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Interconfigurational energies in transition-metal atoms using gradient-corrected density-functional theory

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The rapid variation of charge and spin densities in atoms and molecules provides a severe test for local-density-functional theory and for the use of gradient corrections. In the study reported in this paper, we use the Langreth, Mehl, and Hu (LMH) functional and the generalized gradient approximation (GGA) of Perdew and Yue to calculate *s*-*d* transition energies, 4*s* ionization energies, and 3*d* ionization energies for the 3*d* transition-metal atoms. These calculations are compared with results from the local-density functional of Vosko, Wilk, and Nusair. By comparison with experimental energies, we find that the gradient functionals are only marginally more successful than the local-density approximation in calculating energy differences between states in transition-metal atoms. The GGA approximation is somewhat better than the LMH functional for most of the atoms studied, although there are several exceptions.

I. INTRODUCTION

In the 25 years since Hohenberg and Kohn proved that the ground-state effects of electron exchange and correlation can be expressed in a unique functional of the charge and spin densities[1] that are calculable from a single-particle equation,[2] there have been many efforts to approximate this functional and to use it in quantum calculations for atoms, molecules, and especially, periodic solids. Most density functionals have been developed through theories of the homogeneous electron gas,[3] and these are known as *local*-spin-density approximations (LSDAs), because at each point in space the exchange-correlation potential and energy density are determined from the charge and spin densities at that specific point only. This approach has been unexpectedly successful. For atomic and molecular properties (ionization and excitation energies, molecular geometries, binding energies, etc.) and for the structural properties of condensed matter (cohesive energies, lattice constants, etc.) the LSDA is typically at least as accurate as Hartree-Fock descriptions, and is usually better.[4]

Nevertheless, the LSDA is usually far from "chemical accuracy," and the search for better functionals has taken several directions. Density averaging,[5] semiempirical exchange-correlation parametrizations,[6] and the self-interaction correction methods[7,8] are among the various approaches that have been introduced. Series expansion of the local density functional to include gradients of the charge and spin densities is an obvious means of extending the LSDA,[9,10] but such expansions have been disappointing because they usually disrupt the sum rules[11,12] that make the LSDA as successful as it is.

Wave-vector and real-space analysis of the electron gas have recently led to two new gradient schemes which retain the sum-rule properties of the LSDA. The first was developed by Langreth and Mehl,[13] later extended to the spin-polarized case by Hu and Langreth (LMH).[14] The second functional was formulated by Perdew and Yue,[15,16] and in this paper is called the generalized gradient approximation (GGA). The details of these derivations can be found in papers[13-16] describing their development. Each gradient method expresses the exchange-correlation energy, E_{xc}, in terms of the local charge and spin densities and their gradients. In the LMH functional, E_{xc} takes the form (all equations are in Hartree atomic units)

$$E_{\mathrm{xc}}[n(\mathbf{r})] \approx E_{\mathrm{xc}}^{\mathrm{LSDA}}[n(\mathbf{r})] + \frac{\pi}{16(3\pi^2)^{4/3}} \int d^3r \left[\frac{-7}{9(2^{1/3})} \left[\frac{|\nabla n_+(\mathbf{r})|^2}{n_+^{4/3}(\mathbf{r})} + \frac{|\nabla n_-(\mathbf{r})|^2}{n_-^{4/3}(\mathbf{r})} \right] + \frac{2}{d} e^{-F} \frac{|\nabla n(\mathbf{r})|^2}{n^{4/3}(\mathbf{r})} \right] ,$$

where the following definitions are used:

$$d=2^{-1/2}[(1+\zeta)^{5/3}+(1-\zeta)^{5/3}]^{1/2}$$

$$\zeta=\frac{(n_{+}-n_{-})}{n},\quad n=n_{+}+n_{-}$$

$$F=\frac{(9\pi)^{1/6}f|\nabla n(\mathbf{r})|}{n^{7/6}},\quad f=0.15\ \ (\text{this work})\ .$$

The GGA functional for E_{xc} is expressed as

$$E_{\text{xc}}^{\text{GGA}}=E_{x}^{\text{GGA}}+E_{c}^{\text{GGA}}$$

with an exchange contribution of

$$E_{x}^{\text{GGA}}[n(\mathbf{r})]=A_{x}\int d^{3}r\,n^{4/3}F^{\text{GGA}}(s)\ ;$$

$$\mathbf{s}=\frac{\nabla n}{2k_{F}n}\ ,\quad k_{F}=[3\pi^{2}n(\mathbf{r})]^{1/3},\quad A_{x}=-\frac{3}{4}\left[\frac{3}{\pi}\right]^{1/3},$$

