should be least comparable to our calculations by definition: this method is thought to give results only for the ground state, and the physical significance of the Kohn-Sham orbitals is always a point of discussion. Yet both methods have been applied almost without exception within the local-density approximation, e.g., the results are consistent with a description of the system with single-determinantal wave functions,[13–15] similar to our model Hamiltonian introduced in Sec. III.

For the free ion case Slater found some correspondence between hyper-Hartree-Fock calculations (which contain average multiplet effects) and $X\alpha$ calculations (which employ a mean-field Hamiltonian).[23,30,48] The extension of the $X\alpha$ method to ions in a solid is found by means of the MS$X\alpha$ method.[11,23] For transition-metal-doped semiconductors, spin-polarized results by this method were obtained by Hemstreet and Dimmock for GaAs:Cr,[4] by Dal Pino, Fazzio, and Leite for GaAs:Mn,[49] by Fazzio and Leite for GaAs:M (M=Fe, Co, Ni, Cu),[50] and by DeLeo, Watkins, and Fowler for $3d$ impurities in Si.[3] However, the muffin-tin approximation used in these calculations gives rise to a problem: from Eqs. (10a)–(10d) it is obvious that our model deals with an anisotropic Hamiltonian, whereas the muffin-tin approximation employs a spherically averaged potential in the atomic sphere where most of the d wave-function is localized. Calculations according to the so-called discrete variational $X\alpha$ (DV$X\alpha$) method[26] are more suitable as the muffin-tin constraint of the potential is dropped. Unfortunately most of these calculations are carried out in the so-called SCC (self-consistent charge) approximation,[51] where each orbital is spherically averaged around its central atom again. Thus a comparison is difficult. However, for the more ionic compound semiconductor ZnS, only results obtained by this method exist. ZnS is more suitable for any comparison as covalency does not prevail (i.e., the d character of the orbitals is thought to be dominant) and crystal fields are of moderate strength. Hence we shall take the results of Freidman *et al.* for Fe, Co, and Ni in ZnS (Ref. 27) to discuss the model described in Sec. III. Since energy-level diagrams like Fig. 5 are not available for these calculations, we compare ground-state properties such as the exchange splittings $\Delta_e^{\uparrow\downarrow}$ and $\Delta_t^{\uparrow\downarrow}$.

In Fig. 6 the results of Ref. 27 and our values derived by Eqs. (11a) and (11b) for ZnS are displayed. We either used the parameters of a Tanabe-Sugano approach as derived by several authors [Fig. 6(b)] or employed the parameters of O'Neill to consider any differential hybridization of *e* and t_2 orbitals[38] [Fig. 6(c)]. For comparison the free ion parameters for *B* and *C* were also used [Fig. 6(a)]. In all cases the occupation numbers were chosen to give a high-spin ground state. It is obvious from these figures that the free ion values for $\Delta_e^{\uparrow\downarrow}$ and $\Delta_t^{\uparrow\downarrow}$ [Fig. 6(a)] are reduced in the solid since the orbitals are thought to be expanded. Furthermore, the DV$X\alpha$ results [Fig. 6(d)] are comparable in magnitude to our estimates. For the actual values one notices the following behavior. There are still maximum values for the exchange splitting in the middle of the series. However, one now has to fill two shells according to Hund's rule, which gives rise to some typical features: for the lighter atoms we observe the exchange splitting to be larger for the *e* than for the t_2 orbitals. This is reasonable as the *e* shell is filled first. Later these properties are reversed as the *e* shell is full and there is only a polarization due to a partially filled t_2 shell. The same is observed in the case which allows for the expansion of t_2 orbitals compared with the *e* orbitals [Fig. 6(c)]. For the DV$X\alpha$ method, where only results for the heavier elements exist, we do not recognize this trend: here we still have $\Delta_e^{\uparrow\downarrow} > \Delta_t^{\uparrow\downarrow}$. As explained above this is surprising: the overlap among the *e* and t_2 orbitals is expected to be smaller than among the orbitals of the subshells themselves, thus the polarization should be larger for the t_2 shell once the *e* shell is full. We attribute this difference to the fact that the DVXα calculations used a spherically averaged potential. This is supported by the results of Adachi *et al.* for perovskite-type compounds K*Me*F_3 (*Me*=Cr, Mn, Fe, Co, Ni, Cu), where almost equal exchange splittings were found for *e* and t_2 orbitals.[26]

