PHYSICAL REVIEW A, **66**, 032508 (2002)

Density-functional theory and atomic multiplet levels

M. Weinert,[1,2] R. E. Watson,[1] and G. W. Fernando[3,4]
[1]*Department of Physics, Brookhaven National Laboratory, Upton, New York 11973*
[2]*Department of Physics, University of Wisconsin-Milwaukee, Milwaukee, Wisconsin 53201*
[3]*U-46, Physics Department, University of Connecticut, Storrs, Connecticut 06269*
[4]*Institute of Fundamental Studies, Hantana Road, Kandy, Sri Lanka*

(Received 30 January 2002; published 27 September 2002)

The multiplet splittings resulting from Hund's rules effects for open-shell atomic d^n configurations are investigated within density-functional theory. The calculated results are compared to experiment, Hartree-Fock, and Slater-Condon-Racah fits. Marked systematic errors are found in the local-spin-density (LSDA) and generalized-gradient (GGA) results arising from the failure of the LSDA/GGA single-particle Hamiltonian to commute with L, M_L, and S, which are good quantum numbers for the exact wave functions. The shortcomings of LSDA/GGA for the middle of the transition-metal row ions are more severe than those seen in previous work that concentrated on open p shells, even for multiplet levels with single-determinant wave functions. A number of issues confronting density-functional-based theories are addressed; in particular, it is demonstrated that any exchange-correlation functional that depends on the charge and spin densities alone is incapable of describing multiplet effects correctly.

DOI: 10.1103/PhysRevA.66.032508 PACS number(s): 31.15.Ew, 31.10.+z, 71.45.Gm

I. INTRODUCTION

With the recent increased interest in magnetic properties of complex materials, electronic structure calculations for magnetic solids are increasingly confronted with the need to treat spin, orbital, and spin-orbit effects on an equal basis. This raises the issue of how Hund's rule effects are to be best incorporated in band theory calculations. As a prelude to consideration of these effects in solids, it is useful to understand them for the case of free atoms. In this paper, density-functional theory (DFT) [1], in its local-(spin-)density (LSDA) [2] and generalized-gradient (GGA) [3] approximations, will be juxtaposed against Hartree-Fock theory and experiment for open-shell transition-metal ions.

One of the great successes of the Hartree-Fock approximation is to be found in the Slater-Condon-Racah theory of atomic multiplets [4]. Derived in the era before atomic calculations had become available for open-shell ions, the theory provided a very good description of the observed multiplet splittings. Using single- and multideterminant wave functions having total spin and orbital angular momenta S, L, M_S, and M_L as good quantum numbers, the Slater-Condon-Racah theory involved fitting the observed spectra in terms of a few radial Coulomb integrals, i.e., the Slater F^k. With the advent of Hartree-Fock calculations, it became clear [5] that the F^k of the fits had been screened by correlation effects, leading to values which were smaller than the bare integrals.

In contrast, the LSDA/GGA, as will be discussed in this paper, do not reproduce the multiplet structure well; in particular, degenerancies (and hence splittings) are given incorrectly in the LSDA. This issue has been recognized for many years and motivated several related approaches [6–9] for dealing with multiplets. These previous authors [6–9] addressed the question of multiplet splittings within the LSDA, concentrating on systems with open p shells [6–8]; with the exception of some work on the d^2 configuration [9], the open d (and f) shells important to magnetism have not been considered. In addition to these Slater-Condon-Racah and density functional approaches, various methods such as the time-dependent density-functional theory (TDDFT) and effective action-based approaches have been used to calculate selected atomic multiplets and excitation energies in some molecules [10]. Our results also will have important consequences for such studies, especially when local-density theory (or a similar variant of DFT or a hybrid functional) is used to approximate the frequency-dependent exchange-correlation kernel.

The success of Hartree-Fock theory in dealing with Hund's rules in atoms arises from the inclusion of aspherical interelectronic exchange in which the energy depends on whether the orbital moment of one electron is parallel or antiparallel to that of the other. As will be discussed later, this contribution cannot be described when the interelectronic potential is derived from the electron and spin densities alone. One way to remedy this defect is to add a current density term to the LDA scheme [11], but a practical implementation is still not available. Another approach is to replace the appropriate open shell aspherical LSDA/GGA terms by their (bare or screened) Hartree-Fock counterparts [4]. (A crude, but computationally convenient [12], approximation of limited validity is discussed in Appendix A.) Yet another approach, introduced by Ziegler *et al.* [6], von Barth [7], and Wood [9], is to constrain the LSDA/GGA calculations such that the atomic states of the same multiplet of given L and S, but differing M_L and M_S, are degenerate. In this paper, we extend this constrained approach to open d shells, and find that the lessons learned in the p shell systems are not directly transferable to transition-metal systems.

In the p shell ions considered previously [6–8], only three different multiplet states of L and S may be constructed for a given open p^2, p^3, or p^4 shell, and thus only two independent multiplet level splittings arise. The restriction to two splittings makes these cases a limited test of any theory. Many more multiplet levels arise in open d or f shells, thus allowing a better sampling of how well a given theory separately accounts for Hund's first and second rules, as well as allowing for possibly new phenemona. An additional complication plagues comparisons between theory and experiment for open *p* shells, particularly the $2p$ atoms: consider an s^2p^2 configuration for which there are ^3P, ^1D, and ^1S multiplets with the associated (^1S-^3P) and (^1D-^3P) level splittings. As noted [13] by Condon and Shortley, the experimental ratios of these splittings (and their p^3 and p^4 counterparts) deviate markedly from the predictions of Slater-Condon-Racah theory, which was attributed to the strong mixing [14] between near-lying atomic levels arising from different atomic configurations, e.g., the $2s^22p^2$ with the $2p^4$. Neither density-functional nor Hartree-Fock theory as standardly applied deals with such configuration-interaction effects. Going to the multiplet splittings of open *d* or *f* shells does not completely avoid distortions due to analogous "degenerate" configuration mixing, but its overall impact is usually less.

In discussing various approximations, it is useful to deal with cases for which there are experimental data [13] for comparison. There are very few data for open *f* shells except for the cases of several $4f^2$ and $4f^3$ ions among the rare earths. In contrast, there is a substantial body of transition-metal data, particularly across the $3d$ row. For that reason, the transition metals will be considered in this paper. Wood [9] considered the d^2 levels of Ti and Zr in his LSDA investigation of multiplet splittings, but to our knowledge these are the only transition-metal estimates made prior to the present paper. While valuable to have, Wood's investigation provides an incomplete indication of what happens for the transition-metal elements.

