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Applications of Engel and Vosko's generalized gradient approximation in solids

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Recently, Engel and Vosko have proposed an alternative form of a generalized gradient approximation (GGA) [Phys. Rev. B **47**, 13 164 (1993)] within density-functional theory. This version of the GGA (EV93) was obtained by optimizing the exchange-correlation potential V_{xc} instead of the corresponding energy E_{xc}. We have applied this functional to various solids and found that equilibrium lattice constants generally are far too large in comparison to experiment, so that the total-energy aspect is unsatisfactory. However, EV93 describes FeO and CoO as antiferromagnetic insulators, while the local-spin-density approximation or the Perdew-Wang version of the GGA yields a metallic ground state. EV93 favors magnetism, e.g., the spin susceptibility of V is increased, but Pd remains nonmagnetic in agreement with experiment.

I. INTRODUCTION

In the last years several generalized gradient approximations (GGA) within the density-functional theory (DFT) (Ref. 1) have been developed. In many cases there is a significant improvement over the local-spin-density approximation (LSDA). For example, within LSDA the cohesive energies of most solids and binding energies of molecules are usually overestimated and consequently the respective equilibrium distances are often too short[2] or the ground state of iron is predicted[3] to be the nonmagnetic fcc rather than the ferromagnetic bcc phase observed experimentally. Application of various forms of GGA,[2,4–7] especially that due to Perdew and Wang (PWII) (Ref. 7) improve cohesive energies and equilibrium distances[2,8] and has also led to the correct ground state of Fe.[9–11] Although it was found that in systems (such as Pd), where LSDA already predicts good equilibrium volumes, GGA yields too large values[8,12] or overestimates magnetism,[12] a recent comprehensive study of 3*d*, 4*d*, and 5*d* elements showed substantial overall improvement over LSDA.[13]

Another shortcoming of LSDA calculations is that, for example, the undoped parent compounds of the high-T_c superconductors (e.g., $YBa_2Cu_3O_6$, La_2CuO_4, or $CaCuO_2$) are found to be nonmagnetic metals instead of antiferromagnetic (AF) insulators[14,15] or that the insulating AF transition-metal oxides (like MnO, CoO, or NiO) are computed to be metallic or show only a tiny gap.[16] In these cases PWII yields results closer to experiments such as that for the transition-metal (TM) oxides for which we achieved recently a significant improvement and an almost insulating ground state for CoO,[17] whereas $CaCuO_2$ is driven in the right direction but remains a nonmagnetic metal.[15] Therefore the improvements due to GGA within PWII seem to be so small in these cases that stronger corrections are needed.

In 1993 Engel and Vosko[18] analyzed various versions of GGA exchange potentials and argued that, due to its particularly simple form, GGA's are not able to simultaneously reproduce both the exchange energies E_x and the exchange potentials V_x. They showed that the success of PWII is mainly based on error cancellation in the integrand leading to E_x rather than on the reproduction of the exact exchange potential. Therefore they constructed a new functional form of GGA (denoted as EV93 below) and attempted to better reproduce V_x in atoms even at the expense that E_x agrees less. They determined their potential by firstly calculating the exact V_x (for some atoms) within the so-called optimized-potential model[19–22] (OPM) and secondly they used the virial relation for E_x (Refs. 23 and 24) to construct their new GGA, which now reproduces V_x considerably better. Since they cannot calculate the exact correlation potential V_c within the OPM method they suggested using the standard LSDA-V_c rather than adding gradient corrections for the correlation part as done in PWII.

In this paper we apply EV93 to a wide range of solids and compare the results to PWII and standard LSDA calculations. Firstly, we present total-energy calculations and related quantities such as lattice parameters or bulk moduli for some selected examples (Li, Al, Fe, Nb). Secondly, we concentrate on the energy-band structure (FeO, CoO, $CaCuO_2$) and demonstrate that a significant improvement towards an insulating ground state can be achieved for FeO and CoO. Finally, we report on calculated spin magnetic moments (FeO, CoO, Fe, Ni) and magnetic properties (Pd, V) using EV93.

