PHYSICAL REVIEW B VOLUME 49, NUMBER 3 15 JANUARY 1994-I

Why the local-spin-density approximation fails to predict the energy bands of Gd correctly

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(Received 12 August 1993)

All energy-band calculations of Gd show seven very-narrow minority-spin $4f$ bands just above the Fermi energy. We show that this resonance is an artifact of the local-spin-density approximation and suggest that it is the reason that all calculations have yielded electronic densities of states at the Fermi energy larger than the experimental value.

The local-spin-density approximation (LSDA) for exchange and correlation (xc) often yields remarkably good results, in spite of its many flaws. Occasionally, however, these flaws are sufficient to cause results which differ markedly from experiment. The LSDA potential $V^{\rm LSDA}_{\rm xc}$ tends to underestimate the xc-potential and this underestimate increases with the spatial localization of the eigenstate upon which $V^{\rm LSDA}_{\rm xc}$ is operating. Thus atomic total energies are underestimated by more than crystalline, resulting in overestimates of cohesive energies; core eigenvalues lie too close to the Fermi energy; energy gaps in insulators and semiconductors are underestimated. Because of its nonlinear form, one cannot rigorously separate the LSDA energy functional $E^{\rm LSDA}_{\rm xc}[\rho_\uparrow,\rho_\downarrow]$ into self-interaction and other-electron interaction terms. Nevertheless if one makes the self-interaction correction[1] (SIC)

$$E^{\rm SIC}_{\rm xc}=E^{\rm LSDA}_{\rm xc}[\rho_\uparrow,\rho_\downarrow]-\Sigma_{\alpha\sigma}\{U[\rho_{\alpha\sigma}]+E^{\rm LSDA}_{\rm xc}[\rho_{\alpha\sigma},0]\}\ , \tag{1}$$

where U is the Coulomb interaction and $\rho_{\alpha\sigma}$ is the charge density of a single occupied orbital with spin σ and one uses $V^{\rm SIC}_{{\rm xc},\alpha\sigma}=\delta E^{\rm SIC}_{\rm xc}/\delta\rho_{\alpha\sigma}$, much improved results are obtained.[2] A second flaw of the LSDA is that it underestimates magnetic energy. For iron it predicts the ground state is paramagnetic face centered cubic rather than ferromagnetic body centered cubic. Although the correct ground state has been obtained[3,4] using gradient corrections[5] to the LSDA, we have pointed out[6] that this flaw arises directly from the nonlinearity of $V^{\rm LSDA}_{\rm xc}$. Consider an expansion of $V^{\rm LSDA}_{x}$ in the core region where $\rho_{\rm core}\gg\rho_{\rm val}$. Then (in Ry)

$$\begin{aligned}V^{\rm LSDA}_{x,\sigma}&=-2(6/\pi)^{1/3}(\rho_{{\rm core}\ \sigma}+\rho_{{\rm val}\ \sigma})^{1/3}\\&\approx-2(6/\pi)^{1/3}(\rho^{1/3}_{{\rm core}\ \sigma}+\rho_{{\rm val}\ \sigma}/3\rho^{2/3}_{{\rm core}\ \sigma})\ ,\end{aligned} \tag{2}$$

so that the exchange between valence electrons in the core region is reduced by a factor of $\frac{1}{3}(\rho_{{\rm val}\ \sigma}/\rho_{{\rm core}\ \sigma})^{2/3}$ from the LSDA potential they would see in the absence of core electrons. Since screening of valence-valence exchange interactions by core electrons is negligible, this consequence of the LSDA is unphysical. But because the total $V^{\rm LSDA}_{\rm xc}$ seen by valence electrons in the core region tends to overestimate the true xc potential, the effects of this are unimportant except in ferromagnetic systems where it causes a reduction of the magnetic energy.

All energy-band calculations[7–12] of Gd of which we are aware have seven narrow majority-spin $4f$ bands passing through the bottom of the conduction bands and seven narrow minority-spin $4f$ bands lying just above Fermi energy. Their densities of states at the Fermi energy, $N(E_F)$, range between 25 and 47 states/Ry, exceeding the experimental value of 21.35 states/Ry.[6] If many-body contributions were included in the calculated $N(E_F)$, the discrepancies would be expected to be even larger. In particular, Singh[7] recently obtained f band manifolds centered 0.5 eV above and 4.5 eV below E_F, each of which has a width of 0.7 eV, but without spin-orbit splitting the widths became 0.2 and 0.4 eV for the occupied and unoccupied manifolds, respectively. He obtained $N(E_F)=27.1$ states/Ry of which about 5 states/Ry were due to minority $4f$ hybridization. Photoemission data shows[13] that the majority $4f$ bands lie 8 eV below E_F; this is just another example of a LSDA core eigenvalue lying too close to E_F.

