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Ground-state properties of third-row elements with nonlocal density functionals

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The cohesive energy, the lattice parameter, and the bulk modulus of third-row elements are calculated using the Langreth-Mehl-Hu (LMH), the Perdew-Wang (PW), and the gradient expansion functionals. The PW functional is found to give somewhat better results than the LMH functional and both are found to typically remove half the errors in the local-spin-density (LSD) approximation, while the gradient expansion gives worse results than the local-density approximation. For Fe both the LMH and PW functionals correctly predict a ferromagnetic bcc ground state, while the LSD approximation and the gradient expansion predict a nonmagnetic fcc ground state.

The local-spin-density (LSD) approximation of the density functional (DF) formalism[1] provides a rather accurate description of the ground-state properties of the elementary *spd* bonded metals.[2] Some aspects of the description are, nevertheless, less satisfactory. For instance, the cohesive energy is too large, in particular for the $3d$ metals, where the errors can be a few eV. The lattice parameter is also slightly underestimated and for the $3d$ metals this error is typically 3–4%. Finally, the LSD approximation incorrectly predicts that for Fe the fcc structure has a lower total energy than the bcc structure.[3] It is therefore interesting to test alternative functionals for the $3d$ metals.

An early attempt to improve the LSD approximation was the gradient expansion approximation (GEA).[1] Calculations for atoms[4,5] and a jellium surface[6] show, however, that the GEA does not improve the LSD approximation, if the calculated *ab initio* coefficients of the gradient correction[4,7,8] are used. The errors in the GEA have been studied by Langreth and Perdew[6,9] and by Perdew.[10] Based on this analysis Langreth and Mehl[11] and Hu and Langreth[12] (LMH), as well as Perdew[13] and Perdew and Wang[14] (PW), have proposed modified gradient expansions for the exchange-correlation energy.

The LMH and PW functionals have only been tested in rather few cases, but they give encouraging results for the ground-state properties in these cases. For atoms it was found that both total energies and removal energies are improved in the LMH functional compared with the LSD approximation.[11,12] The PW functional gives a further improvement in the total energy of atoms.[13,14] The binding energies of the first row diatomic molecules are also improved by both functionals.[15,16] In a study of the band structure of V and Cu, Norman and Koelling[17] found that the LMH potential gave an improvement in the Fermi surface for V but not for Cu. The deviation of the band structure from photoemission results also increased somewhat for Cu. The ground-state properties were not studied. For Si von Barth and Car[18] found a similar error (factor 2) in the band gap as in the LSD approximation, while the cohesive energy (4.89 eV) was improved over the LSD result (5.19 eV) compared with experiment (4.63 eV).

The usefulness of the LMH, PW, and GEA functionals relative to the LSD approximation has remained a matter of controversy.[19] It is therefore interesting to apply these approximations to the $3d$ metals. Here we study the cohesive energy, the lattice parameter, and the bulk modulus. We also compare the total energies of the fcc and bcc phases for Fe. We find that for these properties the LMH and PW functionals generally give a substantial improvement compared with LSD approximation, while the GEA gives worse results. In particular, we find that the ground state of Fe has a bcc lattice structure. In most cases the PW functional gives somewhat better results than the LMH functional.

Langreth and Perdew[9] used a wave-vector analysis to study the contribution to the exchange-correlation energy from different wave vectors k. They found that while the GEA is quite accurate for large values of k, it gives a large unphysical contribution for small values of k. To correct for this error, Langreth and Meth[11] proposed a method where the gradient corrections for the correlation energy were put to zero for $k < k_c$. For the cutoff k_c they used the value $k_c = f\,|\nabla n/n\,|$, where n is the electron density and $f = 0.15$ is an empirical constant used for all systems. Perdew[13] introduced a somewhat different correlation energy functional, which goes over to the GEA in the limit of small density gradients, as it should, and which contains contributions beyond the random-phase approximation (RPA). Perdew and Wang[14] and Perdew[10] studied the exchange hole in the gradient expansion and introduced cutoffs, which impose a sum rule[20] on the hole as well as the condition that the hole is nonpositive. The LMH exchange-correlation functional can be written as