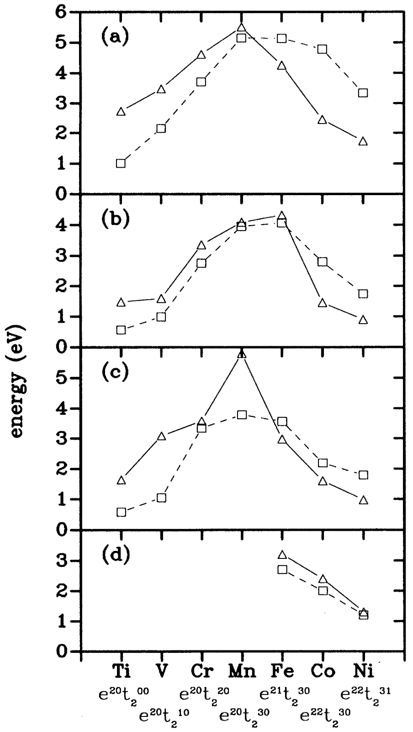

FIG. 6. Single-electron exchange splittings $\Delta_e^{\uparrow\downarrow}(\triangle)$ and $\Delta_t^{\uparrow\downarrow}(\square)$ for the high-spin ground-state configurations (indicated below the element labels) of 3*d* impurities in ZnS as calculated from Eqs. (11a) and (11b) [except (d)]: (a) free ion case (parameters from Ref. 31); (b) Tanabe-Sugano approach [parameters from Refs. 57 (Ti), 58 (V), 59 (Cr), 60 (Mn), 61 (Fe), and 42 (Co, Ni)]; (c) O'Neill-Allen approach (Ref. 38); and (d) DV$X\alpha$ results (Ref. 27).

As far as density-functional approaches are concerned, it is worth noting that Oshiyama, Hamada, and Katayama-Yoshida calculated an exchange splitting of $\Delta_e^{\uparrow\downarrow}=3.2$ eV for the d^4 ($e^{20}t_2^{20}$) ground state of Cr in ZnS,[52] a value very similar to our results of Fig. 6(b) (3.4 eV) and Fig. 6(c) (3.6 eV), respectively.

As one proceeds to more covalent compounds we expect our results to be less comparable to mean-field calculations because covalency becomes more important. Conversely, since we presented our model semiempirically, we can estimate from experiment what order of magnitude the (intracenter) exchange splittings should have to be consistent with experiment. Taking 3*d* impurities in GaAs as an example, very low exchange splittings of the order of some 0.2 eV were calculated by the MS$X\alpha$ method[4,49,50] (though determined for the "3+" charge state), one order of magnitude less than in Fig. 6. We compare this to a reduction of the Racah parameters. Since in most cases not many transitions are observed for 3*d* transition-metal-doped GaAs to determine these parameters accurately, we restrict our discussion to the "2+" charge state of Co in GaAs (transitions due to neutral Co have not yet been observed). The ratio of the Racah parameter *B* in the two host semiconductors ZnS and GaAs in $B_{\mathrm{GaAs}}/B_{\mathrm{ZnS}}=0.62$, the ratio for C being similar,[42,53] which does not suggest a change of the exchange splitting by one order of magnitude. We conclude that in the MS$X\alpha$ results covalency was overestimated since the intracenter exchange interaction was underestimated.

Even more diverging results are expected for Si doped with transition-metal impurities. Apart from DeLeo, Watkins, and Fowler's MS$X\alpha$ calculations, spin-polarized results were obtained by density-functional methods by Katayama-Yoshida and Zunger for the interstitial,[54] by Zunger and Lindefelt for the substitutional,[55] and by Beeler, Anderson, and Scheffler for both types of centers.[56] Unfortunately, no internal transitions have yet been observed for 3*d* impurities in Si. Hence a comparison is not possible for these materials.