As far as we know, the existence of the minority $4f$ resonance bands just above E_F has never been questioned but we will show here that their existence is almost certainly an artifact of the LSDA. Singh's calculation indicates that in their absence the calculated $N(E_F)$ might be very close the experimental value. The physical reason for this artifact is very simple and is common to all multiplicative xc potentials. Consider the Hartree-Fock exchange potential for the (α,σ) state,

$$V^{\rm HF}_{\alpha\sigma}({\bf r})=-\sum_{\beta}\int\psi^*_{\beta\sigma}({\bf r}')\psi_{\alpha\sigma}({\bf r}')\frac{1}{|{\bf r}-{\bf r}'|}d{\bf r}'\frac{\psi_{\beta\sigma}({\bf r})}{\psi_{\alpha\sigma}({\bf r})}\ . \tag{3}$$

Slater[14] suggested multiplying this by $\rho_{\alpha\sigma}({\bf r})/\rho({\bf r})$ and summing over α to obtain the multiplicitive potential,

$$V^{\rm AFA}_{\sigma}=-\sum_{\alpha,\beta}\int\frac{\psi^*_{\beta\sigma}({\bf r}')\psi_{\alpha\sigma}({\bf r}')}{|{\bf r}-{\bf r}'|}d{\bf r}'\frac{\psi^*_{\alpha\sigma}({\bf r})\psi_{\beta\sigma}({\bf r})}{\rho({\bf r})}\ , \tag{4}$$

where the AFA stands for averaged Fock approximation, a designation we[15] have used to distinguish this from other Slater exchange potentials. Because of the $\rho_{\alpha\sigma}$ weight-

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ing, in the core region V_σ^{AFA} is essentially an average of core $V_{\alpha\sigma}^{\mathrm{HF}}$'s and in the valence region an average of valence $V_{\alpha\beta}^{\mathrm{HF}}$'s. A core $V_{\alpha\sigma}^{\mathrm{HF}}$ is larger in the core region than a valence $V_{\alpha\sigma}^{\mathrm{HF}}$, if only because of the self-interaction term. Thus V_σ^{AFA} is too attractive for valence electrons in the core region. $V_{x\sigma}^{\mathrm{LSDA}}$ is $\frac{2}{3}$ of Slater's[14] local-density approximation to V_σ^{AFA} and although it underestimates the self-interaction, it is still too attractive for valence electrons in the core region. For ordinary valence electrons this excess attractiveness is of little consequence, both because these electrons have only a small fraction of their integrated density inside the core region and because they must remain orthogonal to the core electrons of the same symmetry, which prevents them from collapsing into the core region. The $4f$ electrons are a special case. For a given potential they are corelike, higher in energy than in $5s$ and $5p$ core electrons, but more localized. For a potential only slightly less attractive in the core region they become Rydberg-like states, much higher in energy and much more delocalized than the $6s$ valence states.

We have solved the spin-orbit averaged[16] Hartree-Fock-Dirac[17] equation for Gd in the $4f_\uparrow^7 5d_\uparrow 6s_\uparrow 6s_\downarrow$ configuration as well as the spin-orbit-averaged[16] Dirac equation in the LSDA using von Barth–Hedin[18] correlation with Hedin-Lundqvist parameters.[19] The eigenvalues are listed in Table I. Because with the LSDA, unoccupied states see the same potential as occupied ones, the LSDA $4f_\downarrow$ and $5d_\downarrow$ states are well bound. In the HF approximation unoccupied states have no self-interaction term and the $4f_\downarrow$ state is unbound. In order to bind the HF $4f_\downarrow$ state we occupied it in a $4f_\uparrow^7 4f_\downarrow 6s_\uparrow 6s_\downarrow$ configuration. Its eigenvalue of -0.866 eV is only slightly below the -0.860 eV obtained for an occupied $5f_\uparrow$ state. In Fig. 1, the HF potentials of $4f_\uparrow$ and $4f_\downarrow$ electrons from Eq. (3) are compared with the $V_{x,\sigma}^{\mathrm{LSDA}}$. Because of the large $l(l+1)/r^2$ term in these radial potentials, there is only a narrow region in which they are strongly attractive. The majority HF potential lies lowest in this region. The majority LSDA potential lies higher because of its underestimate of the self-interaction. The LSDA potential for the unoccupied minority $4f$ state, which should have no self-interaction, sees the same potential as every other minority-spin state and therefore has a large self-interaction component. Thus on the scale of Fig. 1 it lies only slightly above the majority LSDA potential. This, however, is enough to make the minority $4f$ eigenvalue lie 5.2 eV above the majority (in Table I), demonstrating the relevance of atomic calculations to crystalline calculations[7] where the splitting of the $4f$ manifolds was 5 eV. The minority $4f$ HF state was treated as occupied, but it is so diffuse that its self-interaction is extremely weak and its potential much higher than any of the other's in the attractive region. Finally, we note that the majority $4f$ HF potential lies below all the other potentials even at large $\mathbf{r}$. This is merely a consequence of the fact that $V_{\alpha\sigma}^{\mathrm{HF}}(\mathbf{r}) \to -\infty$ as $\psi_{\alpha\sigma}(\mathbf{r}) \to 0$.