$$F^{\text{GGA}}(s)=\left[1+\frac{0.0864s^{2}}{m}+bs^{4}+cs^{6}\right]^{m},$$

$$s=|\mathbf{s}|,\quad m=\tfrac{1}{15},\quad b=14,\quad c=0.2\ ,$$

and spin polarization is obtained by using

$$E_{x}[n_{+},n_{-}]=\tfrac{1}{2}E_{x}[2n_{+}]+\tfrac{1}{2}E_{x}[2n_{-}]\ .$$

The correlation portion of the GGA functional is

$$E_{c}^{\text{GGA}}[n_{+},n_{-}]=E_{c}^{\text{LSDA}}[n_{+},n_{-}]+\int d^{3}r\,d^{-1}C(n)e^{-\Phi}\frac{|\nabla n|^{2}}{n^{4/3}}\ ,$$

where $C(n)$ is defined as

$$C(n)=0.001\,667+\frac{0.002\,568+\alpha r_{s}+\beta r_{s}^{2}}{1+\gamma r_{s}+\delta r_{s}^{2}+10^{4}\beta r_{s}^{3}}\ ,$$

$$r_{s}=\left[\frac{3}{4\pi n}\right]^{1/3},$$

$$\alpha=0.023\,266,\quad \beta=7.389\times10^{-6}\ ,$$

$$\gamma=8.723,\quad \delta=0.472\ ,$$

and Φ is defined as

$$\Phi=1.745\tilde{f}\left[\frac{C(\infty)}{C(n)}\right]\frac{|\nabla n|}{n^{7/6}},\quad \tilde{f}=0.11\ .$$

The exchange-correlation potential v_{xc} needed to solve the Kohn-Sham equations self-consistently can be obtained from the above expressions by functional differentiation:

$$v_{\text{xc}}^{\pm}=\frac{\delta E_{\text{xc}}}{\delta n_{\pm}}\ .$$

Explicit LMH and GGA equations for v_{xc} GGA may be found in the original papers.[13–16]

These functionals have been found to offer improvement over the LSDA for exchange and correlation energies in atoms and molecules.[13,15–17] The gradient functionals also display a property not found in the LSDA—for atoms with partially filled subshells (but not half-filled), the energy calculated using a nonspherical charge density is lower than that computed using a spherically averaged charge density.[18] Local-spin-density functionals are much less sensitive to spherical averaging.[19] The binding energies of first-row dimers are reduced by the lowered reference atom energies, thereby correcting part of the trend in overbinding predicted for these molecules by LSDA calculations.

In this paper we test the gradient functionals for their ability to predict interconfigurational energies of atoms Ca through Zn. Gunnarsson and Jones have also reported results from calculations of transition-metal interconfigurational energies using local-density models[20] and self-interaction correction (SIC) functionals,[21] and the present local-density results agree well with those results from their work.

II. METHOD OF CALCULATION

Calculations reported here were carried out using the augmented-Gaussian-basis (AGB) method.[22] Uncontracted 14s-8p-6d Gaussian basis functions with screening constants from Wachters[23] were used. Electron-nuclear matrix elements were evaluated analytically, and electron-electron matrix elements were calculated using Gaussian integral algorithms[22] and numerical integration over a radial mesh of 180 points distributed over 15 concentric shells. For atoms with axial symmetry, six angular points were used for each radial point to integrate the unique range of the polar angle from 0 to $\pi/2$, and for atoms without axial symmetry the unique octant was integrated using 36 angular points per radial point, with six points each for the dipolar and azimuthal angles over the range 0 to $\pi/2$.

For comparison with gradient results, the Vosko-Wilk-Nusair (VWN) local functional was chosen to represent the LSDA.[24] The VWN functional was also used as the local portion of the gradient functionals in both the LMH[25] and the GGA calculations.

Both spherical and nonspherical charge densities were used with the GGA functional. In a spherical density calculation, the d orbitals were equally occupied, producing a spherically averaged charge density. When a calculation without spherical averaging is carried out, a choice must be made concerning the state of coupling between the orbital and spin angular momentum for the electron configuration of interest (Russell-Saunders states in lighter atoms). For each electron configuration considered in this paper, we addressed only the state with lowest energy, which is given by Hund's rule of maximum multiplicity. The energy of the lowest state of a given electron configuration can be evaluated from one or more single determinant wave functions. For example, a d^2 configuration gives rise to ^3F, ^3P, ^1G, ^1D, and ^1S states. The energy of the ground state, ^3F ($L=2$, $S=1$), can be computed using a d orbital population in which $M_L=3$ and $M_s=1$, or one for which $M_L=2$ and $M_s=1$.

A problem arises in density functional theory due to the dependence of present functionals on the physical

TABLE I. Comparison of energy differences (in eV) between formally degenerate single determinants belonging to the lowest-energy atomic state for the electron configuration listed, using nonspherical charge and spin densities with the GGA and LMH functionals. (See text for further details.)