V. SPIN-MODIFIED MULTIPLET APPROACHES

Contemporary multiplet theory is based on basis sets of single-electron spin orbitals which have equal spatial parts for spin orbitals having opposite spin. To account for the expectation that minority-spin electrons should have a more extended orbital than majority-spin electrons, since the former are repelled by the Coulomb repulsion to outer spheres, it is therefore straightforward to look for a way this constraint may be relaxed. One could object that in modifying the radial functions of e and t_2 orbitals due to the crystal field one does not include any occupational dependence of the orbitals. But here the situation is entirely different: whereas the spin is directly dependent on the filling of a shell under consideration, the differential expansion of e and t_2 orbitals is a result of the influence of the ligands. In other words, we want to consider the intracenter correlation in some way, and the correlation between the impurity and the ligand electrons is expected to be much smaller.

Biernacki proposed the introduction of different Slater-like single-electron orbitals not only for the radial parts of e and t_2 orbitals, but also for different spin orientation.[39] Apart from the problem that the single-electron energies for spin-up and -down orbitals change and new approximations and/or parameters have to be used, we note that care is also needed in considering the consequences for the two-electron integrals. In Biernacki's approach the matrix elements are modified similarly to the Koide and Pryce formalism, dependent on the starting wave functions. However, this approach no longer provides for the degeneracy of the matrix elements on the M_S values of the wave functions. As an example, let us take wave functions within one shell only: Among others the e^2 configuration gives rise to the following multiplet wave functions:

$$\Psi_1(e^2,{}^1A_1)=\frac{1}{\sqrt{2}}(|\Theta\uparrow\Theta\downarrow\rangle+|\varepsilon\uparrow\varepsilon\downarrow\rangle)\ ,$$

$$\Psi_2(e^2,{}^3A_2,M_S=1)=|\varepsilon\uparrow\Theta\uparrow\rangle\ ,$$

$$\Psi_3(e^2,{}^3A_2,M_S=0)=\frac{1}{\sqrt{2}}(|\Theta\uparrow\varepsilon\downarrow\rangle+|\Theta\downarrow\varepsilon\uparrow\rangle)\ .$$

Ψ_2 and Ψ_3 should be degenerate, which they are in usual multiplet theory. However, if the matrix elements are thought to be spin polarized as treated in Ref. 39 one obtains, apart from the desired modification for $\langle\Psi_1\|\Psi_1\rangle$ and $\langle\Psi_2\|\Psi_2\rangle$, that $\langle\Psi_2\|\Psi_2\rangle\neq\langle\Psi_3\|\Psi_3\rangle$.

It is not the aim of this paper to treat the problem in its most general case. However, we outline here the important steps that have to be considered. First it is essential to realize that spin-polarized spatial orbitals are not required for all multiplet levels. In the example described above, the degeneracy is restored by considering not the value of m_s for the different orbitals, but of S_e of the total wave function. It is unreasonable to take the same single-electron orbitals for Ψ_1 and Ψ_3, as the latter wave function still represents $S_e=1$ as Ψ_2 does. Hence there is no spin polarization to be considered for Ψ_3, one has to take the same radial wave functions for $|\varepsilon\uparrow\rangle$ and $|\varepsilon\downarrow\rangle$, and the same radial wave functions for $|\Theta\uparrow\rangle$ and $|\Theta\downarrow\rangle$. As far as Ψ_1 is concerned one may now assume other orbitals than for the other two cases, since $S_e=0$. Yet there is no net spin polarization, no majority spin. As a consequence one still has the same orbitals for spin-up and spin-down, but both e orbitals are expected to be expanded compared with Ψ_2 and Ψ_3 because of the larger Coulomb repulsion. Therefore the matrix element as a whole should be scaled, and not only the spin-down orbital as in Ref. 39. Formally both approaches seem to be equivalent when only the wave functions with highest M_S values are taken for each multiplet level. However, this holds only for some cases, as in our example. For configurations containing more electrons this becomes obvious: in comparing matrix elements of the type $\langle e^{00}t_2^{30}\|e^{00}t_2^{30}\rangle$, i.e., $S_{t2}=\frac{3}{2}$, and $\langle e^{00}t_2^{21}\|e^{00}t_2^{21}\rangle$, i.e., $S_{t2}=\frac{1}{2}$, it is inadequate to modify only the matrix elements of the second integral that contain the minority-spin electron. Once one scales the matrix elements different space orbitals for the majority-spin electrons should be considered for the second case as well. Now the situation is rendered more sophisticated, as not all electrons have parallel spin or all spins cancel. In setting up the starting wave functions one has to treat the majority- and minority-spin electrons as belonging to two inequivalent shells, i.e., there are still two electrons belonging to one basis function set with t_2 symmetry, whereas the third electron belongs to a different basis set of t_2 symmetry. Nevertheless Pauli's exclusion principle must be obeyed, guaranteeing that no additional multiplet levels evolve. Additionally the multideterminantal wave function will change its character as the coefficients of the single-determinantal wave functions are now dependent on the degree of spin polarization. A further problem arises from nonorthonormalization of some of the involved single-electron orbitals. Integrals of the type $\langle\varepsilon\uparrow|\bar{\varepsilon}\uparrow\rangle$, where $\varepsilon\uparrow$ represents a majority-spin electron and $\bar{\varepsilon}\uparrow$ a minority-spin electron, do not necessarily vanish or are equal to 1. Furthermore it should be noted that electron and hole configurations are no longer necessarily equivalent. The multiplet ${}^3T_1$ of $e^{00}t_2^{20}$ does not require the use of spin-polarized orbitals, whereas ${}^3T_1$ of $e^{22}t_2^{31}$ does.