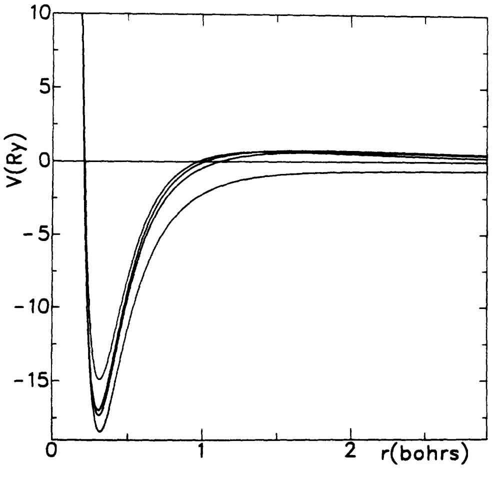

FIG. 1. Radial potentials seen by Gd $4f$ electrons. From highest to lowest in the region of their minima they are HF minority, LSDA minority, LSDA majority, and HF majority. All potentials are in the $4f_\uparrow^7 5d_\uparrow 6s^2$ configuration except for the HF minority, which is in the $4f_\uparrow^7 4f_\downarrow 6s^2$ configuration.

TABLE I. Majority- (↑) and minority- (↓) spin eigenvalues of Gd (in eV) calculated with the LSDA and in the HF approximation. The atomic configuration is $4f_\uparrow^7 5d_\uparrow 6s_\uparrow 6s_\downarrow$ except that the HF $4f_\downarrow$ state, which is unbound in that configuration, has been calculated in the $4f_\uparrow^7 4f_\downarrow 6s_\uparrow 6s_\downarrow$ configuration.

↑ LSDA	↓		↑ HF	↓
−50.845	−47.595	$5s$	−63.369	−58.327
−28.277	−25.691	$5p$	−35.860	−31.502
−10.802	[−5.627]	$4f$	−22.838	(−0.866)
−3.234	[−2.077]	$5d$	−6.647	
−4.587	−3.972	$6s$	−5.761	−5.015

In Fig. 2 the majority HF and LSDA and minority LSDA $4f$ eigenfunctions are plotted. They all look like core orbitals and as expected their peak heights fall in the same order as the depth of their potentials. In Fig. 3 the HF minority $4f$ wave function ($4f_\uparrow^7 4f_\downarrow 6s^2$ configuration) is compared with the majority $5f$ wave function ($4f_\uparrow^7 5f_\uparrow 6s^2$ configuration). For large r the two

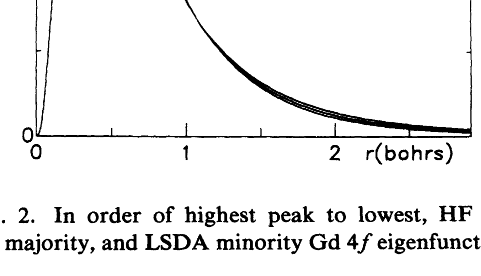

FIG. 2. In order of highest peak to lowest, HF majority, LSDA majority, and LSDA minority Gd $4f$ eigenfunctions.