II. METHOD

In LSDA the exchange-correlation energy (E_{xc}) and the corresponding exchange-correlation potential V_{xc} is just a functional of the local electron-spin densities $n_\uparrow$ and $n_\downarrow$,

$$E_{xc}^{\mathrm{LSDA}}[n_\uparrow,n_\downarrow]=\int n\epsilon_{xc}(n_\uparrow,n_\downarrow)d^3r \ . \tag{1}$$

In the EV93 formalism the exchange energy reads

$$E_x^{\mathrm{EV93}}[n_\uparrow,n_\downarrow]=\sum_{\sigma=\uparrow,\downarrow}\int e_x^{\mathrm{LSDA}}(n_\sigma)f(\xi_\sigma)d^3r \tag{2}$$

with

$$f(\xi_\sigma)=\frac{1+a_1\xi_\sigma+a_2\xi_\sigma^2+a_3\xi_\sigma^3}{1+b_1\xi_\sigma+b_2\xi_\sigma^2+b_3\xi_\sigma^3}\ , \tag{3}$$

where $a_1,\ldots,a_3$ and $b_1,\ldots,b_3$ are constants, which are taken from Ref. 18, and

$$\xi_\sigma=\left[\frac{\nabla n_\sigma(r)}{2k_{F\sigma}(r)n_\sigma(r)}\right]^2 , \tag{4}$$

$$k_{F\sigma}=[6\pi^2 n_\sigma(r)]^{1/3} . \tag{5}$$

The correlation energy is taken from LSDA and therefore the exchange-correlation energy in EV93 is

$$E_{\rm xc}^{\rm EV93}=E_x^{\rm EV93}+E_c^{\rm LSDA} . \tag{6}$$

Limited tests where we added the PWII correlation correction $E_c^{\rm PWII}$ to $E_{\rm xc}^{\rm EV93}$ changed rather little the results, e.g., the equilibrium lattice parameters decreased only by about 0.5% (towards the PWII result). Therefore we base our present investigation on Eq. (6).

We use the full-potential linearized augmented-plane-wave method as embodied in the WIEN93 (Ref. 25) code in a scalar relativistic version without spin-orbit coupling and implement the formalism described above for $E_{\rm xc}$ and the corresponding $V_{\rm xc}$. For the present evaluation of EV93 it is important to include all required gradients, radial as well as angular, which is made possible since WIEN93 is a full potential method.

III. TOTAL ENERGIES AND BULK MODULI

In the present study we performed total-energy calculations for Al as a typical simple metal, for Nb as prototype of a (nonmagnetic) 4*d* transition metal, and for Li and Fe, for which two different structures, bcc and fcc, are reported to have only a small energy difference. The corresponding equilibrium distances and bulk moduli were calculated by fitting Murnaghan's equation of state to the calculated total energies and are compared to experiment, and within the three models (LSDA, PWII, and EV93).

For all calculations we used a sufficiently fine *k* sampling in the irreducible Brillouin zone (IBZ), a large enough basis set of about 100 plane waves (per atom) corresponding to $R_{MT}|\mathbf{k}+\mathbf{K}_{\rm max}|=9.0$, and included local orbitals[26] for the semicore (Fe 3*s*, 3*p* and Nb 4*s*, 4*p*) states in order to guarantee good convergence.

Our results for Li, Al, Fe, and Nb are summarized in Table I including the corresponding deviations from experiment. While LSDA yields lattice constants that are about 1–3% too small as usual, PWII results agree within 1% with experiment. For EV93 lattice constants are obtained that are by far too large (except for Li). The corresponding bulk moduli show an analogous behavior, but opposite in direction: for LSDA calculations they are too large, PWII agrees well with a deviation less than 25% (comparable to the accuracy of the experiment), but using EV93 yields bulk moduli that are much too small (again with the exception of Li). The reason for Li being atypical might be that it is one of the lightest atoms with only three electrons, that have mostly *s* character. Notice that our results for both LSDA and PWII are in excellent agreement with previous calculations.[2,8]

It is well known that LSDA calculations for Fe predict a paramagnetic fcc ground state rather than the experimentally observed ferromagnetic bcc phase. It has been shown,[9–11] that PWII is able to correct this shortcoming and to obtain the right ground state. We reproduced these results and added calculations with the EV93 potential. Figure 1 shows the different total energy curves for Fe with respect to the bcc equilibrium using the three models. Although EV93 still gives the correct ground state, it overestimates the lattice constant significantly as already discussed above. Results of the exchange splitting and the magnetic moment will be discussed in Secs. IV and V.