$$E_{\mathrm{xc}} = E_{\mathrm{xc}}^{\mathrm{LSD\text{-}RPA}} + J\int d^3r \left[-\frac{7}{9} 2^{-1/3} \left(\frac{(\nabla n_\uparrow)^2}{n_\uparrow^{4/3}} + \frac{(\nabla n_\downarrow)^2}{n_\downarrow^{4/3}} \right) + \frac{2}{d} \frac{(\nabla n)^2}{n^{4/3}} e^{-F} \right], \qquad (1)$$

where $E_{\mathrm{xc}}^{\mathrm{LSD\text{-}RPA}}$ is the exchange-correlation energy in the LSD approximation using RPA electron gas data, $n_\uparrow$ and $n_\downarrow$ are the spin densities, $n = n_\uparrow + n_\downarrow$, $J = \pi/[8 \times (3\pi^2)^{4/3}]$, and $F = 2\sqrt{3} f\,|\nabla n\,|/nk_{FT}$, with $k_{FT} = 2(3n/\ \pi)^{1/6}$. We further have $d=2^{-1/2}[(1+\xi)^{5/3}+(1-\xi)^{5/3}]^{1/2}$, where $\xi=(n_\uparrow-n_\downarrow)/n$ is the spin polarization. Densities and lengths are expressed in the units a_0^{-3} and a_0, respectively, where a_0 is the Bohr radius, and energies in Ry. By putting $f=0$ (or $F=0$) in (1) we can recover the normal gradient expansion. The coefficients in this gradient expansion differ slightly from those obtained by Rasolt,[8] due to approximations introduced in the wave-vector expansion for $0<\xi<1$. The PW exchange functional is written as

$$E_x[n]=A_x\int d^3r\, n^{4/3}(\mathbf{r})F(s)\,, \tag{2}$$

where $A_x=-\frac{3}{2}(3/\pi)^{1/3}$, $s=|\nabla n|/[2(3\pi^2)^{1/3}n(\mathbf{r})^{4/3}]$, and $F(s)=(1+as^2+bs^4+cs^6)^m$, with $a=1.296$, $b=14$, $c=0.2$, and $m=\frac{1}{15}$. For a spin-polarized system the exchange energy is obtained from $E_x[n_\uparrow,n_\downarrow]=\frac{1}{2}E_x[2n_\uparrow]+\frac{1}{2}E_x[2n_\downarrow]$. The correlation energy is given by

$$E_c[n_\uparrow,n_\downarrow]=E_c^{\text{LSD-CA}}+\int d^3r\frac{1}{d}e^{-\Phi}C(n)\frac{|\nabla n|^2}{n^{4/3}}\,, \tag{3}$$

where $E_c^{\text{LSD-CA}}$ is the LSD correlation energy with the Ceperly-Alder parametrization,[21]

$$C(n)=0.003\,334+2\frac{0.002\,568+\alpha r_s+\beta r_s^2}{1+\gamma r_s+\delta r_s^2+10^4\beta r_s^3}\,,$$

with $r_s=(4\pi n/3)^{-1/3}$, $\alpha=0.023\,266$, $\beta=7.389\times10^{-6}$, $\gamma=8.723$, $\delta=0.472$ is the coefficient in the gradient expansion,[22] and

$$\Phi=1.745\tilde{f}[C(\infty)/C(n)]\,|\nabla n|/n^{7/6}\,,$$

with $\tilde{f}=0.11$.

The results presented here were calculated self-consistently using the linear muffin-tin orbital (LMTO) method in the atomic-spheres-approximation[23] (ASA). This widely used method has been described in length elsewhere[23] and we shall therefore only give some technical details of how the calculations were performed. The main approximations in the LMTO-ASA method are as follows: First, the potential and the total energies are calculated from spherically averaged charge densities; and second, the Wigner-Seitz cell is approximated by a sphere. We shall later comment on the former approximation. The latter approximation was corrected by including the so-called combined correction term[23] which also corrects for the neglected higher partial waves. The basis consisted of *spdf*-LMTO's for all elements except potassium where *spd*-LMTO's were used. We employed the linear tetrahedron method[24] for the *k*-space integrations and this was implemented so that no misweight of any *k* points occurred. Moreover, simple correction for the approximate linearity of the energy bands between the *k* points were also included.[25] A mesh of about 200 irreducible *k* points were used except for iron where about 500 points were used. A doubling of these meshes led to changes in the total energies of the order of a few tenths of a mRy. Also in the atomic calculations a spherical averaged density was used. This influences the cohesive energy for V and Fe, but not for K, Ca, and Cu, which have spherically symmetric atoms.