In atomic Hartree-Fock theory, the Hamiltonian commutes with L, S, M_L, and M_S; the many-electron wave functions with these quantum numbers are linear combinations of Slater determinants. The total energy of a given state depends on L and S, but not on M_L or M_S (provided spin-orbit coupling is neglected). While the calculated ordering in energy of the multiplet levels is not always in accord with experiment, the orderings do reproduce Hund's first and second rules. The situation is different for the LSDA/GGA calculations where the single-particle Hamiltonian commutes with neither L nor S. Following the previous investigations [6–9], we will require that the wave functions used for the LSDA/GGA energy estimates be eigenfunctions of L, S, M_L, and M_S, i.e., have the same symmetry properties as the Hartree-Fock (single- or multideterminant) wave functions. One consequence of applying the LSDA or GGA to such wave functions is that the energies obtained for states differing only in M_L and/or M_S will differ, contrary to experimental fact. This deficiency in the LSDA already occurs for the single-electron $p,d, \ldots$ states of the hydrogen atom which have different energies depending on the particular m_ℓ considered [15]. These considerations have implications for LSDA/GGA band structure calculations for solids when spin or orbital magnetic effects are of concern.

In general there is a single determinant associated with the states of maximum allowable L for some S appropriate to a d^n (or p^n or f^n) configuration, with $M_L=L$ and $M_S=S$. In other words, restricting consideration to single determinants allows a sampling of the multiplet splittings between states of differing *S*, but not between differing *L* for some given *S*. Also, except for the half-filled d^5 (and f^7 and p^3) configuration, more than one single-determinant state may be constructed for the Hund's rule ground state. These single determinants are associated with different M_L (each having the maximum M_S) and LSDA/GGA estimates yield *different* values for their total energies, similar to the case of the hydrogenic states [15]. Thus, LSDA/GGA estimates of the multiplet excitations from the multiplet ground state to levels describable as single determinants involve a *spread* in energy depending upon which ground state single determinant is used. In part because of the choice of systems considered, the results of the earlier work [6–9] suggested that the LSDA works well in predicting the multiplet splittings between single-determinant levels; for the open *d* shells in the middle of the transition-metal rows, however, we show that the LSDA/GGA is not as successful.

II. CHARGE AND SPIN DENSITIES: CONSEQUENCES FOR MULTIPLET LEVEL SPLITTINGS

In this section, we present cases where (a) any local-density approximation and (b) any density functional (local or nonlocal) that depends on the charge and spin densities only *must* fail to describe the multiplet splitting correctly. A blurring of the roles of Coulomb and exchange effects, within the Hartree-Fock treatment, will also be noted. These results have important implications for the development of exchange-correlation functionals for the successful description of spin and orbital effects.

First consider the d^4 (or d^6) configuration. There are three wave functions that can be written as single determinants for the ground state ^5D level, all with $M_S=2$, but $M_L=0$, 1, 2:

$$\Psi(^5D)_{0,2}=\Phi(2^+,1^+,-1^+,-2^+), \tag{1}$$

$$\Psi(^5D)_{1,2}=\Phi(2^+,1^+,0^+,-2^+), \tag{2}$$

$$\Psi(^5D)_{2,2}=\Phi(2^+,1^+,0^+,-1^+), \tag{3}$$

where the subscripts indicate the M_L and M_S values and 2^+, for example, indicates that the single determinant Φ contains an electron orbital having $m_\ell=2$ and $m_s=+\frac{1}{2}$. Note that each of these single determinants has a spherical density except for a single hole of a given $|m_\ell|$ corresponding to the M_L value. A simple calculation gives that the hole densities for the second and third wave functions, are given by

$$Y_{21}^*(\hat{r})Y_{21}(\hat{r})=\frac{15}{32\pi}[\sin 2\theta]^2 \tag{4}$$

$$Y_{22}^*(\hat{r})Y_{22}(\hat{r})=\frac{15}{32\pi}[\sin^2\theta]^2. \tag{5}$$

The simple mapping of $\sin^2\theta \leftrightarrow \sin 2\theta$ transforms one density into the other (at some different point in space) on a point by point basis. Hence, *any* local approximation will give identical results for these two exchange-correlation energies.

(Nonlocal density functionals will not have this defect since the gradients are different.) Since the charge densities are different for the three single-determinant states, they have different Coulomb energy contributions; however, since the local-density exchange-correlation energy contributions for $M_L=1$ and $M_L=2$ are *identical*, the energies of these degenerate states must be different, causing a nonphysical splitting of the degeneracy. Note that this example is fundamentally different from the common case—such as the single-particle (and thus single-determinant) hydrogenic states [15]—where the Coulomb and exchange-correlation terms are each different and the splitting comes from an incomplete cancellation because of defects in the exchange-correlation functional. For this common case, it is possible, at least in principle, to define an artificial (and probably nonphysical) local exchange-correlation functional that would give the correct degeneracies for a set of states. For the two ^5D states discussed above, this is not possible and there must be a splitting. It is important to emphasize that this splitting happens even for single determinants where previous work has argued that the LSDA should be applicable. In addition, note that the magnitude of the splitting depends on the Coulomb terms alone and is independent of the choice of LSDA functional.

Even a nonlocal exchange-correlation functional that depends on the charge and spin densities alone will not give the correct multiplet splittings since there exist *different* states, belonging to different multiplets, that have *identical* charge and spin densities. Although the existence of sets of such states does not appear to have been recognized previously, such situations are not at all rare: there are two such sets for the P and D levels of the p^2 and p^3 configurations; ^3F and ^1G in d^2; $(^5D,^1I)$, $(^5D,^3H,^1I)$, $(^5D,^1F)$ for d^4; and $(^6S,^2S)$, $(^4G,^4F)$, $(^2I,^2H)$ for d^5. (Other cases exist, but depend on the mixing of the various states of common S and L.) Clearly any method that cannot distinguish between these different states cannot obtain the correct multiplet splittings. The current density *can* distinguish between these states, and thus may provide a way to treat multiplet effects correctly within a (current) density-functional approach.