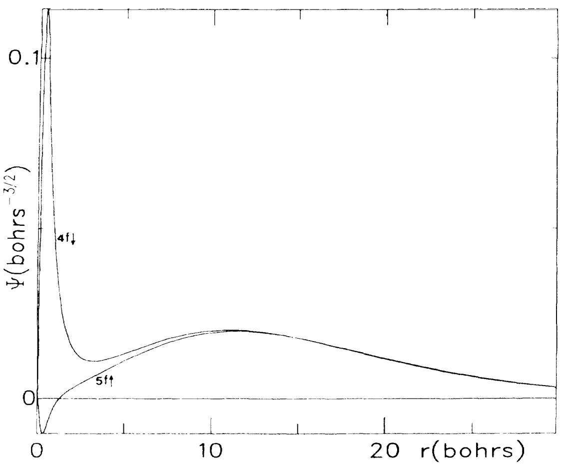

FIG. 3. Comparison of occupied HF $4f$ minority and $5f$ majority Gd eigenfunctions.

functions are indistinguishable so that one should no more expect $4f_\downarrow$ resonances in the crystal than $5f_\uparrow$ resonances. One might argue that a HF potential is not appropriate for electrons in a crystal because of the screening of the valence exchange interaction and we would agree. However, the screening of the core exchange is weak and in the direction to reduce the attractive potential in Fig. 1. Thus an improved potential for the valence electrons in the crystal can be obtained by combining Hartree-Fock exchange with the core electrons (with the majority $4f$ electrons treated as core electrons) with either a LSDA xc potential[20] among themselves or an AFA +correlation potential[15] among themselves. In either case the potential will be less attractive than the HF potential of the $4f_\uparrow^7 4f_\downarrow 6s^2$ configuration so that the $4f_\downarrow$ wave function will not be sucked into the core. The amount by which $N(E_F)$ will be reduced from Singh's[7] value is not just his 5 states/Ry due to minority $4f$ hybridization but will depend in detail on the exact nature of the calculated energy bands around E_F. In fact, the required reduction will be greater than 5 eV to account for the many-body corrections to the band mass. A second feature that the correct band structure must contain is the two small pieces of Fermi surface observed in de Haas–van Alphen (dH–vA) measurements.[21] Singh's bands have two small holes pieces around the K and M points in the Brillouin zone (BZ). Singh argues that for these pieces to be present hybridization with the nearby $4f$ minority bands is required. With a HF core potential, the center of the minority $4f$ bands will be much higher in energy but the bands will be much broader. Hybridization will remain, but it is unlikely that the position, relative to E_F, of the two states at K and M will not be changed significantly even though both these levels and E_F are expected to rise with respect to the bottom of the energy bands. Note, however, that the dH–vA data have not been interpreted to give the position of the two small pieces of Fermi surface in the BZ or even if they are hole or electron pieces. Singh's narrow minority $4f$ bands repel bands from above as well as below so that it is quite possible that new pieces of Fermi surface (either electron or hole) will appear somewhere in the BZ.

We note that the $4f_\uparrow$ HF eigenvalue appears much too low relative to the $4f_\uparrow$ LSDA eigenvalue since the calculated LSDA $4f_\uparrow$ bands[7] are only 3.5 eV above the photoemission results.[13] However[22] $\epsilon_{\alpha\sigma}=\delta E/\delta f_{\alpha\sigma}$ in the LSDA where E is the total energy, $\epsilon_{\alpha\sigma}$ is the eigenvalue, and $f_{\alpha\sigma}$ the occupation of the (α,σ) state. As long as $\partial E/\partial f_{\alpha\sigma}$ is constant over the range $0 \leq f_{\alpha\sigma} \leq 1$, $\epsilon_{\alpha\sigma}$ represents an excitation energy. On the other hand the HF $\epsilon_{\alpha\sigma}$ represents the energy to remove the (α,σ) electron when the other electrons are not allowed to respond.[23] Because of inherent difficulties in obtaining total energies from the spin-orbit averaged Dirac equation, we estimated the relaxation energy by comparing the nonrelativistic HF $4f_\uparrow$ eigenvalue of -28.456 eV with $\Delta E = E(4f_\uparrow^7 5d_\uparrow 6s^2) - E(4f_\uparrow^6 5d_\uparrow 6s^2) = -21.587$ eV. Adding this relaxation energy of 6.869 eV to the relativistic eigenvalue of -22.838 eV yields an estimated HF $4f_\uparrow$ excitation energy of 15.967 eV which is 5.176 eV more than the LSDA eigenvalue. Assuming this difference carries over to the crystal, our estimated crystalline $4f_\uparrow$ excitation energy is 1.676 eV larger than the experimental result.

In conclusion, we have shown that the $4f$ majority bands that have been calculated by many workers[7–11] in the LSDA lie too high in energy but are otherwise correct while the minority $4f_\downarrow$ resonance manifold that they all find just above E_F does not even exist. The removal of this manifold is expected to greatly improve the agreement between the calculated and measured $N(E_F)$.

This work was supported by the University of Texas Center for High Performance Computing, the Welch Foundation (Houston, TX), and the NSF under Grant No. DMR 9015222 and DMR9313645.

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