For Li the situation is somewhat similar to Fe, since at low temperature there are two phases which are close in energy, namely, the bcc and the close-packed 9*R* crystal structure, where the latter is slightly lower in energy. The 9*R* phase can be simulated by the similar but simpler closed-packed fcc structure.[27] We compare the energy per atom of these two phases using our three models and find that the fcc structure is about 2.37 meV (LSDA), 1.78 meV (PWII), or 1.3 meV (EV93) lower in energy than the bcc structure so that in this case all three models

TABLE I. Lattice constants *a* (a.u.) and bulk modulus *B* (GPa) of bcc Li, fcc Al, bcc Fe, and bcc Nb and corresponding deviations (%) with respect to experiment.

	Li		Al		Fe		Nb	
	a	*B*	*a*	*B*	*a*	*B*	*a*	*B*
LSDA	6.356	15	7.540	84	5.229	270	6.167	199
dev. (%)	−3.3	+15	−1.5	+17	−3.3	+57	−1.1	+17
PWII	6.494	12	7.654	74	5.355	215	6.274	177
dev. (%)	−1.2	−8	0	+3	−1.0	+25	+0.6	+4
EV93	6.668	13	7.907	55	5.924	75	6.591	119
dev. (%)	+1.5	0	+3.3	−24	+9.6	−56	+5.7	−30
expt.	6.57[a]	13[b]	7.653[c]	72[c]	5.405[c]	172[c]	6.236[c]	170[c]

[a] Reference 33.

[b] Reference 34.

[c] Reference 35.

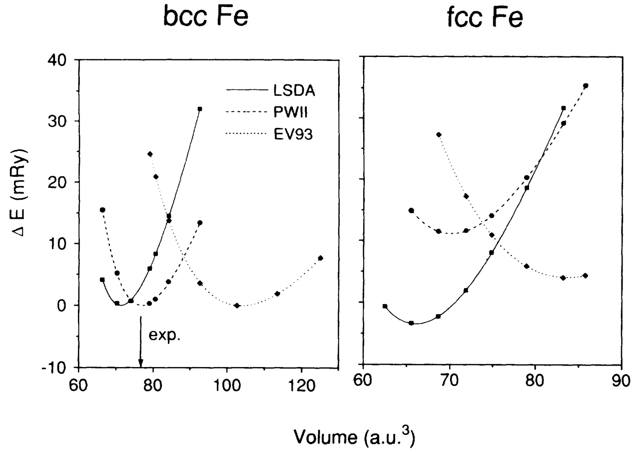

FIG. 1. Total energy (mRy) of Fe (with respect to the bcc equilibrium) in the bcc (left panel) and fcc (right panel) structure as a function of volume for LSDA (squares, solid line), PWII (circles, dashed line), and EV93 (diamonds, dotted line).

predict the correct ground state.

In general, however, EV93 total-energy calculations do not yield good results, but we should remember that EV93 was not constructed to reproduce total energies well.

IV. EFFECTS ON THE BAND STRUCTURE

Since EV93 was developed to yield a better V_x we now want to demonstrate that it really improves results such as the band structure which mainly depends on the accuracy of V_x. For that purpose we choose the two TM oxides, FeO, and CoO, which LSDA finds to be AF metals in contrast to experiment. We have shown recently[17] that with PWII a direct gap opens up in CoO with a remaining small indirect band overlap, while for FeO one needs an additional potential shift to stabilize an insulating solution. EV93, however, leads to an insulating state for both compounds, FeO and CoO. (Computational details are similar to our previous paper.)[17]

The TM oxides crystallize in the sodium chloride structure (neglecting the sometimes observed small distortions) and are insulators with the AF II structure, where the spin alignment is parallel within and AF between consecutive (111) planes (see Fig. 1 of Ref. 17). In the cubic nonmagnetic case the d levels split into e_g and t_{2g} states but in the trigonal AF II structure[16] of these TM oxides the t_{2g} bands are further split into bands corresponding to a twofold e_g (denoted below as e_g') and an a_{1g} symmetry.[16] This lower symmetry can lead to an insulating ground state which we investigate for FeO.