To discuss the relative role of Coulomb and exchange terms, let us consider the d^2 (and d^8) configuration in which Ti^{2+} occurs. This ion was considered by Wood and will be discussed in the next section. The configuration combines to form ^3F, ^3P, ^1G, ^1D, and ^1S multiplet levels, with the ^3F and the ^1G states having single-determinant wave functions:

$$\Psi(^3F)_{31}=\Phi(2^+,1^+), \tag{6}$$

$$\Psi(^3F)_{21}=\Phi(2^+,0^+), \tag{7}$$

$$\Psi(^1G)_{40}=\Phi(2^+,2^-). \tag{8}$$

The other states are combinations of more than one determinant; e.g., the ^1S state is

$$\Psi(^1S)_{00}=\frac{1}{\sqrt{5}}\{\Phi(2^+,-2^-)-\Phi(2^-,-2^+)+\Phi(1^-,-1^+)-\Phi(1^+,-1^-)+\Phi(0^+,0^-)\}. \tag{9}$$

Consider the Hartree-Fock exchange coupling between the 2^+ and 1^+ electrons of Eq. (6), which is [16]

$$E_{exch}=-\frac{6}{49}F^2(dd)-\frac{5}{441}F^4(dd), \tag{10}$$

where the F^2 and F^4 are Slater radial integrals [16] which involve a common d radial function for the electrons of the open shell. If the m_ℓ of the second electron is flipped from $+1$ to -1, with the result that the new determinant belongs to a different multiplet, then the exchange coupling is

$$E_{exch}=0F^2(dd)-\frac{35}{441}F^4(dd). \tag{11}$$

While the electron charge (and hence the d-d Coulomb interaction) and spin densities are the same for the two determinants, exchange samples the energy dependence of the orientation of the two angular momenta, yielding different energies. This behavior is essential to the success of Hartree-Fock theory in predicting the multiplet spectra and maintaining the symmetry of the physical system. However, now consider the exchange energy associated with the electrons of Eq. (7),

$$E_{exch}=-\frac{4}{49}F^2(dd)-\frac{15}{441}F^4(dd), \tag{12}$$

which is quite different from Eq. (10). The Coulomb terms are also different in the two cases, with the result that both single determinants have a total (direct *and* exchange) interelectronic d-d interaction of

$$E_{total}=-\frac{8}{49}F^2(dd)-\frac{9}{441}F^4(dd). \tag{13}$$

Although the exchange terms explicitly depend on the relative signs of m_ℓ of each electron, there is an interplay between Coulomb and exchange contributions to the L, S, M_L, and M_S dependence of the multiplet energies that leads to the degeneracy among the different levels of a multiplet. The situation becomes even more complicated when considering multideterminant states where there are energy contributions arising from matrix elements between determinants. The implication of these observations is that, even within a given multiplet, the Coulomb and exchange contributions for the different members can vary widely, making an unambiguous distinction between exchange and direct Coulomb contributions problematic.

In this section we have indicated some of the difficulties that density functionals must address when dealing with the multiplet effects accompanying Hund's first two rules; in particular, LSDA/GGA-type approximations are incapable of

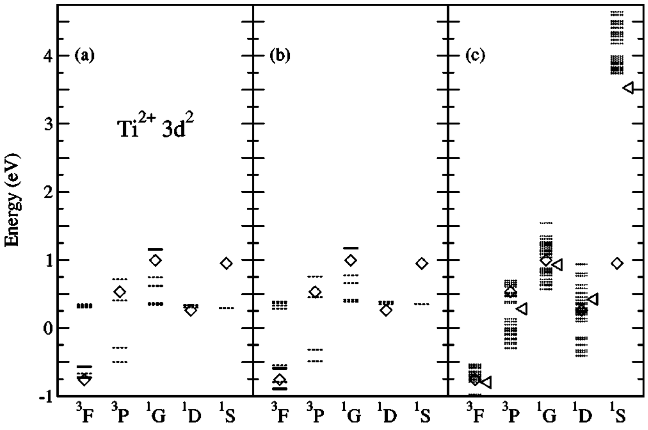

FIG. 1. Experimental (◇) and calculated multiplet energy levels for Ti^{2+} d^2 where the zero of energy is the center of gravity of the set of levels. (a) LSDA predictions for single- (—) and multi- (— — —) determinant wave functions of good S, L, M_S, and M_L. (b) Same, but with gradient terms (GGA) included in the energies. (c) Comparison of the predictions of the Wood-type diagonal sum rule (· · · · · · ·) and von Barth–type (◁) constraints to experiment as discussed in text.

correctly describing these effects. Hartree-Fock theory, with exchange terms that depend on the signs as well as the magnitudes of the m_ℓ values, is in a much better position to deal with multiplet energies. It should, of course, be remembered that local-density theory was not derived to deal with the sets of degenerate states encountered here, but these types of states are of importance in calculations in solids.

III. Ti^{2+} 3d^2 MULTIPLETS

Given Hartree-Fock-like single- and multideterminant wave functions, with L, S, M_L, and M_S as good quantum numbers, the charge and spin densities may be constructed, and then the LSDA/GGA energies may be calculated (see Appendix B). The LSDA results for Ti^{2+} are shown in Fig. 1(a) and compared with experiment [17,18]. (Note that levels with $\pm M_L$ or $\pm M_S$ are degenerate.) The solid lines indicate the results for single determinant wave functions and the ^3F-^1G splitting is in reasonable accord with experiment, in agreement with previous expectations [6,7,9]. This is not the case if other levels are considered. The most striking feature of the results is the separation of the $M_S=1$ levels (below $-\frac{1}{4}$ eV) into one stripe and those for $M_S=0$ into another. The M_S dependence of the energies—*not* L and S—dominates the results. The consequences of including gradient terms (GGA) [3] in the estimates is shown in Fig. 1(b). Although there are changes in details, inclusion of the gradient corrections has had little effect on the predictions, with the M_S striping maintained. There is little tendency for the predictions to reproduce experiment other than yielding the overall spread in the spectra.