Species	GGA	LMH	Species	GGA	LMH
One electron beyond filled or half filled			Two electrons beyond filled or half filled		
Sc (s^2d^1)	0.016	0.019	Sc (s^1d^2)	0.148	0.115
Sc$^+$ (s^1d^1)	0.017	0.020	Ti (s^2d^2)	0.216	0.179
Ti$^+$ (s^2d^1)	0.019	0.022	Ti$^+$ (s^1d^2)	0.225	0.187
Cr (s^0d^6)	0.023	0.130	V^+ (s^2d^2)	0.276	0.235
Mn (s^1d^6)	0.015	0.021	Fe (s^1d^7)	0.257	0.133
Fe (s^2d^6)	0.021	0.026	Co (s^2d^7)	0.311	0.260
Fe$^+$ (s^1d^6)	0.022	0.046	Co$^+$ (s^1d^7)	0.320	0.233
Co$^+$ (s^2d^6)	0.024	0.029	Ni$^+$ (s^2d^7)	0.367	0.311
One electron fewer than filled or half filled			Two electrons fewer than filled or half filled		
V (s^1d^4)	0.014	0.018	Ti (s^1d^3)	0.210	0.183
V$^+$ (s^0d^4)	0.021	0.045	V (s^2d^3)	0.283	0.248
Cr (s^2d^4)	0.019	0.020	V$^+$ (s^1d^3)	0.292	0.256
Cr$^+$ (s^1d^4)	0.019	0.021	Cr$^+$ (s^2d^3)	0.351	0.307
Mn$^+$ (s^2d^4)	0.024	0.023	Co (s^1d^8)	0.327	0.315
Ni (s^1d^9)	0.022	0.045	Ni (s^2d^8)	0.392	0.340
Ni$^+$ (s^0d^9)	0.023	0.046	Ni$^+$ (s^1d^8)	0.400	0.373
Cu$^+$ (s^1d^9)	0.026	0.040	Cu$^+$ (s^2d^8)	0.505	0.397
Cu (s^2d^9)	0.026	0.026			
Zn$^+$ (s^2d^9)	0.030	0.028			

"shape" of the electron density.[26] In these calculations, the energies from two single determinants were averaged.[27] Both single determinants were pure, formally degenerate components of the same atomic angular momentum state. The simplest example is the case of Sc. Occupation of any of the five d orbitals gives one of the ten components of the ^2D ground state. In a density-functional calculation, however, the energy for an atom with the d_{z^2} orbital occupied will differ slightly from the energy of an atom with any of the other d orbitals occupied. Although it would be preferable to develop a symmetry-dependent density-functional theory (DFT), we have chosen to simply average the results for these determinants.

Table I illustrates the magnitudes of such DFT-induced nondegeneracies for transition-metal atoms and ions in various configurations. There are four categories: (a) one electron beyond an empty or half-filled shell (d^1 and d^6), (b) one electron fewer than a half-filled or full shell (d^4 and d^9), (c) two extra electrons (d^2 and d^7), and (d) two missing electrons (d^3 and d^8). The energy separation of different microstates of cases (a) and (b) are relatively small (<0.05 eV). Energy differences can be as much as ten times larger for cases (c) and (d) than for (a) and (b). Discrepancies are about the same for GGA and LMH.

TABLE II. s-d transition energies (eV) calculated with nonspherical and spherical GGA (NSGGA and SGGA), Langreth-Mehl-Hu (LMH), and Vosko-Wilk-Nusair (VWN) functionals. The number in parentheses after the experimental values is the estimated relativistic correction to be applied to each of the calculations. The number in parentheses after the calculated values is the error (after applying the relativistic correction).

Expt. (rel.)	NSGGA	SGGA	LMH	VWN
Ca 2.52 (0.08)	1.76 (−0.68)	1.89 (−0.55)	1.27 (−1.17)	1.73 (−0.71)
Sc 1.43 (0.12)	0.70 (−0.61)	0.91 (−0.40)	0.06 (−1.25)	0.69 (−0.62)
Ti 0.81 (0.14)	0.04 (−0.63)	−0.03 (−0.70)	−0.74 (−1.41)	−0.27 (−0.94)
V 0.25 (0.17)	−0.59 (−0.67)	−0.91 (−0.99)	−1.49 (−1.57)	−1.17 (−1.25)
Cr −1.00 (0.21)	−1.70 (−0.49)	−1.74 (−0.53)	−2.66 (−1.45)	−2.03 (−0.82)
Mn 2.15 (0.20)	1.05 (−0.90)	1.25 (−0.70)	0.57 (−1.38)	1.05 (−0.90)
Fe 0.87 (0.26)	0.04 (−0.57)	0.39 (−0.22)	−0.39 (−1.00)	0.16 (−0.45)
Co 0.42 (0.30)	−0.38 (−0.50)	0.46 (−0.58)	−0.85 (−0.97)	−0.71 (−0.83)
Ni −0.03 (0.36)	−0.84 (−0.45)	−1.30 (−0.91)	−1.37 (−0.98)	−1.57 (−1.18)
Cu −1.49 (0.43)	−2.06 (−0.14)	−2.16 (−0.24)	−2.60 (−0.68)	−2.44 (−0.52)
Mean absolute error:	−0.56	−0.58	−1.19	−0.82