Figure 2(a) shows the d bands of FeO within LSDA, where the lowest three bands correspond to the t_{2g} spin-up manifold followed by the e_g spin-up subbands; around the Fermi energy, E_F, we find the t_{2g} and, higher up in energy, the e_g spin-down bands. The size of the circles is proportional to the a_{1g} spin-down character of the respective states. Within the t_{2g} spin-down manifold there is a strong mixing of a_{1g} and e_g' character since the a_{1g} character appears in two bands above and one band below E_F.

When we apply EV93 we obtain, depending on the starting configuration, two stable states of comparable energy, namely, a metallic [Fig. 2(b)] or an insulating [Fig. 2(c)] one. Starting from the self-consistent LSDA density we obtain the metallic state with the band structure shown in Fig. 2(b) where E_F falls within the e_g' bands and the a_{1g} band is well separated and shifted to higher energies. However, if one starts the calculation by artificially occupying this a_{1g} band, then a stable self-consistent solution is found [Fig. 2(c)] that is an insulator with a gap of 0.29 eV. The a_{1g} subband remains occupied and has almost pure a_{1g} symmetry. Within our computational accuracy the total energy of the insulating and metallic state is the same so that we cannot decide about the ground state.

In the case of CoO, which has one valence electron more than FeO, the band splitting of the t_{2g} spin-down manifold is qualitatively the same as that of the metallic FeO [Fig. 2(b)], where E_F lies above the e_g' bands. We have already shown[17] that PWII leads to an almost insulating ground state with a small indirect band overlap, but EV93 yields an insulator with a gap of 0.48 eV.

For CaCuO$_2$, a parent compound of the high-T_c superconductors, the situation is even worse than for the TM oxides, since LSDA calculations cannot even recover the AF state. Singh and Pickett[15] have shown that an AF state can be obtained by artificially adding and subtracting a constant shift to the spin-up and spin-down nonspherical ($L=4$, $M=0$) part of the potential ($L4$ field).

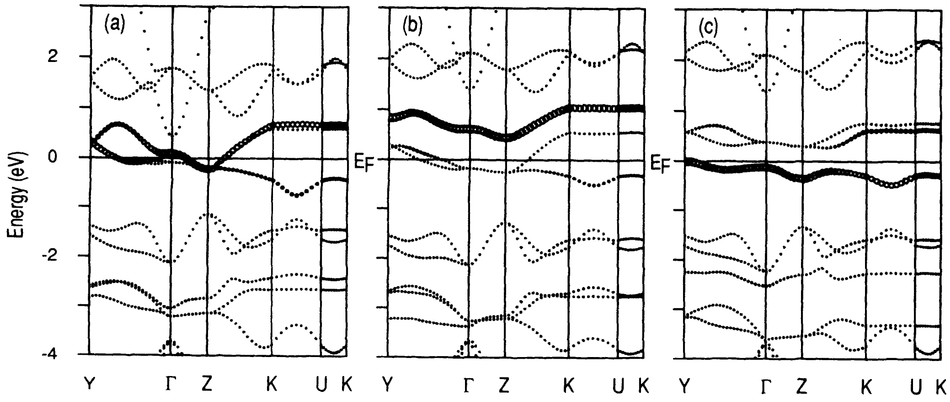

FIG. 2. Band structure of FeO for LSDA (a) and EV93 (b), (c). The size of the circles is proportional to the a_{1g} spin-down character of each state.

Applying this procedure with a $L4$ field of 50 mRy we obtain with LSDA, PWII, or EV93 moments of 0.117, 0.186, and $0.286\mu_B$, respectively. Within EV93 this moment vanishes only slowly during the iteration cycles when the $L4$ field is switched off. Note that a fine k grid of more than 60 k points in the IBZ is required indicating that EV93 favors the AF solution more than LSDA or PWII.

We have also investigated the exchange splitting in Fe and Ni, where LSDA agrees for Fe but yields about twice the experimental splitting for Ni.[28] This situation does not improve using EV93 (nor with PWII).

V. MAGNETIC PROPERTIES

Firstly, we summarize in Table II the spin magnetic moments of FeO, CoO, Fe, and Ni which are computed at the experimental volume using EV93 and compare them with the LSDA, PWII results, and experiment. In general EV93 leads to larger moments with respect to PWII and LSDA. The Ni moment is hardly affected, since it is a strong ferromagnet, but for Fe the moment increases above the experimental value. For the oxides a comparison with experiment is difficult, since the experimental moments contain orbital contributions, while our calculation (within a scalar relativistic approach) gives only spin moments. In the case of CoO orbital contributions are claimed to be more than $1\mu_B$ (Refs. 29 and 30) and increase with increasing localization of the bands.[30] Note that for FeO and CoO the choice of atomic sphere radii determines the attribution of the spin density to a particular atom and thus the respective magnetic moment depends on R_{MT} (2.0 a.u. for Fe and Co).