An approach to resolving the striping is to require that the states of differing M_L and M_S, but the same L and S, have the same energy, E_i. Following Wood [9], one way is to invoke the diagonal sum rule, i.e., the trace of a matrix is invariant. In the case of $M_L=M_S=0$ [see Eq. (9)], there are five single determinants, with energies ε_j. From the diagonal sum rule,

$$\sum_j \varepsilon_j = \sum_i E_i, \tag{14}$$

where, for $M_L=M_S=0$, the right hand side is a sum over the energies of the five d^2 multiplet states. There is such a sum rule, involving varying numbers of states, for each M_L and M_S appropriate to d^2. Combining these sum rules, subject to requiring a single E_i for a given L and S, results in more equations (9) than the number (5) of multiplet state energies. Wood made a particular choice of equations and solved those five. The choice, however, is not unique and the results of making the various possible choices are plotted in Fig. 1(c). Several things have happened by enforcing the diagonal sum rule. With the requirement of a single E_i, the $M_S=0$ stripe of levels for ^3F has disappeared, as has the $M_S=1$ stripe for ^3P. However, different choices of the set of equations to solve lead to a quite large spread in level positions.

In addition, the set of energy values obtained for ^1S has risen some 3–4 eV so that theory lies well above experiment for this level. It should be noted that ^1S enters only the $M_L=M_S=0$ equation and is obtained *after* the other four levels are solved for from the other equations. It might thus be concluded that the ^1S energy suffers from the shortcomings, numerical and physical, of enforcing the Hartree-Fock requirement of a single energy per multiplet state upon the other LSDA/GGA-based levels.

The diagonal sum rule is just one of a number of Hartree-Fock relationships between the single determinant ε_j and multiplet energies E_i. In general there are more equations than unknowns if each of the ε_j are considered to be independent. In Hartree-Fock theory, there are degeneracies and simple relations among the energies of the determinants, thereby reducing the number of independent equations so that the problem is well defined. Ziegler *et al.* [6] considered cases where the number of different determinant energies (calculated within the LSDA) are the same as the number of different multiplets energies so that a unique solution can be found. Because of this restriction on the number of independent energies, their method is appropriate for systems such as small molecules that have lower symmetry (and degeneracies) than found in atoms. von Barth [7] in his treatment of the p^n ions extended this approach and did a least deviation fit of the full set of equations. To these, he suggested applying even more constraints based on Hartree-Fock wave function information. By considering the unitary transformation between the Hartree-Fock eigenfunctions Ψ_j, which are proper eigenfunctions of L, S, M_L, and M_S, and the single determinants one can write

$$\Phi_i = \sum_j \beta_{ij}\Psi_j. \tag{15}$$

Multiplying this equation on the left by the Hartree-Fock Hamiltonian, then by Φ_i, and integrating, we have

$$\varepsilon_i = \sum_j \beta_{ij}^2 E_j, \tag{16}$$

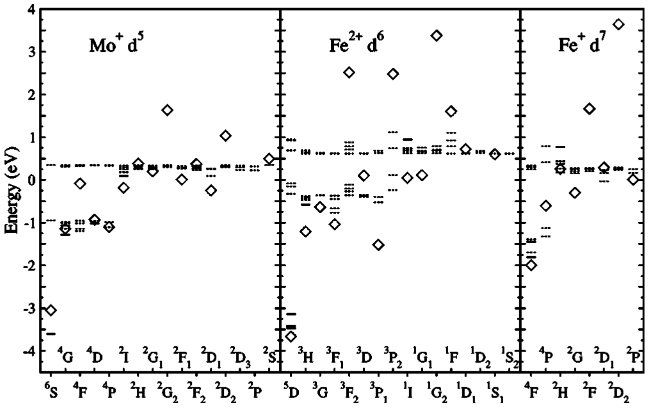

FIG. 2. Comparison of the calculated GGA single- (—) and multi- (— — —) determinant multiplet levels to experimental (◇) values for Mo$^+$, Fe$^+$, and Fe^{2+}. The energy zero of a given set of multiplet levels is the center of gravity of that set.

where we have made use of the fact that the Hartree-Fock energies E_j are diagonal in terms of the Ψ_j. The result is a set of equations having Hartree-Fock constraints on the combination of single determinants. The consequence of fitting this larger set of equations is indicated by the triangles of Fig. 1(c). Agreement with the earlier fit is quite good and the predictions of the multiplet splittings (relative to the ^3F level) of the ^1G, ^3P, and ^1D, but *not* the ^1S, levels are in accord with experiment; e.g., the order in which the multiplet levels lie is almost correct. The misplacement of the ^1S level, however, is significant numerically and is a indicator that the constrained LSDA-type approaches do not work as well for the *d* shells as for the *p* shells.

IV. RESULTS: d^3 TO d^7 CONFIGURATIONS

Going from the d^2 configuration (and its over-half-filled *d* shell counterpart d^8) to the other configurations introduces a significant complication not encountered in the previous section. In the d^3 (d^7), d^4 (d^6), and d^5 configurations there exist pairs of multiplet states which are of the same symmetry and which have matrix elements coupling them. Thus, the final set of states and their energies depend on the strength of this mixing. Pairs of ^2D states exist for the d^3 (d^7) and d^5 cases, while for d^4 (and d^6) over half the multiplet states are members of such pairs, i.e., ^3F, ^3P, ^1G, ^1D, and ^1S. The mixing matrix elements between the multiplet states, along with their individual energies, have been evaluated with both the LSDA and GGA (cf. Appendix B).

The equivalent of Fig. 1(b) is shown for three representative ions in Fig. 2. Two of these are monovalent ions whose d^n spectra are overlapped by $d^{n-1}s$ multiplet levels, many of which are of common *L* and *S*. Some of the experimental levels are expected to be moved by "degeneracy" configuration mixing between these levels, but should have little effect in ascertaining the trends to be observed here. The M_S dependent striping seen in Fig. 1 has become more pronounced, especially for the half-filled d^5 shell of Mo$^+$. With the exception of the two ^2D multiplets involved in mixing, all the d^5 states have spherical charge densities; hence the