TABLE III. s ionization energies from the s-rich electron configuration ($4s^2 3d^{n-2} \Longrightarrow 4s^1 3d^{n-2}$) which is the experimental ground state for all except Co, Ni, and Cu. The entries of Cr*, Ni*, and Cu* are for ionizations from experimental ground states of Cr, Ni, and Cu ($4s^1 3d^{n-1} \Longrightarrow 4s^0 3d^{n-1}$). All energies are in eV and the column designations are the same as for Table II. The numbers in parentheses after the experimental values are the relativistic corrections, and after the calculated values are the errors after making the relativistic correction.

Expt. (rel.)	NSGGA	SGGA	LMH	VWN
Ca 6.11 (0.02)	6.38 (0.29)	6.38 (0.29)	5.98 (−0.11)	6.22 (0.13)
Sc 6.56 (0.02)	6.76 (0.22)	6.77 (0.23)	6.29 (−0.25)	6.60 (0.06)
Ti 6.83 (0.04)	7.04 (0.25)	7.05 (0.26)	6.51 (−0.28)	6.89 (0.10)
V 7.06 (0.03)	7.28 (0.25)	7.29 (0.26)	6.71 (−0.32)	7.12 (0.09)
Cr 7.28 (0.04)	7.49 (0.25)	7.49 (0.25)	6.88 (−0.36)	7.33 (0.09)
Cr* 6.76 (0.09)	7.55 (0.88)	7.55 (0.88)	7.51 (0.84)	7.48 (0.81)
Mn 7.43 (0.05)	7.67 (0.29)	7.67 (0.29)	7.03 (−0.35)	7.52 (0.14)
Fe 7.90 (0.06)	8.20 (0.36)	8.21 (0.37)	7.59 (−0.25)	8.07 (0.23)
Co 8.28 (0.08)	8.66 (0.46)	8.68 (0.48)	8.08 (−0.12)	8.54 (0.34)
Ni 8.67 (0.11)	9.08 (0.52)	9.10 (0.54)	8.56 (0.00)	8.97 (0.41)
Ni* 7.62 (0.15)	8.43 (0.96)	8.44 (0.97)	8.18 (0.71)	8.26 (0.79)
Cu 9.04 (0.13)	9.52 (0.61)	9.52 (0.61)	9.06 (0.15)	9.40 (0.49)
Cu* 7.72 (0.15)	8.50 (0.93)	8.50 (0.93)	8.22 (0.65)	8.35 (0.78)
Zn 9.39 (0.16)	9.84 (0.61)	9.84 (0.61)	9.39 (0.16)	9.71 (0.48)
Mean |error| (without Cr*, Ni*, and Cu*)	0.37	0.38	0.21	0.23
Mean |error| (all)	0.49	0.50	0.33	0.35

III. RESULTS

The experimental values used for assessment of errors in the functionals are $(2J+1)$ weighted averages of energies of the spin-orbit (J) states for the pertinent electron configuration, taken from Moore.[28] The transition and ionization energies and their errors are given in Tables II–IV, and the relativistic correction used to construct Figs. 1–3 are in parentheses following the experimental values.[29–31]

A. 4*s*-3*d* transitions

We first address the case of s-d transfer energies, defined by

$$\Delta_{sd} = E(\text{core}, 4s^1 3d^{n-1}) - E(\text{core}, 4s^2 3d^{n-2}) ,$$

where n is the number of valence electrons in the atom (2 for Ca through 11 for Cu). The LSDA has a well-documented tendency to overstabilize $3d$ orbitals relative to $4s$ orbitals and thereby understates the $4s$-$3d$ transition energy.

TABLE IV. d ionization energies from the s-rich electron configuration ($4s^2 3d^{n-2} \Longrightarrow 4s^2 3d^{n-3}$) which is the experimental ground state for all except Co, Ni, and Cu. The entries of Cr*, Ni*, and Cu* are for ionizations from experimental ground states of Cr, Ni, and Cu ($4s^1 3d^{n-1} \Longrightarrow 4s^1 3d^{n-2}$). All energies are in eV and the column designations are the same as for Table II. The numbers in parentheses after the experimental values are the relativistic corrections (the negative indicates that the relativistic correction makes the transition lower in energy), and after the calculated values are the errors after making the relativistic correction.