At this stage it is obvious that we have already passed the limit of what a semiempirical approach might be able to describe. This can be illustrated with the aid of a much less general model: a dependence on spin may be introduced by using one set of ten spin-unpolarized orbitals $\varepsilon\uparrow$, $\varepsilon\downarrow, \ldots, \zeta\uparrow, \zeta\downarrow$ for each set of S_e, S_{t2}, S. Just considering the consequences for the diagonal matrix elements, this leads for d^N configurations to 6 (d^2, d^8), 9 (d^3, d^7), or 15 (d^4, d^5, d^6) sets of ten Griffith parameters, i.e., 60, 90, or 150 parameters, which just describe the intracenter electronic repulsion. From this it becomes clear that as a semiempirical approach the introduction of spin-polarized single-electron orbitals to multiplet theory is not sensible as either too many parameters have to be considered or too many approximations have to be introduced (not to mention the treatment of the single-electron parameters), so that a quantitative improvement becomes rather doubtful. We conclude that such an approach does not promise to lead to substantial progress. Coming back to our motivation for investigating the introduction of spin-dependent modification of crystal-field theory as described in Sec. I, we therefore favor the first explanation of why other versions of crystal-field approaches, including hybridization, in some way lead to no improvement in the description of low-spin levels, e.g., the models themselves might be the reason for this discrepancy.

VI. CONCLUSION

We have given average multiplet energies for spin-dependent strong-field $e^{m\uparrow m\downarrow}t_2^{n\uparrow n\downarrow}$ configurations. Differences in these energies have been compared with a single-electron mean-field Hamiltonian which was set up similar to Slater's spin-polarized hyper-Hartree-Fock treatment of the free ion. High-spin states were shown to be properly represented by this Hamiltonian, but deviations occur for low-spin levels. The difference is due to nonequivalent averaging procedures. Exchange splittings were deduced from the single-electron approach, and the way these splittings can be linked to spin-flip energies, as defined by average multiplet energies, was discussed. Conversely, it is possible to calculate the exchange splittings with the aid of parameters deduced from experiment. As an example we discussed the case of ZnS doped with 3*d* transition metals. For more covalent systems we expect a larger discrepancy between our approach and mean-field calculations including additional orbitals more explicitly. The wave functions are considered to become too different. On the other hand our estimates of the exchange splittings can be used to show what order of magnitude is expected from experimentally deduced parameters.

Furthermore we have indicated how a possible spin-polarized modification of energy matrices for the Coulomb interaction among strong-field $e^m t_2^n$ configurations could be introduced consistently with multiplet theory. However, if the corresponding parameters have to be determined experimentally we do not consider this approach to be useful as either too many approximations or too many parameters are involved.

---

[1] N. Samarth and J. K. Furdyna, Proc. IEEE **78**, 990 (1990).

[2] A. Zunger, Solid State Phys. **39**, 275 (1986).

[3] G. G. DeLeo, G. D. Watkins, and W. B. Fowler, Phys. Rev. B **25**, 4962 (1982); **25**, 4972 (1982).

[4] L. A. Hemstreet and J. O. Dimmock, Phys. Rev. B **20**, 1527 (1979).

[5] J. W. Richardson, T. F. Soules, D. M. Vaught and R. R. Powell, Phys. Rev. B **4**, 1721 (1971).