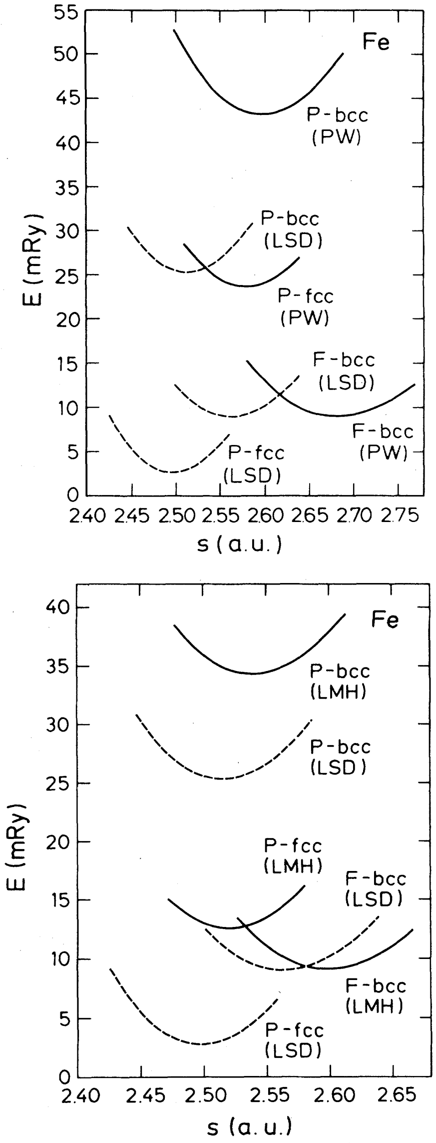

FIG. 1. Calculated total energy of paramagnetic (*P*) bcc and fcc and ferromagnetic (*F*) bcc iron as a function of the Wigner-Seitz radius (*s*). The dotted curve corresponds to the LSD approximation and the solid curve corresponds to the LMH and PW approximations. The curves are displaced in energy so that the minimum for the *F* bcc coincides.

In Fig. 1 the total energy of Fe as a function of the Wigner-Seitz radius is shown for the paramagnetic fcc and bcc phases and the ferromagnetic bcc phase calculated in the LSD, LMH, and PW approximations. We first observe that both the LMH and PW functionals correctly predict a ferromagnetic bcc ground state, while the LSD approximation predicts a fcc ground state. The Wigner-Seitz radius is also improved substantially, in particular in the PW approximation. In contrast, the GEA is worse than the LSD approximation. The GEA predicts that the fcc phase is about 8 mRy (LSD 6 mRy) below the bcc phase, and the error in the Wigner-Seitz radius is more than twice as large as in the LSD approximation.

To analyze the improvements in the PW and LMH functionals, we notice from Fig. 1 that both functionals add an energy contribution which is roughly linear in the Wigner-Seitz radius s to the LSD functional. This term is

$$\Delta E(s) = As + B , \qquad (4)$$

where $A \sim -40$ and $A \sim -160$ mRy/a_0 for the LMH and PW functionals, respectively. Using the experimental bulk modulus, we deduce that the Wigner-Seitz radii are increased by about 0.04 and 0.14a_0 in the LMH and PW functionals, respectively, in rather good agreement with the full calculations. Since the bcc phase is ferromagnetic while the fcc phase is weakly antiferromagnetic or paramagnetic, the Wigner-Seitz radius is larger in the bcc phase. In the LSD approximation the difference is about 0.07a_0. Because of the additional term (4) in the nonlocal functionals, the larger Wigner-Seitz radius of the bcc phase favors this phase. We can estimate this gain to be about 3 and 11 mRy in the LMH and PW functionals, respectively. In addition, both the LMH and PW functionals favor a magnetic moment also for a fixed Wigner-Seitz radius. This can be seen by comparing the energy gain in going from the paramagnetic to the ferromagnetic phase in the LSD approximation and in one of the nonlocal functionals at a fixed Wigner-Seitz radius. We estimate this gain to be 7 and 5 mRy in the two functionals. From this we conclude that relative to the LSD approximation the LMH and PW functionals favor the bcc phase over the fcc by about $3+7=10$ and $11+5=16$ mRy, respectively, which is rather close to what is obtained in the full calculations. We note that the term depending on the Wigner-Seitz radius (4) contributes about $\frac{1}{3}$ and $\frac{2}{3}$ of the full effect in the LMH and PW functionals, respectively. The spin part of the magnetic moment calculated at the experimental lattice parameter is found to be 2.30μ_B (LMH) and 2.32μ_B (PW), compared with 2.23μ_B in the LSD approximation and 2.21μ_B experimentally. The (small) increase in the magnetic moment in the LMH and PW functionals is consistent with the somewhat greater tendency of these functionals to favor the ferromagnetic phase for Fe.