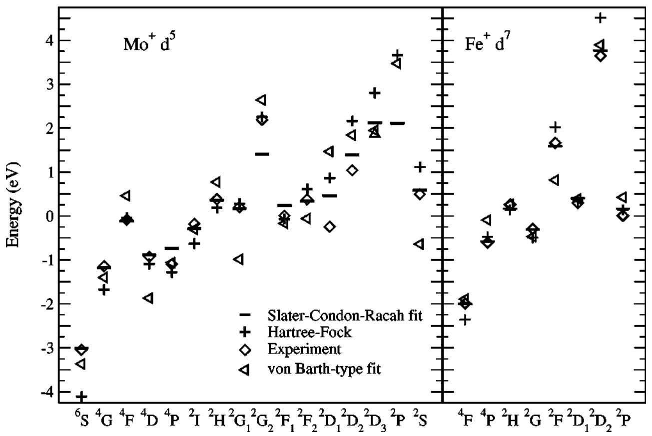

FIG. 3. Calculated Hartree-Fock (+), Slater-Condon-Racah fits (—), and von Barth–type predictions (◁) for the multiplet levels of Mo$^+$ and Fe$^+$ compared to experiment (◇). The energy zero is the center of gravity of all multiplets. For the Mo$^+$ $^2D_3$ multiplet, an experimental ^2D value (△, which overlaps the ◁) attributed to the d^4s configuration is also given (see text).

deviations from having a single-valued energy for a given M_S arise from aspherical exchange-correlation terms due to the aspherical components of the spin density. Here we have the most graphic example of the inability of LSDA/GGA energies, derived for wave functions of well-defined *L*, *S*, M_L, and M_S, to replicate the Hartree-Fock success in its overall mapping of the experimental level positions. Limiting consideration to the LSDA/GGA predictions for the single-determinant cases also shows poorer agreement with experiment than was encountered for the d^2 ion; in general, the calculated single-determinant splittings differ from experiment by ~0.5 eV.

There is some tendency for the experimental levels to fall in broad bands of their own. As was the case in Fig. 1 with the ^3P level, there are quartets in the d^3, d^7, and d^5 cases which are out of line in that their experimental energies coincide with those values calculated for states which have been assigned the lower M_S value [19]. There are, in addition, some levels which lie well above the main group of low-spin levels, but there is no hint of this tendency in the LSDA/GGA predictions.

Two of the ions just considered are shown in Fig. 3 where the Hartree-Fock predictions, the Slater-Condon-Racah (where F^2 and F^4 are fitted independently) and von Barth–type fits, and experiment are compared. The agreement with experiment is typical of other examples which could have been chosen. With its interelectronic interactions unscreened by correlation effects, Hartree-Fock theory overestimates the overall multiplet splitting while doing well in predicting the ordering of the multiplet levels. The von Barth–type predictions avoid the striping of Fig. 2 and do quite well in reproducing the trends in multiplet level behavior, although some of the predictions are as much as an eV out of position relative to experiment. The Hartree-Fock and von Barth–type fits are comparable in quality, but both are poorer than the Slater-Condon-Racah fits.

When comparing the Hartree-Fock and Slater-Condon-Racah results it should be noted that the splitting between the centers of gravity of different spin manifolds, i.e., differing S, is proportional to the sum F^2+F^4, while the variation in position of individual levels in a manifold depends on the separate behavior of F^2 and F^4. The Slater-Condon-Racah fits have improved both the overall exchange splitting and the positions of individual levels, resulting in good agreement with experiment, as seen for Fe^+. Going to the higher range in spin multiplicity of Mo^+, there are three low-spin levels ($^2G_2$, $^2D_1$, and $^2D_2$) for which experiment and the Slater-Condon-Racah fits are in poor agreement. (There is another low lying ^2D level in the Mo^+ spectrum attributed to the d^4s, but possibly belonging to the d^5, configuration, that is in excellent agreement with the remaining fitted $^2D_3$ level; this level does not mix with the other two ^2D levels.) Problems have also been encountered in the fits for the ^2D levels of other d^5 ions. Omitting this set of three d^5 levels, the Slater-Condon-Racah fits for the d^2 through d^8 ions show agreement with experiment like, and often better than, that seen in Fig. 3. The bulk of the experimental data [17] for which such comparisons may be made resides in the $3d$ row and for Mo; the data are sparse for other $4d$ and $5d$ ions.

The Slater-Condon-Racah fits of Fig. 3 involved all the reported experimental levels, but other choices can be made. For example, consider the d^4, d^5, and d^6 ions where there is one (ground state) multiplet of maximum S plus sets of multiplets with two smaller S values. Fits have been done for the set of multiplet levels of a given S relative to the ground state multiplet. The purpose, then, is to fit the F^2 and F^4 to best represent the L dependence within a given S manifold. The results of such fits yield sums F^2+F^4 which are almost identical, but very slightly smaller for the small S manifold, indicating a slight increase in the screening of the exchange splitting. In contrast, the ratios of the Slater parameters, F^4/F^2, vary markedly: in the case of Mo^+ the ratio is 0.88 for the fit of all levels, 0.67 for the fit of the quartets, and 0.92 for the doublets. A similar situation holds for the d^2, d^3, d^7, and d^8 ions for which there are only two S manifolds.

It would thus appear that estimates of the screening of such interelectronic interactions depend significantly on what subset of multiplet levels is considered. In solids, for example, one is often concerned with states of less than maximum S and, as a rule, of less than maximum L for that S.

V. DISCUSSION

Because of the larger number of multiplet levels of varying L and S, the open d shells provide a better test of multiplet theory than do the open p shells. The middle of the transition-metal rows shows the M_S striping of the multiplet energies to be more narrowly defined relative to the overall multiplet splittings (Fig. 2) and problems arise concerning the single-determinant states. Previous work on p shell systems indicated that LSDA energies could yield multiplet splittings in accord with experiment for multiplets that can be represented as single determinants. Contrary to this perception, the LSDA/GGA single-determinant energy splittings of Fig. 2 for d shell systems are *not* in agreement with experiment. If interest is not limited to states of maximum L for a given S, then the multideterminant character of Hartree-Fock theory, as developed for atoms by Slater, Condon, and Racah, cannot be avoided. As shown here, the introduction of gradient terms has little effect on the LSDA predictions of the splittings.