[6] A. Fazzio, M. Caldas, and A. Zunger, Phys. Rev. B **30**, 3430 (1984).

[7] J. W. Allen, in *Proceedings of the 7th International Conference on the Physics of Semiconductors, Paris, 1964*, edited by M. Hulin (Academic, New York, 1964), p. 781.

[8] S. Watanabe and H. Kamimura, Mater. Sci. Eng. B **3**, 313 (1989).

[9] G. Piccoli, A. Chomette, and M. Lannoo, Phys. Rev. B **30**, 7138 (1984).

[10] O. Gunnarsson, O. K. Andersen, O. Jepsen, and J. Zaanen, Phys. Rev. B **39**, 1708 (1989).

[11] K. H. Johnson, J. Chem. Phys. **45**, 3085 (1966); K. H. Johnson and F. C. Smith, Jr., Phys. Rev. B **5**, 831 (1972); J. C. Slater and K. H. Johnson, *ibid.* **5**, 844 (1972).

[12] P. Hohenberg and W. Kohn, Phys. Rev. **126**, B864 (1964); W. Kohn and L. J. Sham, *ibid.* **140**, A1133 (1965).

[13] T. Ziegler, A. Rauk, and E. J. Baerends, Theor. Chim. Acta **43**, 261 (1977).

[14] U. von Barth, Phys. Rev. A **20**, 1693 (1979).

[15] M. Lannoo, G. A. Baraff, and M. Schlüter, Phys. Rev. B **24**, 943 (1981).

[16] J. H. Wood, J. Phys. B **13**, 1 (1980).

[17] J. Hubbard, D. E. Rimmer, and F. R. A. Hopgood, Proc. Phys. Soc. London **88**, 13 (1966).

[18] A. Fujimori, F. Minami, and S. Sugano, Phys. Rev. B **29**, 5255 (1984); A. Fujimori and F. Minami, *ibid.* **30**, 957 (1984); A. Fujimori, M. Saeki, N. Kimizuka, M. Taniguchi, and S. Suga, *ibid.* B **34**, 7318 (1986); A. Fujimori, N. Kimizuka, T. Akahane, T. Chiba, S. Kimura, F. Minami, K. Siratori, M. Taniguchi, S. Ogawa, and S. Suga, *ibid.* **42**, 7580 (1990).

[19] G. J. M. Janssen and W. C. Nieuwpoort, Phys. Rev. **38**, 3449 (1988).

[20] J. Zaanen, G. A. Sawatzky, and J. W. Allen, Phys. Rev. Lett. **55**, 418 (1985).

[21] L. Ley, M. Taniguchi, J. Ghijsen, R. L. Johnson, and A. Fujimori, Phys. Rev. B **35**, 2839 (1987).

[22] A. Bouhelal and J. P. Albert, Solid State Commun. **69**, 713 (1989); J. Cryst. Growth **101**, 528 (1990); Physica B **185**, 255 (1993).

[23] J. C. Slater, *Quantum Theory of Molecules and Solids, Vol. 4: The Self-Consistent Field for Molecules and Solids* (McGraw-Hill, New York, 1974).

[24] *Theory of the Inhomogeneous Electron Gas*, edited by S. Lundqvist and N. H. March (Plenum, New York, 1983).

[25] J. Callaway and N. H. March, Solid State Phys. **38**, 135 (1984).

[26] H. Adachi, S. Shiokawa, M. Tsakada, C. Satoko, and S. Sugano, J. Phys. Soc. Jpn. **47**, 1528 (1979).

[27] S. P. Freidman, V. I. Sokolov, E. Z. Kumaev, and V. A. Gubanov, Opt. Spectrosc. **57**, 512 (1984).

[28] S.-H. Wei and A. Zunger, Phys. Rev. B **35**, 2340 (1987).

[29] J. C. Slater, Phys. Rev. **165**, 655 (1968).

[30] J. C. Slater, Phys. Rev. **165**, 658 (1968).

[31] J. S. Griffith, *The Theory of Transition Metal Ions* (Cambridge University Press, Cambridge, 1964).

[32] Y. Tanabe and S. Sugano, J. Phys. Soc. Jpn. **9**, 753 (1954); **9**, 766 (1954).