The calculated ground-state properties of third row elements are shown in Table I. The Wigner-Seitz radius is generally increased, as one would expect from correction (4), which appears for all the elements considered. For the LMH functional we find $A \sim -13$ (K), -20 (Ca), -50 (V), and -40 (Cu) mRy/a_0 and for the PW functional $A \sim -7$ (K), -20 (Ca), -120 (V), and -130 (Cu) mRy/a_0. The LMH functional removes about $\frac{1}{3}$ of the error in the LSD approximation. The PW functional gives a further improvement in most cases, but there is an overcorrection towards the end of the series. The bulk modulus is also improved by the LMH and PW functionals, although there is a tendency by the PW functional to overcorrect the LSD errors. For the cohesive energy, finally, there are substantial improvements for all the elements investigated, except K where the LSD error already is very small. In particular, the PW functional gives a very substantial reduction in the errors for Ca, V, Fe, and Cu. It has earlier been observed that inclusion of the nonspherical components of the density lowers the energy of first row atoms in the LMH and PW functionals.[16] For V and Fe, which have nonspherical atoms, we expect the nonspherical effects to be more important in the atom than in the solid, while the opposite should be true for K, Ca, and Cu, which have spherical atoms. If the observations[16] for the first row atoms also apply here, we would expect this to reduce the calculated cohesive energy for V and Fe but to increase it for K, Ca, and Cu. These corrections would go in the right direction for both the LMH (except for Ca and Cu) and the PW functionals.

TABLE I. The equilibrium Wigner-Seitz radii (a.u.) (s), the bulk modulii (kbar) (B) calculated at the experimental value of s, and the cohesive energies (eV/atom) (E_c) for some third row elements as measured (expt) and calculated in the LSD approximation, using the LMH and PW exchange and correlation functions. The total energies for the solids as well as for the atoms were calculated using a spherically symmetrized charge density.

	K	Ca	V	Fe	Cu
$s_{\rm expt}$	4.862	4.122	2.818	2.662	2.669
$s_{\rm LSD}$	4.656	3.982	2.730	2.562	2.592
$s_{\rm LMH}$	4.929	4.018	2.763	2.598	2.626
$s_{\rm PW}$	4.809	4.026	2.822	2.681	2.714
$B_{\rm expt}$	31.8	152	1620	1684	1310
$B_{\rm LSD}$	29.4	114	1482	1525	982
$B_{\rm LMH}$	40.0	148	1603	1721	1394
$B_{\rm PW}$	36.6	155	1825	1674	1678
$E_{c,\rm expt}$	0.94	1.83	5.29	4.31	3.50
$E_{c,\rm LSD}$	1.06	2.43	8.07	6.96	4.72
$E_{c,\rm LMH}$	0.71	2.26	7.41	6.20	3.98
$E_{c,\rm PW}$	0.81	1.70	6.27	5.01	3.37

In this paper we have studied the ground-state properties of some third row elements using the LMH, PW, and GEA functionals. We find systematic improvements using the LMH and PW functionals, which typically remove half the errors in the LSD approximation, while the GEA is worse than the LSD approximation. In particular, the LMH and PW functionals correctly predict a bcc ground state for Fe. Since these functionals are relatively easy to implement, we believe that they represent a promising alternative to the LSD approximation for the calculation of ground-state properties of solids.

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