Expt. (rel.)	NSGGA	SGGA	LMH	VWN
Sc 8.00 (−0.10)	9.02 (0.92)	8.89 (0.79)	9.08 (0.98)	9.01 (0.91)
Ti 9.92 (−0.10)	10.88 (0.86)	10.61 (0.59)	11.00 (0.98)	10.75 (0.73)
V (−0.14)	12.09	12.18	12.34	12.35
Cr 12.40 (−0.17)	13.25 (0.68)	13.65 (1.08)	13.62 (1.05)	13.84 (1.27)
Cr* 8.29 (−0.17)	9.19 (0.73)	9.23 (0.77)	9.54 (1.08)	9.36 (0.90)
Mn 14.30 (−0.15)	15.03 (0.58)	15.05 (0.60)	15.42 (0.97)	15.26 (0.81)
Fe 10.71 (−0.20)	12.23 (1.32)	12.03 (1.12)	12.08 (1.17)	12.22 (1.31)
Co 12.88 (−0.22)	14.11 (1.01)	13.71 (0.61)	14.05 (0.95)	13.94 (0.84)
Ni	15.21	15.32	15.32	15.57
Ni* 8.70 (−0.25)	9.92 (0.97)	10.40 (1.45)	9.94 (0.99)	10.54 (1.59)
Cu 15.04 (−0.30)	16.68 (1.34)	17.20 (1.86)	17.08 (1.74)	17.48 (2.14)
Cu* 10.53 (−0.30)	11.58 (0.75)	11.68 (0.85)	11.66 (0.83)	11.84 (1.01)
Zn 17.30 (−0.55)	18.26 (0.41)	18.35 (0.50)	18.59 (0.74)	18.62 (0.77)
Mean |error| (without Cr*, Ni*, and Cu*)	0.89	0.89	1.07	1.10
Mean |error| (all)	0.87	0.93	1.04	1.12

Figure 1 is a plot of the *errors* (calculated value minus experimental value) for the VWN, LMH, and spherical GGA calculations (SGGA), compared with the nonspherical GGA calculations (NSGGA). Relativistic corrections have been taken from Martin and Hay[29] and Lagowski and Vosko.[30,31] In all cases, the relativistic correction increases the energy needed to promote the 4*s* electron. The magnitude of the correction increases steadily with atomic number from 0.08 eV in Ca to 0.43 eV in Cu. This correction accounts for nearly half of the error in the nonrelativistic, nonspherical GGA calculations for Co, Ni, and Cu.

The error remaining after the relativistic correction is applied is smaller for the nonspherical GGA calculations than for the other functionals, although the improvement is marginal in some cases. The errors in the NSGGA calculation are more nearly uniform across the series than are those from the VWN functional, where the errors vary by about a factor of 2. The magnitude of the errors is also relatively constant in the LMH functional calculations, although the errors are nearly twice as great as those for the NSGGA calculations. The trend of the errors across the series is similar in NSGGA and LMH, with the exception of a slight difference around Cr and Mn.

The comparison between results of spherical and nonspherical GGA calculations in Fig. 1(c) shows that, owing to other errors, nonspherical calculations are not consistently more accurate. The errors in the nonspherical values are, however, slightly more uniform. The trend in the SGGA is similar to that of the VWN calculations,