Symmetry is a large part of the issue. The LSDA/GGA Hamiltonian does not commute with the L, S, and M_L (and m_ℓ) operators; hence, by construction, it does not deal properly with these symmetries for the atomic case unless they are imposed from the outside. The matter is further complicated by the utilization of spin-polarized calculations where orbitals of electrons of different m_s are allowed to be different. If both are occupied, such pairs of electrons then do not make singlet contributions to the spin and S ceases to be a good quantum number. (The same situation applies for L if an m_ℓ-dependent polarization is introduced.) Also, the division into d-d direct Coulomb and exchange terms, even for Hartree-Fock states describable as single determinants, depends on the M_S and M_L of states of common L and S. The fact that the relative roles of direct Coulomb and exchange terms cannot be uniquely defined for such a set of states means that the separate screening of such terms, as has sometimes been contemplated, would destroy the ability of Hartree-Fock theory to predict the multiplet level degeneracies and to maintain symmetry. The interplay of these terms in Hartree-Fock theory, which is so important to its prediction of the degeneracies, has no counterpart in LSDA/GGA theory and is at the root of the M_S striping of Figs. 1 and 2.

The effective exchange coupling in a solid is often defined as $\Delta E/\Delta S$, where $\Delta E(\Delta S)$ is the difference in energy (spin) between two levels. As seen in Fig. 2 for the d^5 and d^6 configurations, when the multiplet states take on more than two S values, the resulting exchange splitting is nonlinear; for example, changing S of the d^5 configuration from $\frac{5}{2}$ to $\frac{3}{2}$ yields a substantially different, i.e., larger, $\Delta E/\Delta S$ than going from $\frac{3}{2}$ to $\frac{1}{2}$. The same holds for both d^4 and d^6 changing $S=2$ to 1 and, in turn, to 0. The nonconstancy of $\Delta E/\Delta S$ with S does not seem to be widely recognized.

These results also have implications for bulk electronic structure calculations. A normal band structure calculation involves a single (large) determinantal wave function made up from a set of occupied one-electron states. It is inherently unable [20] to deal with the multideterminant character associated with the spin and orbital Hund's rule type of effects. The spin-polarized LSDA/GGA scheme has $\langle S_z\rangle$ as a component of spin and thus is matched to the single-determinant character of the band structure wave function [21]. Spin-polarized band calculations for magnetic solids have been very successful in reproducing—and predicting—the spin magnetism, although the question arises of whether the spin S intrinsic to a result equals the calculated $\langle S_z\rangle$ value. Alternative approaches such as "LDA$+U$" and/or "LDA$+I$" have been coming into increased use. The starting point of these schemes is a paramagnetic LDA band calculation to which is appended a self-consistent treatment of magnetic and correlation effects with the introduction of a Hubbard U or a Stoner I term. Double counting of interelectronic interactions is avoided (or largely so) by starting with the paramagnetic bands and screened U or I with values of the order of 1 eV for the $3d$ ions. These approaches add terms to the

Hamiltonian directly, but they still do not obey all the symmetry requirements.

Orbital magnetism in solids arises from spin-orbit coupling and from the incomplete quenching of Hund's second rule effects. Such magnetism is important to magneto-optical effects and to the description of magnetism in the actinides and their compounds. Here density-functional theory is in trouble for the same reasons as for the multiplet levels; it does not differentiate between $\pm m_\ell$ and there are problems with the single-determinant character of the band wave function. As noted in the Introduction and discussed in Appendix A, an approximate scheme for dealing with orbital effects has been introduced for open *d* [22] and *f* [12] shells. The scheme has restricted validity, but is computationally convenient within a conventional band calculation. Ultimately, the multideterminant character of the problem will have to be addressed. A possible step in this direction has been suggested by several recent papers [23] in which the LDA$+U$ approach is extended to include the m_ℓ and m_s dependence in U. Such schemes will require screened F^k matrix elements. The screening will be different for the F^2 and F^4 d-electron terms, and will depend on the ion in question *and* on what set of multiplet levels is important to the physics at hand.

VI. CONCLUSIONS

In this paper, we have considered a number of issues related to multiplets in open-shell atomic d^n configurations. The LSDA/GGA and Hartree-Fock calculations have been compared to both experiment and to Slater-Condon-Racah fits. The use of Hartree-Fock constraints [6,7,9] in the LSDA/GGA enforces the correct degeneracies and removes one of the major defects (the M_S striping) of a straightforward application of the LSDA/GGA to the treatment of multiplets. (The use of the GGA, as opposed to the LSDA, has little effect on the results.) However, even with constraints, the LSDA/GGA results for the d^n configurations are significantly worse than previous work on the *p* shell atoms would suggest, with some levels such as the ^1S state of Ti^{2+} off by 3–4 eV and errors of order 1 eV common. This poorer agreement is related to the greater complexity of the multiplet structure found in the *d* shell compared to *p* shell configurations, and thus the *d* shell systems provide a more stringent test of the various multiplet theories. An important observation is that, contrary to expectations based on the *p* shell systems, even single-determinant states for these d^n configurations are not always well described; in fact, single-determinant states that should be degenerate may be split by $\sim$0.5 eV, with similar errors between different multiplet levels. As demonstrated for the d^4/d^6 configurations, such energy splittings between single-determinant states are an essential feature of any local-density approximation. Even with these shortcomings, these constrained (von Barth–type) fits give results comparable in quality to Hartree-Fock calculations and represent a reasonable (and, at present, probably the best) approach if the limitations are kept in mind.

In addition to extending the constrained LSDA approaches to multiplets of d^n ions, we have also discussed some general issues related to the calculation of multiplets that do not appear to have been recognized previously. The marked systematic errors that are found in the LSDA/GGA results arise from the failure of the LSDA/GGA single-particle Hamiltonian to commute with L, M_L, and S, which are good quantum numbers for the exact wave functions. Complicating the development of new exchange-correlation functionals is that direct Coulomb and exchange contributions cannot be separated uniquely even within a given multiplet. The Slater-Condon-Racah fits suggest that the screening of the interelectronic interactions depends on the spin manifold and the set of multiplet levels that are physically relevant. We have also shown that *any* density functional that depends on the charge and spin densities alone cannot describe multiplet effects correctly, but must depend on other quantities such as the current density. All of these results place important limitations and requirements on the properties that exchange-correlation functionals must satisfy in order to describe spin and orbital magnetic effects in both atoms and solids.

ACKNOWLEDGMENT

This work was supported under Contract No. DE-AC02-98CH10886 with the Division of Materials Sciences, U.S. Department of Energy.