The two transition metals fcc Pd and bcc V are close to a magnetic instability and thus provide a crucial test system for the EV93 potential. As shown above, EV93 seems to enhance magnetic moments and thus it could lead to a magnetic ground state. In order to check whether or not this is true we have performed fixed spin moment (FSM) calculations[31,32] for Pd up to a moment of $0.3\mu_B$ using 2000 k points in the IBZ. As a function of moment the total energy rises monotonically with a very small slope corresponding to a large paramagnetic susceptibility. A paramagnetic ground state but no metamagnetic solution was found with all three models reproducing the earlier results obtained with LSDA and PWII.[12]

For bcc V we performed FSM calculations up to a moment of $1\mu_B$ using a grid of 1000 k points in IBZ, but again no metamagnetic solution was found with EV93. In Fig. 3 we show the magnetic field as a function of moment using the three models. From the slope at zero moment (which is estimated from the FSM calculation at $0.1\mu_B$ with a numerical uncertainty of about 5%), the spin susceptibility can be determined. Using EV93 we obtain a value of 7.5 emu/g, slightly larger than the experimental value of 6.0, but significantly higher than the LSDA (3.8) or the PWII (4.6) values, which agree well with previous calculations.[12] LSDA and PWII calculations drastically underestimate the spin susceptibility, while EV93 overestimates it by 25%.

TABLE II. Spin magnetic moments (μ_B) according to our LSDA, PWII, EV93 calculations and comparison to literature.

	LSDA	PWII	EV93	Expt.
FeO	3.33 (3.43)[a]	3.38	3.41	3.32[b]
CoO	2.36 (2.35)[a]	2.42	2.48	3.35,[c] 3.8[b]
Fe	2.21	2.21	2.31	2.13
Ni	0.600	0.612	0.617	0.57

[a] Reference 16.
[b] Reference 36.
[c] Reference 37.

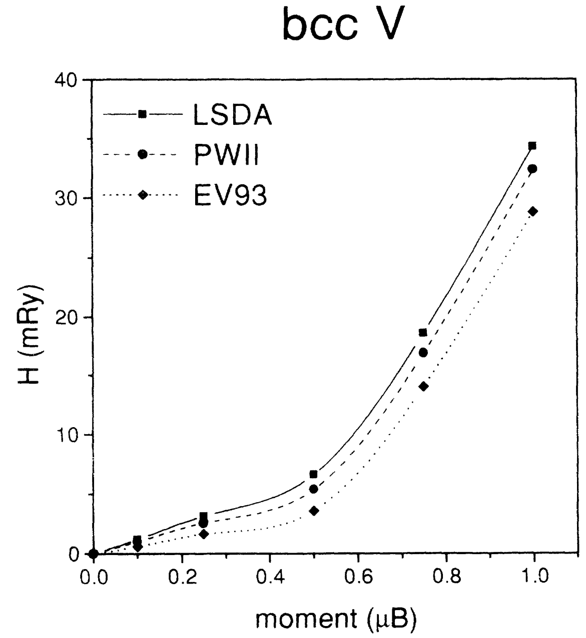

FIG. 3. Stabilizing field H (in mRy) as function of moment based on a FSM calculation for V using the three models.

VI. CONCLUSION

We have tested a new form of GGA derived by Engel and Vosko[18] in various solids. EV93 was designed to give a better exchange potential V_x, but the exchange energy E_x for atoms was less accurately reproduced. In fact, EV93 yields a better band splitting and more localized states for the AF TM oxides as well as an enhancement of magnetism in $CaCuO_2$ and the spin susceptibility of the bcc V. On the other hand, quantities which depend on an accurate description of E_x such as equilibrium volumes and bulk moduli are in poor agreement with experiment, e.g., for the tested systems lattice constants are too large (1.5–9.6 %) and bulk moduli are by far too small (up to 56%). Further analysis of these problems could lead to new insights and hopefully to an optimal form of GGA.

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