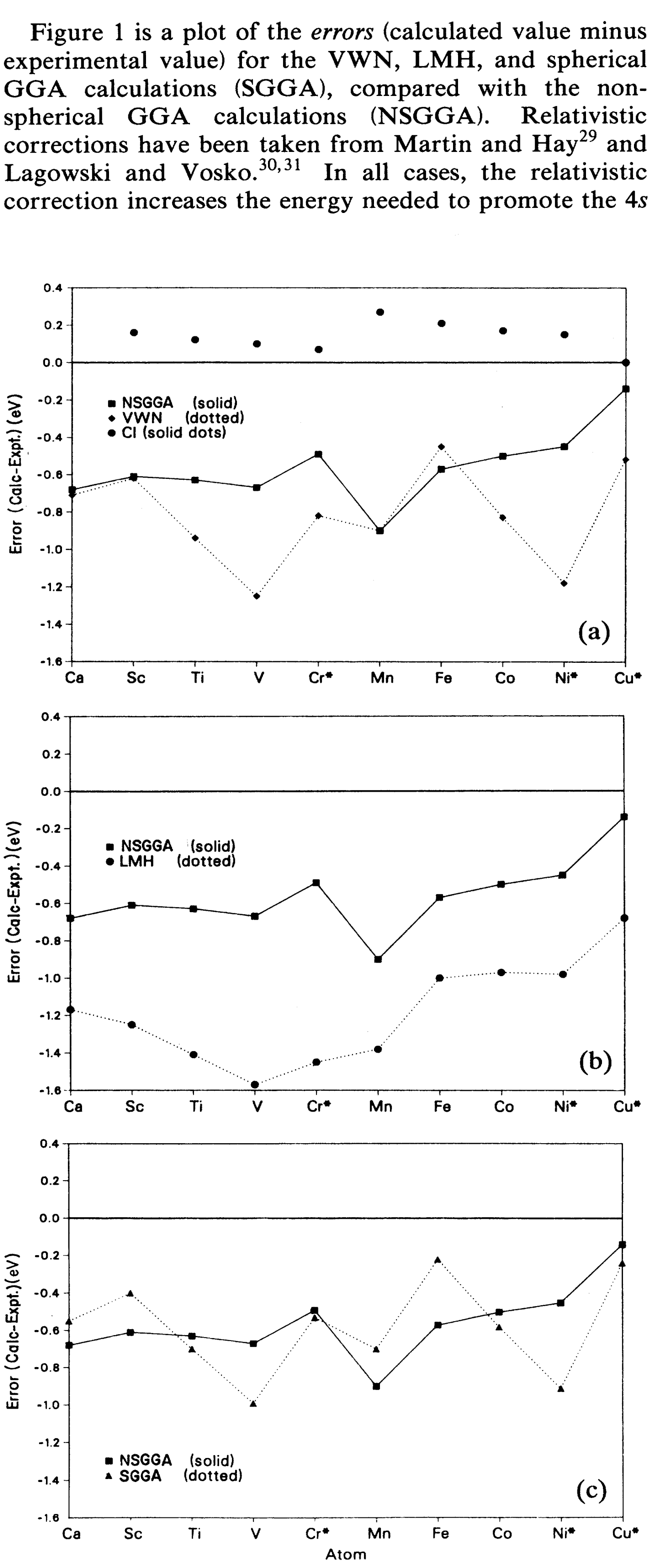

FIG. 1. The error in the calculated *s*-*d* transition energies (calculated value−experimental value) using nonspherical GGA (NSGGA), spherical GGA (SGGA), Langreth-Mehl-Hu (LMH), and Vosko-Wilk-Nusair (VWN) functionals. All energies are in eV. CI denotes configuration-interaction results (Ref. 32).

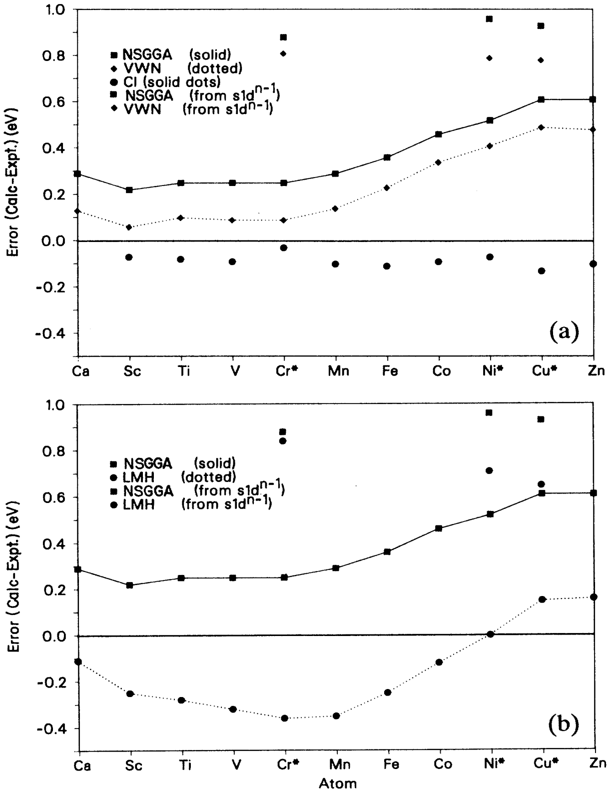

FIG. 2. Errors (in eV) in calculated *s* ionization energies from the experimental ground-state configurations ($4s^23d^{n-2}$ for all atoms except Cr, Ni, and Cu, for which the calculations are for ionizations from the $4s^13d^{n-1}$ state), labeled as in Fig. 1. Unconnected markers for Cr, Ni, and Cu are calculations from the $4s^23d^{n-2}$ state.

Fig. 1(a), although the errors are smaller for the SGGA. This suggests that the greater uniformity of error in the NSGGA and LMH calculations is an indirect consequence of the effect nonspherical charge densities have on the gradient corrections to the local functionals.

Raghavachari and Trucks[32] have reported results of *s*-*d* transition energies for the 3*d* transition-metal atoms from quadratic-configuration-interaction (QCI) calculations, a method which spans single and double excitations iteratively, and triple excitations noniteratively. The results are included in Fig. 1(a); the mean deviation is 0.13 eV for the series Sc–Cu. They also report that Moeller-Plesset perturbation calculations (MP2, MP3, and MP4) give excellent results for Sc–Fe, but give large mean deviations for the rest of the series (1.77 eV for MP4). The Moeller-Plesset calculations for Co, Ni, and Cu are also reported to be very sensitive to the order of the perturbation calculation.