APPENDIX A: ORBITAL EFFECTS

Racah [24] introduced linear combinations of the Slater F^k integrals: B, a combination of the d^n shell F^2 and F^4 integrals, and E^3, a combination of the F^2, F^4, and F^6 appropriate to a f^n shell. The energy splittings between states of maximum allowable spin and varying L depend only on B or E^3. For such states, the energy of an individual level corresponds to

$$E_{av}+\chi L(L+1)\zeta, \tag{A1}$$

where E_{av} is the energy of the center of gravity of the configuration, χ is a simple constant such as $-1/2$, and ζ is B for the case of a *d*-shell or E^3 for an *f*-shell atom. From the variational principle, a one-electron operator of the form

$$\chi\langle L\rangle\zeta\hat{m}_\ell, \tag{A2}$$

can be introduced into a band structure calculation. ($\langle L\rangle$ is the orbital moment and $\hat{m}_\ell$ is the orbital angular momentum operator in the one-electron Hamiltonian.) In schemes [12,22] which add such a term to spin-polarized muffin-tin LSDA calculations, the spin polarization deals with the spin magnetism and this term (plus spin-orbit coupling) is responsible for orbital magnetic effects. In contrast with the LSDA treatment of aspherical effects, where $\pm m_\ell$ are treated identically, the introduction of Eq. (A2) differentiates between up and down orbital angular momenta. Use of this equation avoids the issue of whether orbital effects can be properly described within the single-determinant description intrinsic to band theory. More seriously, however, Eq. (A1) is only occasionally correct in its description of free atom multiplet levels. Given its ready utilization in band calculations, Eq. (A2) will be widely employed, but it seems appropriate to review the circumstances under which it is valid when applied to a set of levels with different values of L but with a common S. Consider four cases associated with open d^n and f^n shells (the behavior of the f^n shell multiplets in their maximum spin manifolds may be easily read off Fig. 1.9 of Ref. [25]; the results for the d^n may be obtained from Refs. [4,26] if one converts the Slater F^k integrals into their Racah combinations).

(i) d^2, d^3, d^7, and d^8. The states of maximum spin are F and P levels whose separate energies do not obey Eq. (A1), but whose energy difference may be written as

$$E(F)-E(P)=\chi\Delta[L(L+1)]B, \tag{A3}$$

where $\chi=-\frac{3}{2}$, the coefficient employed in [22] in calculations of transition-metal oxides. For states of less than maximum S, the states of maximum L are not the lowest lying in energy; Hund's second rule, properly stated, only applies to states of maximum spin. No single value for the coefficient χ describes the splittings between the sets of states of lower S.

(ii) d^4, d^5, d^6, f^6, f^7, and f^8. These configurations have only a single multiplet state of maximum S. In the manifolds of lower spin, the states of maximum L often lie lowest. In such cases, χ is negative when defining the energy of this state with respect to another. However, no single choice of χ defines the splitting between all the L states of any one of these manifolds.

(iii) f^2, f^5, f^9, and f^{12}. There are H, F, and P multiplet states in the maximum spin manifolds. The splittings between the H and F levels have the form of Eq. (A3), with $\chi=-\frac{1}{2}$ and with E^3 replacing B. However, the same expression does not give the energy of the P state correctly with respect to the others.

(iv) f^3, f^4, f^{10}, and f^{11}. These configurations have I, G, F, D, and S states in their maximum spin manifold. The I and S states are the only f^n states which conform to Eq. (A1) and for these $\chi=-\frac{1}{2}$. Although the I state does lie lowest, the order of the energy levels, with L, does not conform with Eqs. (A1)–(A3).

Equation (A2) is justified for only a very limited set of the multiplet levels. However, the very ease of its utilization strongly encourages its use. If a spin-polarized band structure without this term (and without spin-orbit coupling) represents an quenched orbital moment state, the process of turning on this term may be viewed as unquenching; one can perhaps rationalize a choice of χ based on the states involved in the unquenching. Such a choice, however, will not lead to a single value of χ for the open d^n (or f^n) systems, or even a single value for a given atom in different environments.

APPENDIX B: COMPUTATIONAL DETAILS

The radial atomic basis functions were calculated using a standard self-consistent LSDA/GGA relativistic atomic program for spherical densities. LSDA [2,27] or GGA [3] exchange-correlation potentials were used; different choices of exchange-correlation approximations have little effect on the results since the radial wave functions are similar. Likewise, changes in the reference state by, for example, occupying the $d_{5/2}$ rather the the $d_{3/2}$ orbital during the self-consistent atomic calculation, had negligible effect on the calculated multiplet splitting, although the absolute total energy of the atom did change.

Slater determinants of definite M_L and M_S of the open-d-shell electrons are formed by combining these radial functions with spherical harmonics and two-dimensional spinors. These determinants are then combined to form the Hartree-Fock wave functions for the multiplet states. The Hartree-Fock energies given were then calculated using these wave functions, and are in agreement with previous results [4]. Each wave function has well-defined (aspherical) charge and spin densities. These densities were, in turn, used to obtain the LSDA/GGA energies, including all nonspherical contributions to the Coulomb and exchange-correlation energies.

The Slater-Condon-Racah fits were straightforward rms fits employing the expressions to be found in Ref. [4]. The subscript labels in the figures for cases where more than one set of levels for some given S and L are allowed follow Slater's definitions [4].

The zeros of energy in the figures are set at the center of gravity of the multiplets of a given configuration. Obviously all the multiplet level positions are required when determining such a center of gravity. Even in the best cases, typically one or two high-lying levels are missing from the experimental data. To account for these levels, Slater-Condon-Racah fits were made of the available data and the resulting F^k were used to estimate the positions of the missing levels. This procedure introduces only a slight error (of order a few hundredths of an eV) into the calculated centers of gravity because the missing levels are few and of low degeneracy (although high in energy).

---

[1] P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964); W. Kohn and L. J. Sham, *ibid.* **140**, A1130 (1965); for general references, see, e.g., A. K. Rajagopal, Adv. Chem. Phys. **41**, 59 (1980).

[2] U. von Barth and L. Hedin, J. Phys. C **5**, 1629 (1972).

[3] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996).

[4] J. C. Slater, *Quantum Theory of Atomic Structure* (McGraw-Hill, New York, 1960), Vols. I and II; E. U. Condon and H. Odabasi, *Atomic Structure* (Cambridge University Press, Cambridge, England, 1980).