[33] S. W. Biernacki and H.-J. Schulz, Phys. Status Solidi B **103**, K163 (1981); S. W. Biernacki, *ibid.* **118**, 525 (1983); **131**, 349 (1985).

[34] A. G. O'Neill and J. W. Allen, Solid State Commun. **46**, 833 (1983).

[35] S. Koide and M. H. L. Pryce, Philos. Mag. **3**, 607 (1958).

[36] R. R. Sharma, M. H. DeViccaro, and S. Sundermann, Phys. Rev. B **23**, 738 (1981).

[37] D. Durie, C. Barthou, and B. Canny, J. Chem. Phys. **61**, 3043 (1974).

[38] A. G. O'Neill, Ph.D. thesis, University of St. Andrews, 1984.

[39] S. W. Biernacki, Phys. Status Solidi B **132**, 557 (1985); see also S. W. Biernacki and H.-J. Schulz, Z. Phys. B **65**, 429 (1987).

[40] B. D. Bird, E. A. Cooke, P. Day, and A. F. Orchard, Philos. Trans. R. Soc. London Ser. A **276**, 277 (1974).

[41] In contrast to the original definition of $\hat{E}(m,n)$ in Ref. 6, we include single-electron contributions arising from the crystal-field splitting Δ in $\hat{E}(m,n)$ [as in $\hat{E}(m\uparrow,m\downarrow;n\uparrow n\downarrow)$] throughout this paper; there is a printing mistake in the Appendix of Ref. 6: for $N=5$ read $g_{3,2}=-\lambda_t^4-3\lambda_e^2\lambda_t^2-4\lambda_e^4$ instead of $g_{3,2}=-\lambda_t^4-3\lambda_e^2\lambda_t^2-\lambda_e^4$.

[42] H. A. Weakliem, J. Chem. Phys. **36**, 2117 (1962).

[43] J. C. Slater, *Quantum Theory of Atomic Structure* (McGraw-Hill, New York, 1960), Vols. 1 and 2.

[44] B. H. Brandow, Adv. Phys. **26**, 651 (1977).

[45] P. Vogl and J. Baranowski, Acta Phys. Pol. A **67**, 133 (1985); and in *Proceedings of the 17th International Conference on the Physics of Semiconductors, San Francisco, 1984*, edited by J. D. Chadi and W. A. Harrison (Springer, New York, 1985), p. 623.

[46] C. Delerue, M. Lannoo, and G. Allan, Phys. Rev. B **39**, 1669 (1989).

[47] J. Kanamori, Progr. Theor. Phys. **30**, 275 (1963).

[48] J. C. Slater, J. B. Mann, T. M. Wilson, and J. H. Wood, Phys. Rev. **184**, 672 (1969).

[49] A. Dal Pino, Jr., A. Fazzio, and J. R. Leite, Solid State Commun. **44**, 369 (1982).

[50] A. Fazzio and J. R. Leite, Phys. Rev. B **21**, 4710 (1980).

[51] D. E. Ellis, G. A. Benesh, and E. Byrom, Phys. Rev. B **20**, 1198 (1979).

[52] A. Oshiyama, N. Hamada, and H. Katayama-Yoshida, Phys. Rev. B **37**, 1395 (1988).

[53] H. Ennen, U. Kaufmann, and J. Schneider, Solid State Commun. **34**, 603 (1980).

[54] H. Katayama-Yoshida and A. Zunger, Phys. Rev. Lett. **53**, 1256 (1984); Phys. Rev. B **31**, 7877 (1985); **31**, 8317 (1985).

[55] A. Zunger and U. Lindefelt, Phys. Rev. B **27**, 1191 (1983).

[56] F. Beeler, O. K. Anderson, and M. Scheffler, Phys. Rev. Lett. **55**, 1498 (1985).

[57] J. M. Noras, Ph.D. thesis, University of St. Andrews, 1980.

[58] S. W. Biernacki, G. Roussos, and H.-J. Schulz, Acta Phys. Pol. A **73**, 259 (1988).

[59] G. Grebe and H.-J. Schulz, Z. Naturforsch. **29a**, 1803 (1974).

[60] U. W. Pohl, Ph.D. thesis, D83, Technische Universität Berlin, 1988.

[61] M. Skowroński and Z. Liro, J. Phys. C **15**, 137 (1982).