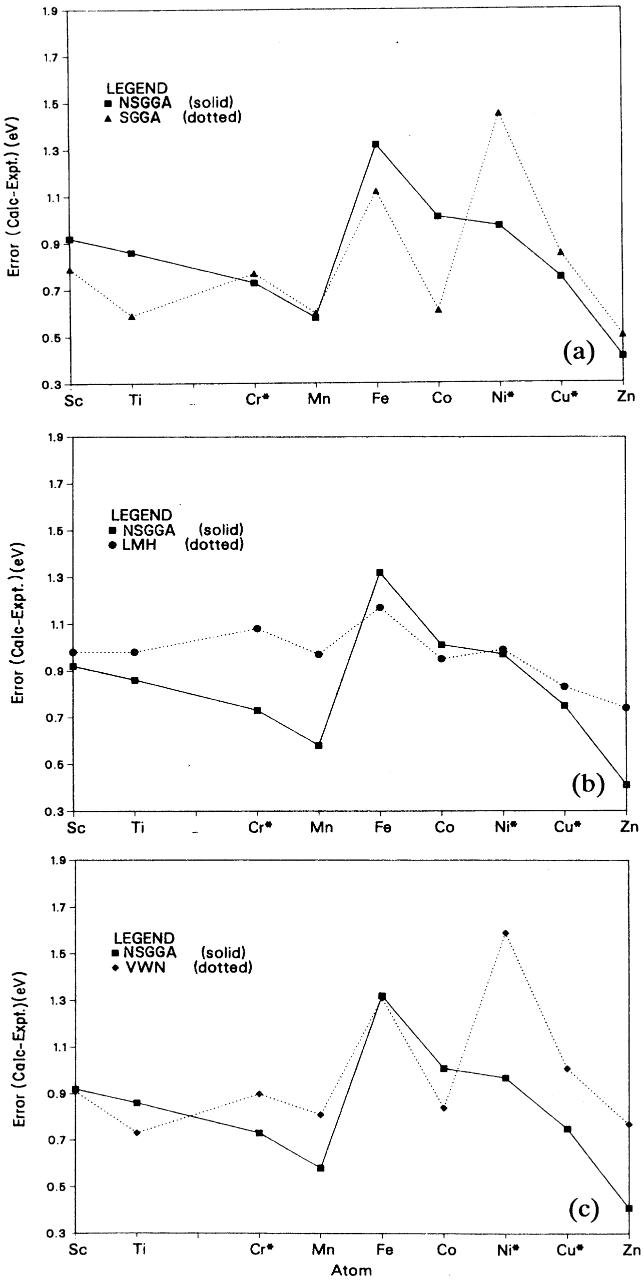

FIG. 3. Errors (in eV) in calculated *d* ionization energies from the experimental ground-state configurations ($4s^23d^{n-2}$ for all atoms except Cr, Ni, and Cu, for which the calculations are for ionizations from the $4s^13d^{n-1}$ state), labeled as in Fig. 1.

B. 4*s* ionizations

In our calculations of *s*-electron removal energies, we have selected the $4s^23d^{n-2}$ configuration as the initial state, although this configuration is not the experimental ground state for Cr, Ni, and Cu. Hence, we define the *s* ionization energy as

$$\Delta_{s\text{-ion}}=E(\text{core},4s^13d^{n-2})-E(\text{core},4s^23d^{n-2})$$

for all atoms. We do not allow for a change in the number of *d* electrons, which does occur experimentally in the lowest-energy ionization of an *s* electron in V, Co, and Ni. The *s* ionizations from the $4s^13d^{n-1}$ state were also calculated for Cr, Ni, and Cu. The resulting errors in the density-functional calculations are shown in Fig. 2 with the $4s^13d^{n-1}$ calculations for Cr, Ni, and Cu shown with unconnected markers.

Relativistic corrections have been introduced into Fig. 2 from literature values.[29–31] Relativistic effects are three to four times smaller for *s* ionizations than for *s*-*d* transitions (except when the number of *d* electrons changes), ranging from 0.02 eV for Ca to 0.16 eV for Zn, all making the ionization more energetic.

The VWN functional gives good results for all the $4s^23d^{n-2}$ ground states, with smaller errors than the GGA functional, which overestimates 4*s* binding. The GGA and LMH functionals are roughly equivalent in magnitudes of error, the GGA overestimating and the LMH underestimating *s* ionization energies for atoms with a $4s^23d^{n-2}$ ground state.

All three functionals display the same trend in errors. The errors across the series are nearly constant up to Mn, and gradually rise thereafter. When calculations of the transition $4s^13d^{n-1}\Longrightarrow 4s^03d^{n-1}$ are performed for Cr, Ni, and Cu, we find these errors to be much greater than for ionization from the $4s^23d^{n-2}$ configuration. These are shown as unconnected markers in Fig. 2. It is curious that the error in the LMH functional is negative for the $4s^23d^{n-2}$ ionizations, but positive for the $4s^13d^{n-1}$ ionizations.

The question arises whether the large error that results when a lone *s* electron is ionized is inherent in these functionals whenever a single 4*s* electron is removed, or whether the error is present only when the 4*s* electron is interacting with *d* electrons with parallel spin. To test this we calculated the *s* ionization energy for the potassium atom (not shown), and found that the error for potassium was much smaller (0.2 and 0.3 eV depending on the functional) than for Cr, Ni, and Cu, indicating that the functionals are subject to considerable error in the calculation of the interaction energy between the 4*s* electron with the 3*d* subshell.