[5] For example, for 3d ions, see R. E. Watson, Phys. Rev. **118**, 1036 (1960).

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

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

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

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

[10] M. Petersilka, U. J. Gossmann, and E. K. U. Gross, Phys. Rev. Lett. **76**, 1212 (1996); R. E. Stratmann, G. E. Scuseria, and M. J. Frisch, J. Chem. Phys. **109**, 8218 (1998); M. Valiev and G. W. Fernando, Phys. Lett. A **227**, 265 (1997).

[11] For example, A. K. Rajagopal and J. Callaway, Phys. Rev. B **7**, 1912 (1973).

[12] M. S. S. Brooks and P. J. Kelly, Phys. Rev. Lett. **51**, 1708 (1983); O. Eriksson, B. Johansson, and M. S. S. Brooks, J. Phys.: Condens. Matter **1**, 4005 (1989); O. Eriksson, M. S. S. Brooks, and B. Johansson, Phys. Rev. B **41**, 9087 (1990).

[13] E. U. Condon and J. H. Shortley, *The Theory of Atomic Spectra* (Cambridge University Press, London, 1953).

[14] Configuration mixing provides a way to correct Hartree-Fock wave functions and energies for the omission of correlation effects. Crudely speaking, these omissions take two forms. The first is the correlation hole by which electrons keep out of each other's way due to their Coulomb repulsion. This is most (least) important for states of minimum (maximum) spin. This omission causes Hartree-Fock theory to overestimate splittings between states of differing spin, i.e., the splittings associated with Hund's first rule. The exchange term of the LSDA/GGA also overestimates these splittings, but its correlation term acts to correct this. The second type of configuration mixing involves pairs of states of the same symmetry which mix strongly because they are nearly degenerate. This mixing has little to do with the construction of an exchange-correlation hole, but instead, in the case of atoms, with the assumption of a shell structure where atomic states are assigned specific configurations. This type of configuration mixing is presumably of importance to the ratios of the p^n atomic level splittings. Condon and Shortley suggested that this was associated with promoting a single valence p electron into a p shell of higher principal quantum number n. However, such single-substitution configuration mixing tends to be weak (because of zero or near zero valued mixing matrix elements). In more recent years it has become accepted that at least for the $2p^n$ atoms the multiplet splitting ratio is significantly affected by strong mixing between the $2s^2 2p^n$ and the $2p^{n+2}$ configurations, i.e., between configurations that differ by the substitution of a pair of orbitals. When going to solids, such substitutions can be between atomic sites and thus bear a relationship to superexchange couplings.

[15] O. Gunnarsson and B. I. Lundqvist, Phys. Rev. B **13**, 4274 (1976).

[16] See Sec. 8.6 and Table 1.6 of Condon and Shortley (Ref. [13]).

[17] C. E. Moore, *Atomic Energy Levels*, Natl. Bur. Stand. (U.S.) Circ. No. 35 (U.S. GPO, Washington, D.C., 1971); J. Sugar and C. Corliss, J. Phys. Chem. Ref. Data **6**, 317 (1977); **6**, 1253 (1977); **8**, 4 (1979); **10**, 197 (1981); **10**, 1097 (1981); **11**, 135 (1982); **17**, 157 (1988); **19**, 539 (1990).

[18] The different J values of a given multiplet are split by spin-orbit terms; the center of gravity of each such set of levels is used here to compare to the calculations without spin-orbit terms.

[19] Considering experiment further, comparison of $\mathrm{Fe}^+ d^7$ and $\mathrm{Zr}^+ d^3$ shows levels tracking each other pretty well, as might be expected. The greatest discrepancy occurs with the ^2P states with the Zr level lying high and that of Fe lying low. Inspection of other d^3 and d^7 spectra indicates trends more consistent with the behavior of Fe, suggesting that the Zr level is unusually high. (The Slater-Condon-Racah fits are also in accord with the ^2P position in the Fe^+ spectrum and not with that for Zr^+.) The reported spectra for these two ions indicate $^2P d^{n-1} s$ levels that lie below the d^n for Zr^+ and above for Fe^+. Configuration mixing of the pairs of levels would thus tend to raise the Zr d^n levels and lower those of Fe, causing a disparity in the direction seen in Fig. 2. Another explanation for the discrepancy is to suggest that wrong configuration assignments were made for one of the ion spectra, i.e., an interchange of the ^2P levels labeled d^{n-1} and d^n. Cases can sometimes be made for reassigning the experimental labeling, but we doubt that it is appropriate here.

[20] Some multideterminant effects can be approximated by the use of a larger single determinant. This statement follows simply from the mathematical result that the determinant can be written as a sum of its cofactors, which are also determinants, but of lower rank. Note, however, that in such a case the relative weights of the different cofactors are fixed, thereby limiting the variational freedom. Which effects can be included in this way remains an open question.

[21] The magnetization density operator is given by

$$\hat{\mathbf{m}}(\mathbf{r}) = g\mu_B \sum_\nu \delta(\mathbf{r}-\mathbf{r}_\nu)\mathbf{s}^\nu,$$

where $\mathbf{s}^\nu$ is the single-particle spin operator for the νth electron. Applying this operator to a single-determinantal wave function, it is straightforward to show that the x and y components of the magnetization density vanish since s_x and s_y generate spin flips. Thus, the magnetization density depends only on s_z and m_s.

[22] M. R. Norman, Phys. Rev. Lett. **64**, 1162 (1990); Phys. Rev. B **44**, 1364 (1991).

[23] I. V. Solovyev, A. I. Liechtenstein, and K. Terakura, Phys. Rev. Lett. **80**, 5758 (1998); T. Shishidou, T. Oguchi, and T. Jo, Phys. Rev. B **59**, 6813 (1999); D. L. Price, B. R. Cooper, S. P. Lim, and I. Avgin, *ibid.* **61**, 9867 (2000).

[24] G. Racah, Phys. Rev. **61**, 186 (1942); **62**, 438 (1942); **63**, 367 (1943).

[25] Z. B. Goldschmidt, in *Handbook on the Physics and Chemistry of Rare Earths*, edited by K. A. Gschneidner, Jr. and L. Eyring (North Holland, Amsterdam, 1978).

[26] See Appendixes 21a and 24 of Ref. [4].

[27] L. Hedin and B. I. Lundqvist, J. Phys. C **4**, 2064 (1971).