Spherical and nonspherical GGA calculations give 4*s* ionization energies within 0.03 eV of one another. The lack of dependence on the sphericity is not surprising given the symmetry of the *s* oribtal.

Li *et al.*[33] have also reported *s* ionization energies for several closed-shell atoms, including Ca and Zn, using a method which computes the exchange-correlation potential from the spatial distribution of the Fermi-Coulomb hole. The Ca and Zn ionization energies by their method are in both cases 0.89 eV lower than our nonspherical GGA results, and are lower than experiment by 0.62 and 0.44 eV, respectively, after relativistic corrections have been applied.

A QCI study of ionizations by Raghavachari and Trucks[34] have found a mean deviation of about 0.09 eV for the transitions relevant to this paper. The error in the QCI values is included in Fig. 2(a). As in the case of *s*-*d* transitions, Moeller-Plesset perturbation theory is reported to be inadequate for ionizations of the highly correlated atoms, Co through Zn.

C. 3*d* ionizations from the experimental ground states

The differences among the density functionals are more prominent when the number of *d* electrons changes. For this reason, we calculated the energies required to ionize *d* electrons from the experimental ground states of all atoms, and from the $4s^13d^{n-1}$ configuration of Cr, Ni, and Cu. Again, no further changes in the electron configuration were allowed. For all atoms we calculated the quantities

$$\Delta_{d\text{-ion}}=E(\text{core},4s^23d^{n-3})-E(\text{core},4s^23d^{n-2})\ ,$$

and for Cr, Ni, and Cu we also calculated the values

$$E(\text{core},4s^13d^{n-2})-E(\text{core},4s^13d^{n-1})\ .$$

As noted above, LSDA calculations predict stronger binding of 3*d* electrons than experimentally observed, and this results in overestimation of the 3*d* ionization energies. In Fig. 3, *d*-ionization results are shown for all 3*d* transition-metal atoms except V—Moore[28] does not tabulate an energy for the $4s^23d^3 \Longrightarrow 4s^23d^2$ ionization.

Relativistic corrections have also been estimated for the removal of a *d* electron. In all cases the relativistic corrections lower the *d* ionization energy. Martin and Hay[29] report that the relativistic correction for *d* ionization from the $4s^23d^{10}$ state of the Zn atom is -0.55 eV, but no data is available for ionization from the $4s^23d^{n-2}$ states of the other 3*d* transition metals. (The negative sign indicates a decrease in transition energy compared to nonrelativistic calculations.) The atomic energies given by Martin and Hay[29] do, however, yield relativistic corrections for *d* removal from atoms in the $4s^13d^{n-1}$ configuration for all 3*d* transition-metal atoms (except Zn). Although we expect that relativistic corrections for the $4s^13d^{n-1}$ ionizations are somewhat smaller than the corrections for the $4s^23d^{n-2}$ ionizations, we have applied the Martin and Hay $4s^13d^{n-1}$ corrections to our calculated $4s^23d^{n-2}$ *d* ionization energies. The results shown in Fig. 3 include this correction.

The errors in the GGA functional [Fig. 3(a)] are about 0.2 eV smaller than those with the VWN functional for Cr, Mn, Co, Cu, and Zn, with much improvement for Ni, and about the same or slightly worse results for Sc, Ti, and Fe. The errors in the LMH functional [Fig. 3(b)] are greater than those in the NSGGA calculation for the first half of the series, but smaller in the second half. Furthermore, the LMH errors are more nearly uniform than either the GGA or the VWN results.

Results shown in Fig. 3(c) indicate that, with the exception of Ni, there is little improvement upon using a nonspherical charge density, although the errors are slightly more uniform. In three cases (Ti, Fe, and Co) errors are greater with the nonspherical densities. As with the *s*-*d* transition, the pattern of errors across the series is much the same for the spherical GGA and VWN functionals, suggesting that the improvement in error uniformity is a consequence of a better description of nonspherical effects within the gradient functionals.

IV. CONCLUSIONS

It is clear that much work remains to be done in deriving a functional which is universally better than the LSDA for transition-metal interconfigurational energies. While inclusion of gradient effects in general leads to improvement over the LSDA, the remaining errors are often large and, most disturbingly, occur in an unpredictable pattern across the series.

Intercomparison of the various gradient functionals shows that the GGA is slightly better in describing *s*-*d* transition energies, but similar to LMH for both 4*s* and 3*d* ionizations. While using nonspherical charge densities is quite beneficial in calculations for the binding energies of first-row dimers,[18] the benefit for the cases in this study is much less pronounced.

These results indicate gradient functionals provide some improvement over the local-density approximation, but the limited degree of success underscores the difficulty in improving on the remarkable accuracy available from the relatively simple local-density approximation.

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